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FIRE-RETARDANT DECORATIVE INKS FOR AIRCRAFT INTERIORS

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ABSTRACT

Commercial and experimental fire retardants were screened as potential fire retardants for acrylic printing inks used on aircraft interior sandwich panels. The fire retardants were selected according to their physical properties and their thermostabilities. A criterion for selecting a more stable fire retardant was established.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to determine thermostabilities. Results showed that the fire retardant formulations are more thermally stable than the acrylic ink control. It was determined that an ink formulation containing a brominated phenol and carboxy-terminated butadiene acrylonitrile which has been modified with a brominated polymeric additive (BPA), yielded the highest limiting oxygen index (LOI) of all the compounds tested. All of the fire-retardant formulations had a higher oxygen index than the baseline acrylic ink did.

INTRODUCTION

Sidewall panels used in the interior of commercial aircraft are decorated with the airline's colors and pattern designs. The carrier for these color pigments and designs is a resin which is screen printed. The ink is mixed in solvents to make it fluid, and is screen printed on a decorative polyvinyl-fluoride (PVF) film. The solvent in the ink is then evaporated by passing the printed film through a drying oven.

The thickness of ink material used is small, at most 0.02 mm for two coats. This study is concerned with the inherent thermal stability of the ink and its effect on ignition and smoke evolution when applied as a film on a substrate of 0.05 mm of polyvinylfluoride film.

This paper describes the evaluation of an acrylic ink containing various fire-retardant agents to gain improved fire resistance without sacrificing process performance.

EXPERIMENT

The ideal fire-retardant agent in an acrylic ink must be (1) soluble in methyl ethyl ketone (MEK); (2) chemically reactive, so it will not leach out or migrate; (3) compatible with the polymeric binders to avoid migration out of thin films; and (4) compliant with existing techniques of applying printing inks (an adaptable solution without capital investments by applicators).

The use of fire-retardant agents in thin films has always been a technical problem. One of the main phenomenon in fire-retardant thin films is the migration of the fire-retardant agent, such as antimony trioxide (Sb_2O_3), to the surface.[1]

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In this study, fire-retardant candidates that might not migrate were screened, such as reactive fire retardants and polymeric fire retardants in which migration (or leaching) is diffusion controlled.

The following criteria were set up for candidate selection:

1. Solubility in MEK (the acrylic ink solvent)
2. Thermostability
3. Reactive vinyl site or polymeric backbone
4. Fire-retardant agents containing halogens or phosphorus or a combination of them
5. Processability with the acrylic ink
6. No interference with the curing cycle of the ink

MATERIALS

Fire-retardant additives were selected from a variety of commercially available additives that met the above criteria. The following fire-retardant additives were used to prepare the ink formulations shown in Table 1.

Brominated Polymeric Additive (BPA) (Formulation 1).

This additive is available at various molecular weights ranging from 660 to 40,000. Chemically, the family has two glycidyl groups, and includes aromatic bromine which is very thermostable. The chemistry and properties of these additives have been described previously.[2] The BPA selected has a 50% bromine content, melting point of 60-70°C, and an epoxy equivalent (EE) of 545. This fire retardant (Formulation 1) was used as the reference in a series of formulations in which the effect of different modifications of the basic polymeric backbone were studied. Two types of modifications were made. The first included the formulation of the basic BPA with brominated phenols and the second included the formulation of these compounds with carboxy-terminated butadiene acrylonitrile (CTBN). They are identified as Formulations 2, 3, 4 and 5, and are discussed below. Formulation 1 is the basic BPA.

BPA-Tribromophenol (BPA-TBP) (Formulation 2).

A brominated phenol in the form of tribromophenol (TBP) was formulated with the BPA. The tribromophenol has a melting point of 95°C and contains 72% bromine. When combined with the BPA, the bromine content of the Formulation was 58.0%. The synthetic scheme for formulating this compound is shown in Figure 1. The BPA is blocked through its diglycidyl end groups with the brominated phenols to yield the BPA-Tribromophenol compound.

BPA-Pentrabromophenol (BPA-PBP) (Formulation 3).

This brominated phenol has a melting point 230°C and contains 82% bromine. When combined with the BPA, the bromine content of the formulation is 63%.

BPA-Rubberized Tribromophenol (BPA-RTBP) (Formulation 4).

In recent research [3], it was found that carboxy-terminated butadiene acrylonitrile (CTBN) rubber improves the fracture toughness of various thermosets [4, 5]; consequently, there was a desire to determine its effect on fire-retardant acrylic inks when it was blended with the BPA control.

Rubber-toughened BPA was synthesized by reacting it with liquid CTBN rubber using ethyl triphenyl phosphonium iodide (ETPPI) as the catalyst to produce a concentration of prereacted rubber in BPA.[3] Molecules with concentrations of up to 50% CTBN were synthesized to obtain a block polymer of

the general type shown in Figure 2. Two of the glycidyl groups have been consumed and the molecular weight has been increased accordingly. The CTBN is entrapped now between two BPA units, thus retaining its elastomeric properties. The resulting block polymer still has two glycidyl ether groups which may be subjected to further modification.

The introduction of CTBN rubber decreases the bromine content of the BPA; therefore, modification with brominated phenols is required to keep an acceptable bromine concentration. As a result, the two glycidyl end groups were further reacted with brominated phenols, using the same catalyst, to produce a polymer that is capped at both sides with the brominated phenoxy group (Fig. 3). This procedure increases the bromine content, the extent of the increase being dependent on the selected brominated phenol and on the loaded amount of the CTBN rubber.

BPA-Rubberized Tribromophenol (BPA-RTBP) (Formulation 5).

The tribromophenol compound was synthesized with the CTBN using the procedure to prepare Formulation 4. However, in this case the CTBN content was increased to 16.2% and the bromine content was decreased to 48.6%.

2,3 Dibromopropyl Acrylate (Formulation 6).

In addition to the BPA modifications, this brominated fire-retardant additive containing 58.8% bromine was evaluated.

Bis(chloroethyl) Vinyl Phosphonate (Formulation 7).

A nonbrominated compound was also studied in order to determine the effect of phosphorus and chlorine on the fire retardancy of the acrylate ink.

The ink formulations shown in Table 1 were calculated and adjusted to contain the same loading of 10% bromine with the exception of Formulation 7, in order to determine the effectiveness of each fire-retardant additive in the final ink formulation. All formulations were also adjusted to contain 60% by weight solids so that the viscosity of all formulations was approximately the same as the acrylic ink control Formulation 0.

Film preparation--Films of acrylic ink containing the fire-retardant additives were prepared by casting on glass plates. Initially the solvent was vacuum evaporated, followed by curing the cast films at 80°C to 100°C for 30 minutes in an air-circulating oven. The thermochemical properties of these films were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and were compared with those of the neat acrylic ink control.

Using the same method, the samples of the various fire-retardant modified ink formulations were cast on sheets of polyvinyl fluoride (PVF) and their limiting oxygen index (LOI) and smoke evolution were measured. The LOI of the coated PVF samples was determined per the American Society of Testing Materials (ASTM) publication D-2863.[6] The smoke evolution of the same samples was also determined using the NBS-Aminco smoke density chamber. The procedure and test method used are described in ASTM publication E662.[7]

The incorporation of the fire-retardant additives into the acrylic ink does not significantly affect the transparency of the cast films. However, there were some difficulties in preparing the cast films as a result of adding the fire-retardant agent to the acrylic ink. In particular, the films obtained from the RTBP in both concentrations of CTBN rubber (Numbers 4 and 5, Table 1) were very tightly attached to the glass plate and could not be peeled off and separated without being destroyed. Therefore, in both cases the glass plates were sprayed with a mold-release dry lubricant; this made it easier to

separate the films from the plates but also reduced their transparency. Formulation number 6, Table 1, was observed to be brittle. The formulations adhered well to the PVF film with the exception of Formulation number 6, Table 1.

TEST RESULTS

The limiting oxygen index (LOI) and the maximum smoke emission (Dm) of specimens consisting of the cast ink films on the PVF film substrate was determined. The PVF film was used for these tests since it is the most common decorative film used in aircraft interiors. Since previous studies [8] have shown that the neat PVF film has an LOI of 25 and Dm of 2.5 and the LOI and Dm values obtained for the ink-coated films were higher than was the PVF film itself, the contribution of the PVF film was considered insignificant for this study.

Limiting Oxygen Index

LOI test results are shown in Table 2. All of the films with formulations of the fire-retardant additive showed a higher limiting oxygen index and, therefore, showed higher resistance to ignitability than did the acrylic ink control (Formulation 0). The unmodified BPA (Formulation 1) had a lower LOI than did the modified BPA (Formulations 2 and 3).

The CTBN modified formulations (Formulations 4 and 5) showed high LOI values. In addition the unmodified BPA had lower LOI than the other fire-retardant formulations containing the dibromopropyl acrylate (Formulation 6) or the phosphonate (Formulation 7).

Smoke Emission

The maximum smoke emission (Dm) when the films are exposed under a non-flaming condition at 2.5 W/cm^2 is shown in Table 3. The formulations are listed in order of increasing maximum smoke density (Dm). There was an increase in the smoke evolution of the cast films using the formulation containing the fire-retardant additives. It has been shown previously [2] that the addition of CTBN to polymers increases the smoke evolution. Formulation 5 with 16.2% CTBN had higher smoke density than Formulation 4 with 12.0% CTBN.

Thermogravimetric Analysis Measurements

Thermogravimetric analysis (TGA) was accomplished using a DuPont 951 TGA cell and 1090 thermoanalyzer at a heating rate of $20^\circ\text{C}/\text{min}$, and nitrogen flow rate of $80 \text{ ml}/\text{min}$. The TGA results are shown in Figure 4.

For comparison purposes one should follow the loss of weight of the control specimen of acrylic ink which starts to lose weight at 120°C . There is a weight loss of approximately 10-12% until the deflection point at 240°C , where specimens start to lose weight rapidly (about 40%) during a temperature interval of 40°C . Table 4 shows a tabulation of the LOI and the remaining weight of the samples at 280°C .

At 280°C , the remaining weight of all the modified BPA formulations (Formulations 3, 4, 5 and 6) was higher than the acrylic ink control indicating a higher thermostability. This is generally in agreement with the LOI test results where the CTBN modified formulations had high LOI values. The BPA-RTBP (Formulation 5) with 16.2% CTBN has the highest remaining weight (78%) of all the formulations tested and exhibited the highest LOI (33.3). The BPA-RTBP (Formulation 4) with 12.0% CTBN has a remaining weight of 72% and LOI of 32.7. The BPA-PBP (Formulation 3) had a higher concentration of

bromine than did the BPA-TBP (Formulation 2) and higher LOI and thermal stability. It is interesting to note that all of these formulations were modifications with brominated phenols introduced in the formulation as a tribromophenol or pentabromophenol. There was no correlation between the limiting oxygen index and the thermal stability of the other formulations (Formulations 1, 6 and 7). The other brominated phenol modified BPA (BPA-TBP, Formulation 2) ranked fourth for thermal stability and fifth for LOI.

It is evident that the most effective fire-retardant formulations were: BPA-RTBP (16.2% CTBN), BPA-PBP, and BPA-RTBP (12.0% CTBN).

Differential Scanning Analysis

The differential scanning analysis (DSC) of the neat cured films (without the PVF) is shown in Figure 5.

The first thermal transformation for the acrylic ink occurs at 51-52°C. All of the formulations showed a similar transformation at 50-60°C. All formulations show a decomposition exotherm in the range of 210-220°C. The information gained from the DSC studies is, therefore, insufficient as a basis for judging the thermal stability of the fire-retardant formulations.

CONCLUSIONS

The fire resistance of the acrylic ink was enhanced by the use of the fire retardants. At equal bromine loading in the final ink formulation, it was determined that the most effective fire retardants were the formulations modified with the CTBN and brominated phenols introduced in the formulation either as a tribromophenol or as a pentabromophenol. This was demonstrated by an increase in the limiting oxygen index of these formulations coated on PVF and the higher thermal stabilities of the neat formulations at 280°C. Formulation 5 containing both the brominated phenol and CTBN was the most effective formulation studied.

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Table 1. Composition of Fire-Retardant (FR) Ink Formulations
Calculated for 100 ml Ink

Formulation	FR additive description	Percent Br,Cl,P or CTBN in FR additive	FR additive, g per 100 ml ink	MEK addition ml ¹	Percent Br,Cl,P in final formulation
0	Acrylic ink (control) ⁷	0	0	0	0
1	Brominated polymer additive (BPA) ⁸	50.0 Br	15.0	18.7	10.0
2	BPA-tribromophenol (BPA) ³	58.0 Br	12.5	15.6	10.0
3	BPA-pentabromophenol (BPA-PBP) ⁴	63.0	11.3	18.8 ²	10.0
4	BPA-rubberized tribromophenol (BPA-RTBP)	53.0 Br	13.9	17.4	10.0
5	BPA-rubberized tribromophenol PA-RTBP)	12.0 CTBN ⁹ 48.6 Br	20.5	34.3	10.0
6	2,3 dibromopropyl acrylate ⁵	16.2 CTBN ⁹ 58.8 Br	12.3	15.3	10.0
7	Bis(chloroethyl) vinyl phosphonate ⁶	13.3 P 30.0 Cl	22.5	28.1	5.0 P 11.2 Cl

¹MEK addition to 100 ml final ink formulation

²50:50 dioxane:MEK

³Tribromophenol (TBP): Great Lakes Chemical Corporation

⁴Pentabromophenol (PBP) Great Lakes Chemical Corporation

⁵2,3 dibromopropyl acrylate: Great Lakes Chemical Corporation

⁶Bis(chloroethyl) vinyl phosphonate: Stauffer Chemical Company

⁷Acrylic ink: K. C. Coatings, Inc.

⁸Brominated polymeric additive: Makhteshim, Ltd.

⁹Carboxy-terminated butadiene acrylonitrile: B. F. Goodrich Chemical Company

Table 2. Relative Limiting Oxygen Index (LOI) of PVF-Ink Formulation in Order of Decreased Oxygen Index

Order of oxygen index	Formulation	Formulation description	LOI
1	5	BPA-RTBP (16.2% CTBN)	33.3
2	3	BPA-PBP	33.0
3	4	BPA-RTBP (12.0% CTBN)	32.7
4	7	Bis(chloroethyl) vinyl phosphonate	32.3
5	2	BPA-TBP	31.3
6	6	2,3 dibromopropyl acrylate	31.2
7	1	BPA	30.2
8	0	Acrylic ink (control)	28.4

Table 3. Relative Smoke Density of PVA-Ink Formulations in Order of Increased Maximum Smoke Density (Dm) at 2.5 W/cm²

Order of smoke density	Formulation	Formulation description	Dm
1	0	Acrylic ink	2.86
2	1	BPA	5.83
3	4	BPA-RTBP (12.0% CTBN)	6.34
4	7	Bis(chloroethyl) vinyl	8.25
5	6	2,3 dibromopropyl	8.98
6	2	BPA-TBP	9.5
7	5	BPA-RTBP (16.2% CTBN)	10.3
8	3	BPA-PBP	11.5

Table 4. Limiting Oxygen Index (LOI) and Weight Loss of PVF Ink Formulations in Order of Decreased Thermal Stability

Order of thermal stability at 280°C	Formulation	Formulation description	LOI	Percent weight remaining at 280°C
1	5	BPA-RTBP (16.2% CTBN)	33.3	78
2	3	BPA-PBP	33.0	72
3	4	BPA-RTBP (12.0% CTBN)	32.7	72
4	2	BPA-TBP	31.3	70
5	0	Acrylic ink (control)	28.4	65
6	1	BPA	30.2	63
7	7	Bis(chloroethyl) vinyl phosphate	32.3	58
8	6	2,3 dibromopropyl acrylate	31.2	51

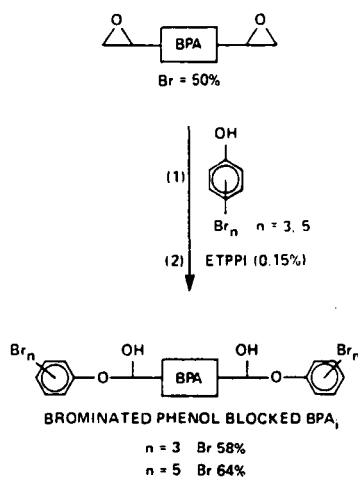


Figure 1. Synthesis scheme of brominated phenol-blocked BPA.

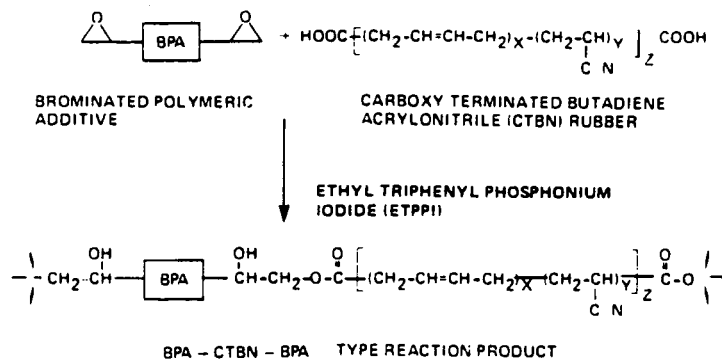


Figure 2. Synthesis scheme of rubber-toughened BPA.

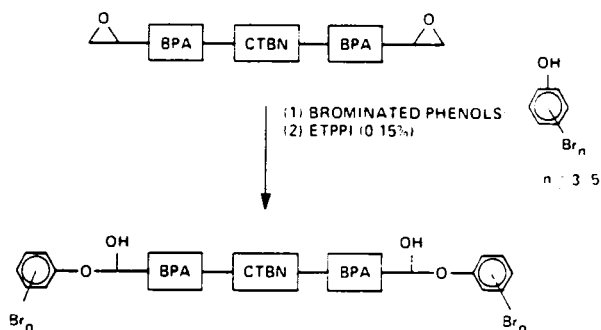


Figure 3. Synthesis scheme of rubber-toughened, brominated phenol-blocked BPA.

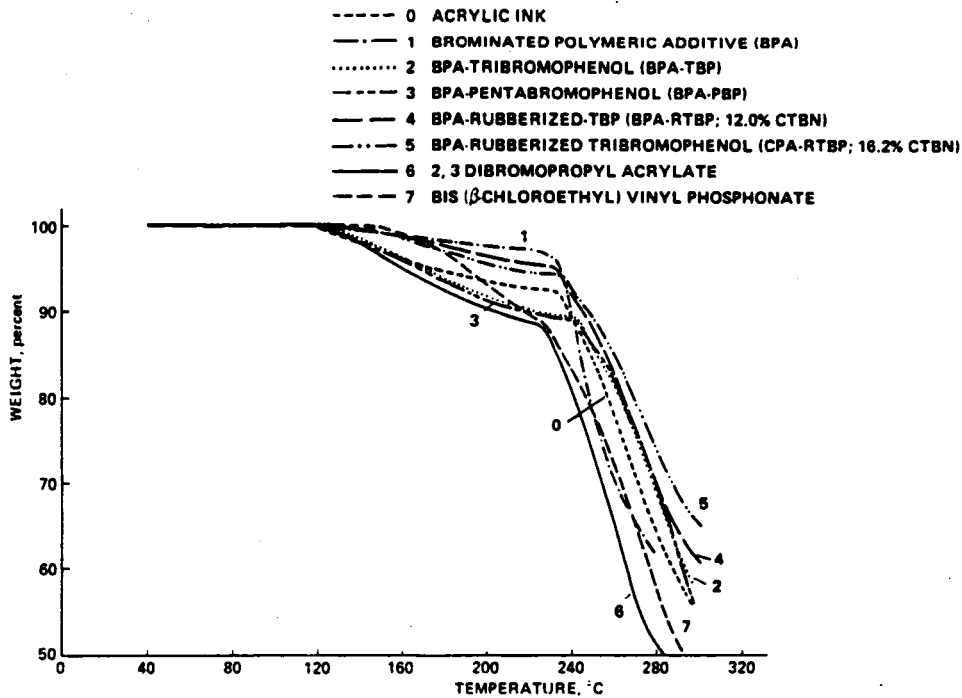


Figure 4. Thermogravimetric analysis of fire-retardant acrylic ink formulations.

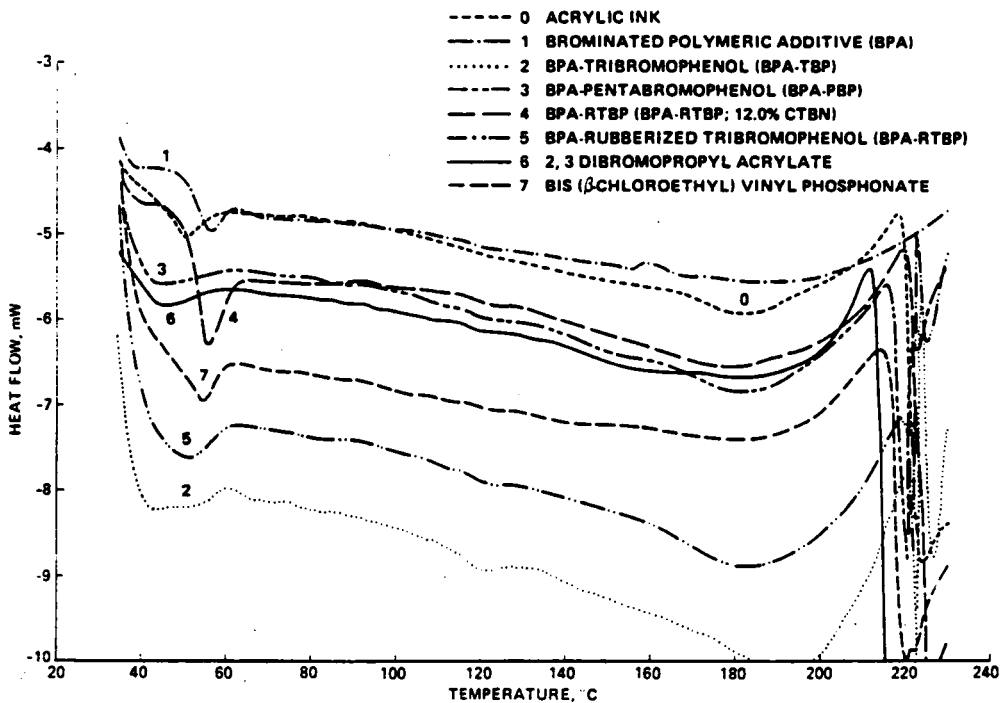


Figure 5. Differential scanning analysis of fire-retardant acrylic ink formulations.

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