What Everyone Should Know About Fire Retardants for Plastics

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Fuel, oxygen, and heat sufficient to raise the material to its ignition temperature must be presented to produce a flame. The effect the fire-retardant system will have on each of these components must be considered during the development of effective fire-retardant polymer formulations.

There are two general approaches to imparting fire retardance to plastic materials – namely reactive and additive. For the purpose of this paper, a *reactive* fire-retardant chemical is defined as one which enters into the chemical reaction and becomes an integral part of the polymer structure. An *additive* fire-retardant chemical is defined as one which can be physically dispersed in a polymer, but does not become part of the polymer structure.

Over the years many chemical compositions have been evaluated as fire-retardant candidates, but only those compounds containing one or more of the following elements – a halogen (usually chlorine or bromine), phosphorus, and nitrogen – have been found to be effective. This does not imply, however, that all chemical compositions containing one or more of these elements can qualify as a desirable fire-retardant material. The list of effective fire-retardants is much smaller.

Recently certain hydrated inorganic materials have been found to provide fire-retardancy for specific applications. Typical is hydrated alumina.

Reactive Fire-Retardants

Reactive fire-retardant intermediates are normally used in the manufacture of fire-retardant grades of unsaturated polyesters, epoxies, and of polyurethane foams.

Polyesters. Simply stated, a polyester resin is the reaction product of a polybasic acid and a polyhydric alcohol. For unsaturated polyesters, a cross-linking agent such as styrene is incorporated into the formulation. Fire-retardant properties can be incorporated into the polyester by selecting certain polybasic acids or polyhydric alcohols. Some of the reactive fire-retardant intermediates used to produce fire-retardant polyesters are (1) chlorendic anhydride, (2) chlorendic acid, (3) tetrachlorophthalic anhydride, (4) tetrabromophthalic anhydride, (5) brominated bisphenol compounds, and (6) brominated neopentyl glycols.

Fire-retardant unsaturated polyesters find application in building panels, boat hulls, ventilation duct work, etc. Three to five percent antimony trioxide can be incorporated into the formulation as an additive to enhance the fire-retardant properties.

Epoxy Resins. A typical epoxy resin intermediate is the reaction product of epichlorohydrin and bisphenol-A. Curing of the epoxy resin intermediate involves a reaction with a hardening agent such as diamines or dibasic anhydrides. Fire-retardant properties can be incorporated into the epoxy resin either via the hardener, such as chlorendic anhydride, or via reactive intermediates, such as brominated bisphenol compounds. Reactive viscosity modifiers such as alkyl phosphates or aromatic phosphites do impart some degree of fire retardance to the cured epoxy formulation.

Fire-retardant epoxy formulations find wide use in electrical and electronic fields.

Polyurethane Foams. A polyurethane foam is the reaction product of an isocyanate and a polyol which has a chemical or mechanical blowing agent incorporated into the formulation. Fire-retardant properties can be imparted to polyurethane foams by replacing part of the conventional polyol with (1) halogenated polyols, (2) halogenated phosphorus-containing polyols, and (3) phosphorus-containing polyols. The degree of fire retardance will depend primarily upon the amount of the fire-retardant reactive polyol used in the final formulation.

Typical applications for fire-retardant polyurethane foams are in insulation and upholstery materials.

Additive Fire-Retardants

The majority of the commercially available non-plasticizing fire-retardant additives are halogen-based, and utilize antimony trioxide as a synergist to obtain optimum fire-retardant properties. There are both positive and negative factors associated with halogen-, phosphorus and nitrogen-type fire-retardant additives:

Chlorine-Based Additives. There are three broad structural catagories in this area – namely aliphatic, cycloaliphatic, and aromatic.

The aliphatic-type materials, such as chlorinated paraffins, are efficient fire-retardant additives where processing temperatures are below 400°F and dripping properties are acceptable. The aliphatic chlorine materials have found wide utility in fire-retardant polyethylene formulations for wire and cable applications. These materials enjoy the largest share of the total fire-retardant additive market.

The cycloaliphatic chlorine additives, based upon hexachloro-cyclopentadiene, are somewhat less efficient than the aliphatic chlorine materials, but have greater thermal stability which permits higher processing temperatures. Non-drip fire-retardant polymer formulations can be achieved with cycloaliphatic chlorine additives. These materials have found widespread application in polypropylene and in other polymers requiring processing temperatures in the order of 450°-500° F.

Interest in the aromatic chlorine products, such as the chlorinated biphenyls, has almost disappeared because of ecology problems. However, for the record, they are less effective as fire-retardant additives than the aliphatic or cycloaliphatic chlorine materials, but have excellent thermal stability. Compounds of this type can be processed upward to 600°F with long residence times.

Bromine Additives. There are two general classes of bromine compounds used as fire-retardant additives – aliphatic and aromatic. Aliphatic bromine additives are very effective as fire retardants. However, these materials have been limited in their use by low processing temperatures and drip characteristics.

Brominated aromatic additives are somewhat less effective than the aliphatic bromine additives, but can be processed at elevated temperatures without thermal degradation. In the past, brominated aromatics did not receive wide acceptance because of their high vapor pressures, resulting in poor heat aging characteristics. This disadvantage has been overcome recently by the introduction of a new generation of aromatic bromine compounds, such as the brominated biphenyls.

Phosphorus-Type Additives. To our knowledge there are few commercial fire-retardant additives available which are based solely upon phosphorus. There are phosphorus-containing additives incorporating phosphorus, bromine, and nitrogen, such as the phosphonium bromide materials. These phosphonium bromide-type additives have not achieved widespread acceptance as yet, but are effective additives for a wide range of polymers. Fire-retardant properties can be achieved with these materials without the use of antimony oxide.

Nitrogen-Type Additives. Ammonium fluoroborate is a nitrogen-type additive which has utility in polyolefins. Antimony trioxide is used in conjunction with ammonium fluoroborate to impart optimum fire-retardant properties.

Typical Formulations. The following formulations illustrate the utility of these materials as fire-retardant additives. The fire-retardant classification for each formulation is included.

Polyethylene (%)	82
Aliphatic Chlorine Source (%)	12
Antimony Trioxide (%)	6
Fire-Retardant Classification	Self-extinguishing; dripping

Polypropylene (%)	60
Cycloaliphatic Chlorine Source (%)	32
Antimony Trioxide (%)	8
Fire-Retardant Classification	Self-extinguishing; non-dripping

Nylon (%)	80
Cycloaliphatic Chlorine Source (%)	12
Antimony Trioxide (%)	3
Zinc Oxide (%)	3
Fire-Retardant Classification	Self-extinguishing; non-dripping

Polypropylene (%)	90
Aliphatic Bromine Source (%)	7
Antimony Trioxide (%)	3
Fire-Retardant Classification	Self-extinguishing; dripping

ABS (%)	80
Aromatic Bromine Source (%)	15
Antimony Trioxide (%)	5
Fire-Retardant Classification	Self-extinguishing; non-dripping

Polystyrene (%)	80
Cycloaliphatic Chlorine Source (%)	15
Antimony Trioxide (%)	5
Fire-Retardant Classification	Self-extinguishing; non-dripping

Polypropylene (%)	80
Phosphonium Bromine-Type, Additive (%)	20
Fire-Retardant Classification	Self-extinguishing; dripping

High-Impact Polystyrene (%)	75
Phosphonium Bromine-Type, Additive (%)	25
Fire-Retardant Classification:	Self-extinguishing; non-dripping

Polypropylene (%)	80
Ammonium Fluoroborate (%)	15
Antimony Trioxide (%)	5
Fire-Retardant Classification:	Self-extinguishing; dripping

Fire-Retardant Plasticizers

Among the plastics, polyvinyl chloride (PVC) is a special case with regard to fire retardancy. Rigid PVC is inherently fire retardant because of the chlorine in the polymer structure. Antimony trioxide may be added to improve its fire-retardant properties.

The addition of plasticizers, such as dioctyl phthalate, to rigid PVC lowers the chlorine content of the formulation, resulting in a more combustible material. A fire-retardant flexible PVC formulation can be achieved by replacing a portion of the conventional plasticizer with a fire-retardant plasticizer. Some of the commonly used fire-retardant plasticizers are (1) tricresyl phosphate, (2) tris (2, 3-dibromopropyl) phosphate, (3) triphenyl phosphate, (4) cresyl diphenyl phosphate, and (5) methylpentachloro stearate. These plasticizers may be used with antimony trioxide if required.

Some of the factors which must be taken into consideration when selecting a fire-retardant plasticizer for flexible PVC applications are (1) fogging, (2) low-temperature flex, (3) aging properties affected by compatibility and vapor pressure, and (4) the degree of fire retardance required for the end use.

Selection Of Fire-Retardant Systems

There are many fire-retardant systems available today. Selection of the best system for a specified end-use application must be based on many factors. Some of these factors to be considered in selecting a fire-retardant system follow:

Fire-Retardant Requirements. The first step in choosing a fire-retardant system is to define the fire-retardant requirements and flame test as dictated by the end-use application. Fire-retardant test methods are reviewed later in the article.

Thermal Stability. The thermal stability requirements of the fire-retardant additive are dictated primarily by the processing characteristics of the base polymer. An additive decomposing at or below the processing temperature of the base polymer cannot be used effectively. Usually discoloration or streaking of the molded or extruded object is a good indication of thermal instability. Excess thermal stability may not be desirable either, since the efficiency of the additive is usually inversely proportional to the thermal stability. Ideally, the fire-retardant additive should decompose near the flame temperature of the polymer composition.

Effect on Physical Properties. The addition of an additive to a thermoplastic polymer will have some effect on the physical properties of the polymer. The selection of the best-suited fire-retardant additive is made on the basis of its effect on the most critical physical property requirements. An accurate prediction of the effect an additive will have on any one of the physical properties of a polymer cannot be made without an actual evaluation. Properties of the fire-retardant additive which change the physical properties of the polymer are (1) particle size of the additive, (2) melting point of the additive, (3) compatibility of additive with polymer system, (4) solubility of additive in polymer at processing temperatures as well as room temperature, (5) physical state of additive (liquid or solid), and (6) effective loading level.

Effect on Electrical Properties. For electrical applications, the base polymer is picked because of its electrical properties. Therefore, the fire-retardant polymer must retain the electrical properties of the base polymer. Factors which adversely affect the electrical properties of the base polymer are (1) water sensitivity of the fire-retardant system, (2) characteristics of the char upon burning, (3) electrical conductivity of the fire-retardant additive, and (4) void formation during processing.

Compatibility. Compatibility of the fire-retardant additive in a polymer formulation cannot be accurately measured. Blooming is usually evidence of the lack of compatibility of the additive with the polymer system. Blooming, over an extended period of time, can reduce the fire-retardant property. Blooming may be a function of the vapor pressure of the additive or its tendency to undergo sublimation.

Aging Characteristics. There are two types of aging tests – heat aging and water aging. The conditions for both heat aging and water aging are dictated by end-use applications. Factors which lead to high weight loss upon heat aging are (1) high vapor pressure of the fire-retardant system, (2) poor compatibility of the additive in a polymer system, (3) sublimation tendency of the additive, and (4) melting point of the additive.

The water aging test measures either weight loss or weight gain. A weight loss indicates the additive is moisture-sensitive and may be leached upon exposure to atmospheric moisture. Weight gain measures the uptake of water by the additive in the polymer system. Either weight gain or weight loss suggests the additive will have an adverse effect upon the electrical properties of the base polymer.

Price/Performance Relationship. This factor is perhaps the most important, and one which may be the most difficult to resolve. So often the choice of an additive is made on price alone, rather than the properties it imparts to the polymer system. To obtain a true price/performance relationship, a great deal of testing and formulation optimization must be carried out.

Fire-Retardant Test Methods

There is much confusion in selecting a reliable flame-test method. Many test methods are available with varying degrees of reproducibility. Therefore, it is advisable to use more than one flame-test method for evaluation purposes. The following tests represent a cross-section of the types of flame-test methods presently being used. These test methods are (1) Underwriters' Laboratories 94 (UL-94), (2) ASTM D-635, (3) Department of Transportation (DOT) 302, (4) Limited Oxygen Index (LOI), and (5) Pill Test.

UL-94. This test was developed by Underwriters' Laboratories for materials used in electrical applications. It can be used to measure both vertical and horizontal flame characteristics; however, the vertical test is more severe and more widely used. This test can be used to measure flameout, afterglow, and dripping characteristics. Flame-retardant ratings are given in accordance with the thickness of the test specimen. Generally speaking, the thicker the test specimen the better the fire-retardant rating.

ASTM D-635. The ASTM D-635 horizontal test method is a laboratory tool in determining relative flammability of rigid plastic over 0.05 inches in thickness. Ratings, based upon ten individual specimens tested, as non-burning, self-extinguishing, and burning are given by this test. This test also distinguished between dripping and non-dripping formulation.

DOT 302. The DOT 302 horizontal test method was developed to measure the flammability of interior components of automobile and truck passenger compartments. This standard, effective September 1, 1972, establishes a 4 inches per minute horizontal burn rate.

LOI. The LOI test method is a vertical test. However, unlike the UL-94 test, the flame is at the top of the specimen. This test is becoming widely accepted as a very reproducible test which can be duplicated from laboratory to laboratory. The LOI test method measures the amount of oxygen required to support combustion and is highly recommended as a screening test. Dripping formulations tend to distort the LOI values.

Pill Test. The pill test is a horizontal flame test method designed to measure the flammability of carpets. The methanimine pill is the constant fuel source for the test. The rating obtained from the pill test is either pass or no pass, with no flame-spread rating developed.

Other test methods which are widely accepted for specific end-use applications are the UL-83 (wire and cable test method), UL-E84 tunnel test, and the NBS chamber test for carpets.

Test specimen conditioning dictated by the fire-retardant test method must be followed.

Compounding of Fire-Retardant Formulations

Uniform dispersion of the fire-retardant system in the polymer formulation is mandatory to obtain consistent fire-retardant properties. Factors to be considered in compounding fire-retardant polymer formulations are (1) particle size of the fire-retardant additive, (2) density of the fire-retardant additive, (3) melting point of the fire-retardant additive, (4) loading level required, (5) solubility of the additive in the system, (6) processing temperatures of the base polymer and the thermal stability of the additive, (7) melt index of the base polymer, (8) type of blending equipment – dry blend vs. melt blend, and (9) other fillers used in the formulation.

To insure obtaining good commercial fire-retardant polymer compositions consistently, it is necessary at some point in the processing for good melt blending to occur. Melt blending can be achieved in batch or continuous melt blend equipment or in a properly designed compounding extruder.

Suppliers of Flame Retardant Products

The listings that follow were developed from responses to two waves of questionnaires sent to companies known to make and thought to make products in the appropriate categories. They include all companies who responded in time, and no others.

Thermosetting resins or compounds which are self-extinguishing or flame resistant or retardant

Allied Chemical Corp., Plastics Div.
BASF Wyandotte Corp.
Bacon Industries, Inc.
Cincinnati Development & Mfg. Co.
Cosmic Plastics Inc.
Diamond Shamrock Chemical Co.
Dow Chemical Co.
Dow Corning Corp.
Durez Div., Hooker Chemical Corp.
El Monte Chemical Co.
Fiberfil Div., Dart Industries
Fiberite Corp.
General Electric Plastics (Pittsfield)
General Electric Plastics (Waterford)
Glastic Corp.
Halby Chemical Co., Inc.
Hardman Inc.
Haysite Div., Synthane-Taylor Corp.
Isochem Resins Co.
Interplastic Corp., Commercial Resins Div.
Marplex, a Hitco Co.
Pacific Resins & Chemicals, Inc.
Plastics Engineering Co.
Premix, Inc.
The Pultrusions Corp.
Raychem Corp.
Ren Plastics, Inc.
Rogers Corp.
Rohm and Haas Co.
Symplastics, Inc.
Tra-Con, Inc.

Thermoplastic resins or compounds which are self-extinguishing or flame resistant or flame retardant

Air Products and Chemicals, Inc., Plastics Div.
Allied Chemical Corp., Plastics Div.
Amoco Chemicals Corp., Plastics Div.
Ampacet Corp.
Carborundum Corp.
Celanese Plastics Div.
Dover Chemical Corp.
Eastman Chemical Products, Inc.
Enjay Chemical Co.
Fiberfil Div., Dart Industries
General Electric Plastics (Pittsfield)
General Electric Plastics (Selkirk)
B.F. Goodrich Chemical Co
Halby Chemical Co., Inc.
Hercules Incorporated
LNP Corp.
Marbon Div., Borg Warner Corp.
Monsanto Polymers & Petrochemicals Co.
Neville Chemical Co.
Novamont Corp.
Pennwalt Corp., Indchem Div.
Phillips Petroleum Co.
Polymer Materials Inc.
K.J. Quinn & Co., Inc.
Raychem Corp.
Rohm and Haas Co.
Swift Chemical Co.
U.S. Industrial Chemicals Co.
Wellman, Inc.

Flame Retardants–Additive Types

Antimony-based

Americhem, Inc.
Anderson Development Co.
Chemetron Corp., Chemicals Group
Dover Chemical Corp.
East Coast Chemicals
Harshaw Chemical Co.
Hooker Chemical Corp.
Humphrey Chemical Corp.
Isochem Resins Co.
M & T Chemicals, inc.
Nichem Corp.
Novamont Corp.
Pacific Resins & Chemicals, Inc.
Podell Industries Inc.
Reed Plastics Corp.

Boron-based

Anderson Development Co.
Buckman Laboratories, Inc.
GAF Corp.–Chemicals Div.
Halby Chemical Co., Inc.
Humphrey Chemical Corp.
Nichem Corp.
Podell Industries Inc.
Reed Plastics Corp.
U.S. Borax & Chemicals Corp.

Halogen-based

Anderson Development Co.
Buckman Laboratories, Inc.
Canadian Industries Ltd.
Cities Service Co.
Diamond Shamrock Chemical Co.
Dover Chemical Corp.
Dow Chemical Co.
East Coast Chemicals Co.
Fine Organics, inc.
GAF Corp.– Chemicals Div.
Great Lakes Chemical Corp.
Halby Chemical Co., Inc.
Hooker Chemical Corp.
Humphrey Chemical Corp.
Isochem Resins Co.
Keil Chemical Co., Inc.
Michigan Chemical Corp.
Monsanto Industrial Chemicals Co.
Nichem Corp.
Novamont Corp.
Pacific Resins & Chemicals, Inc.
Pearsall Corp.
Phillips Petroleum Co.
Raychem Corp.
Reed Plastics Corp.
Universal Oil Products Co.– Chemicals Div.
Velsicol Chemical Corp.
White Chemical Corp.

Phosphorous-based

Anderson Development Co.
Buckman
East Coast Chemicals Co.
GAF Corp.– Chemicals Div.
Great Lakes Chemical Corp.
Hooker Chemical Corp.
Isochem Resins Co.
M & T Chemicals Inc.
Michigan Chemical Crop.
Monsanto Industrial Chemicals Co.
Nichem Corp.
Reed Plastics Corp.
Weston Chemical, Inc.
White Chemical Corp.

Other (Incl. fillers and reinforcements)

A & S Corp. (ammonium sulfamate)
Aluminum Co. of America (hydrated alumina)
Engelhard Minerals & Chemicals Corp.
Humphrey Chemical Corp.
Mineral Products Div., GLFS Co. (hydrated alumina)
Monsanto Industrial Chemicals Co.
N.L. Industries, inc.- Pigment & Chemicals Div.
Ottawa Silica Co. (silica sand & flour)
Phillips Petroleum Co.
Rohm & Haas Co. (plasticizers)
Eli Sandman Co. (fillers & reinforcements)

Flame Retardants–Reactive Types

Halogen-containing

BASF Wyandotte Corp.
Dow Chemical Co.
East Coast Chemicals Co.
GAF Corp.–Chemicals Div.
Great Lakes Chemicals Corp.
Hooker Chemical Corp.
Isochem Resins Co.
Michigan Chemical Corp.
Millmaster Chemical Co.
Monsanto Industrial Chemicals Co.
Neville Chemical Co.
Nichem Corp.
Stauffer Chemical Co., Specialty Chemicals
Swift Chemical Co.
Universal Oil Products Co.– Chemical Div.
Velsicol Chemical Corp.
White Chemical Corp.

Phosphorous-containing

BASF-Wyandotte Corp.
East Coast Chemicals Co.
Great Lakes Chemical Corp.
Hooker Chemical Corp.
Michigan Chemical Corp.
Millmaster Chemical Co.
Nichem Corp.
Podell Industries Inc.
Swift Chemical Co.
Stauffer Chemical Co., Specialty Chemicals
Weston Chemical, Inc.
White Chemical Corp.