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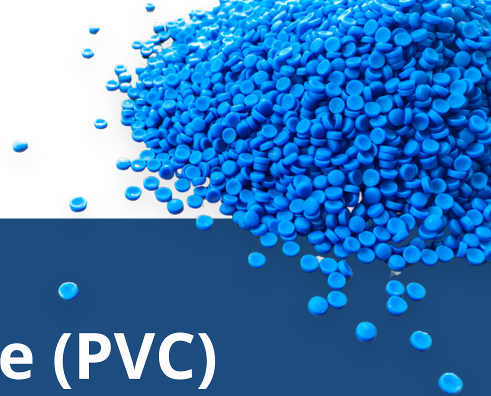

Replacement of brominated flame retardants in polyvinyl chloride (PVC)

What are flame retardants?

The most common, effective and cost-effective method of obtaining fire-resistant polymer materials, in particular PVC compositions, is the use of flame retardants. They are chemicals that are intentionally added to plastic to slow down or prevent the spread of fire. They act through various mechanisms depending on the type of flame retardant used.

The largest group of substances used to reduce the flammability of PVC materials is halogenated flame retardants. Overall, this group accounts for approximately 25% of global production of all flame retardants.

The effectiveness of halogen-containing flame retardants increases in the F-Cl-Br-I series. Chlorine- and bromine-containing compounds are most often used as flame retardants, as they provide the best price/quality ratio.

Bromine-containing flame retardants are much more effective than chlorine-containing ones, since the products of their combustion are less volatile. In addition, chlorine-containing flame retardants emit chlorine in a wide temperature range, so its content in the gas phase is low, and bromine-containing flame retardants decompose in a narrow temperature range, thus ensuring the optimal concentration of bromine in the gas phase. Flame retardants with bromine compounds are easily recycled due to their high level of heat resistance.

Polybrominated diphenyl ethers (PBDE) flame retardants, widely used in PVC formulation, have been the subject of intense scrutiny for negative health effects on humans, animals, and other organisms, particularly because of evidence for biological activity at low concentrations.

Threat level

The production of PVC plastics in Ukraine is estimated at 40-60 thousand tons/year, of which about 20% is produced using halogenated flame retardants. With a flame retardant content of about 0.01% (100 mg/kg), this corresponds to an annual release of 800-1200 kg of halogenated (mostly brominated) flame retardants onto the market and, ultimately, into the environment.

Halogenated flame retardants are released into the environment in a variety of ways – as emissions during production, from products during use, as well as through incineration, leaching from landfills, or recycling at the end of the product's life.

Since their introduction, brominated flame retardants have become widespread global pollutants and have been found worldwide in air, water, soil, sediment, silt, dust, bivalves, crustaceans, fish, amphibians, reptiles, birds, mammals, and human tissue.

The main ways for brominated flame retardants to enter the human body are through food, inhalation, and dust in residential and industrial premises. For the general public, food is considered the main source of exposure. The most brominated flame retardants are highly soluble in lipids, so oily fish, fish oil, and fatty animal products are potential sources of flame retardants.

The results of studies on humans and animals indicate a correlation between exposure to brominated flame retardants and adverse health effects, namely thyroid disorders, hepatotoxicity i neurotoxicity, immunotoxicity, reproductive toxicity, effects on fetal/child development, neurological function, cardiovascular disease and cancer. Therefore, it is very important to replace brominated flame retardants with safer alternatives.

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Safer alternative

The problem of reducing the flammability of plasticized materials based on polymer and copolymers of vinyl chloride is tried to be solved by using heat-stable, flame-resistant and low-volatile plasticizers, which most often are various halogen and phosphorus-containing organic compounds (FOC). It is believed that when using FOC, the reduction in the flammability of polymeric materials mainly depends on the amount of introduced phosphorus, which should be at least 5% by weight in the composition.

Phosphorus-containing flame retardants belong to the group of the most effective flame retardants. Red phosphorus, phosphates and polyphosphates, phosphazenes and polyphosphazenes are most often used as additives to polyvinyl chloride compositions to reduce both the flammability and burnability of materials. The consumption of flame retardants of this type is growing at the fastest rates, which is due to their ability to reduce the flammability of the material and the density of the smoke formed during combustion, as well as the excellent chemical and physical characteristics of the materials, containing FOC-flame retardants, and, as a result, the possibility to obtain materials with reduced fire hazard.

The effect of FOC flame retardants is revealed in the condensed phase and leads to a decrease in burnability and flammability. The mechanism of action of FOC-flame retardants is due to the formation of oxides and acids of phosphorus, which physically protect the underlying layers of the material from the reaction with oxygen, or with the regulation of their oxidation in the direction of the reaction with a significantly lower exothermic effect.

Most phosphorus flame retardants are non-toxic and do not tend to bioaccumulate. They are easily integrated into the polymer matrix without compromising the mechanical properties of PVC.

One of the latest development in FOC-flame retardants is polymeric salt of benzyl[(4-chloromethyl)phenylethyl]phenylethyl(4-vinylbenzyl)phosphonium chloride] that added in an amount of 0,05-0,5 pts wt. into a composition containing 100 pts wt. of PVC; in this case the phosphorus content in the compositions was 0.0003%–0.003% by weight. Its synthesis is based on the use of cheap red phosphorus.

During burning, a protective film is formed on the surface of samples containing the flame retardant. This was proved by the decrease in flammability, loss of mass, increase in ignition delay time, decrease in smoke-generating ability. This film protects the surface of the sample from evaporation of the plasticizer and decomposition of the material itself. A similar effect is achieved by introducing tricresyl phosphate into the composition in a multiple amount corresponding to a phosphorus content of 10.3%.

The latest bio-phosphorus flame retardants are derived from renewable sources, namely lignin, phosphorylated proteins, starch derivatives, and chitosan. They are environmentally safe, are under development, and are promising for use in flexible PVC. The most common non-halogenated alternatives to brominated flame retardants in PVC compositions are shown in Table 1.

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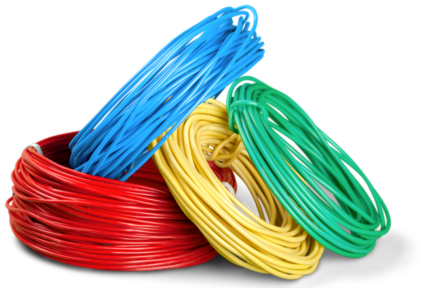

Table 1: Halogen-free alternative flame retardants in PVC

Substance	CAS	Function	Toxicity
Cresyl diphenyl phosphate (CDP)	26444-49-5	Combines the functions of flame retardant and plasticizer. Used in flexible PVC. High thermal stability.	Moderate toxicity
Triphenyl phosphates (TPP): Triaryl phosphates butylated	115-86-6 68937-40-6		
Resorcinol bis(diphenylphosphate) (RDP)	57583-54-7 125997-21-9	Acts as a flame retardant and plasticizer. High stability and low smoke generation. Used in flexible PVC for the production of films, cables and facing materials.	Toxic to aquatic ecosystems
Diethylphosphinic acid, aluminium salt	225789-38-8	Highly effective in combination with other flame retardants. Used in PVC for electrical materials and the cable industry.	Low toxicity
Red phosphorus	7723-14-0	Effective at low doses. Chemically binds to the polymer. Used in rigid PVC for specialized applications.	Practically no environmental impact
Ammonium polyphosphate (APP)	14728-39-9 68333-79-9	Used in rigid and flexible PVC for cables. Stable	Non-toxic, non-bioaccumulative
Melamine polyphosphate	218768-84-4	Used in flexible PVC. The combination of nitrogen and phosphorus increases fire resistance (up to 320°C).	Low toxicity
Melamine cyanurate	37640-57-6	Good thermal stability at prolonged heating up to 300°C.	Moderately toxic
Aluminium trihydroxide (ATH)	21645-51-2	Used in PVC compositions for cable insulation. Thermally stable up to 200°C.	Safe for humans and the environment
Magnesium dihydroxide (MDH)	1309-42-8	Used in PVC compositions for cable insulation. Thermally stable up to 300°C	Safe for humans and the environment

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