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Fluoride Scavenger STF

Melt Processing fluoropolymers releases several harmful and corrosive transformation products. Hydrofluoric acid is among the many acidic transformation products formed. However, less acidic products no less toxic are formed with loss of weight from the polymer. Thermal stabilization of fluoropolymers is sometimes complicated by other additives that tend to compromise the polymer during melt processing by attacking and releasing free acid causing black specks during extrusion. This is the case when basic additives used to provide UV stabilization to polyolefins come in contact with fluoropolymers. Also included in the mix are metallic stearates and primary amides.

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Control of this process has been problematic since classical so called acid acceptors and acid buffers used in traditional polyolefins do not perform the same and are less effective in control of this form of acid formed from fluoropolymers.

Studies with several fluoropolymers show the following:

Polyvinylidene fluoride

Polymeric structure, $-(\text{CH}_2\text{-CF}_2)_n-$

Excellent resistance to degradation at temperatures below 200°. However, Above 350°C, thermal decomposition may occur with hydrogen fluoride evolved. In one study, heating in the range 400 to 530°C resulted in 35% hydrogen fluoride and high yields of products volatile at 25°C. Other reported decomposition products include carbon monoxide, carbon dioxide and organic fluorine.

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Perfluorinated ethylene-propylene copolymers

Polymeric structure, $-(CF_2-CF_2)_n-.....-(CF_2-CF(CF_3))_m-$

FEP is a copolymer of tetrafluoroethylene and hexafluoropropylene. Its structure resembles PTFE except for the random replacement of a fluorine atom with a perfluoromethyl group (CF₃). The introduction of hexafluoropropylene lowers the melting point of PTFE to around 260°C enabling it to undergo conventional melt processing.

Thermal decomposition of FEP is found to start at 205°C to give mainly carbonyl fluoride and trifluoroacetyl fluoride. The rate of decomposition increases with temperature, from 0.0004% per hour at 230°C to 0.3% per hour at 370°C. In humid air carbonyl fluoride is instantly hydrolysed to hydrogen fluoride and carbon dioxide and trifluoroacetic acid and hydrogen fluoride are formed from trifluoroacetyl fluoride. Perfluoroisobutylene has been identified at heating temperatures in the region of 500°C, when decomposition occurs in air.

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Perfluoroalkoxyfluorocarbon resin

Polymeric structure, -CF₂-CF₂-CF(OC₃F₇)-CF₂-

PFA contains a fluorocarbon backbone as its main chain and randomly distributed perfluorinated ether side chains. These added side chains reduce the crystallinity of the molecule; the melting point is 305°C (between that of PTFE and FEP).

Decomposition of PFA is reported to begin at 230°C and the rate is a function of both temperature and time. Reported decomposition products include fluorinated hydrocarbons (fluoro-olefins), carbonyl fluoride (at temperatures around 450°C) and hydrogen fluoride (Kirk-Othmer Encyclopedia of Chemical Technology). Perfluoroisobutylene is reported to be formed at around 500°C when decomposition occurs in air.

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Ethylene chlorotrifluoroethylene

Polymeric structure, $-(\text{CH}_2-\text{CH}_2)_n-\dots-(\text{CF}_2-\text{CFCl})_m-\dots$

Decomposition of ECTFE reportedly begins at 260°C. Thermal decomposition products may include fluorinated hydrocarbons (fluoro-olefins), chlorinated hydrocarbons and hydrogen fluoride. Traces of carbonyl fluoride and carbonyl chloride are evident at around 450°C.

A study of the pyrolysis of polychlorotrifluoroethylene ($-(\text{CF}_2-\text{CFCl})_n-$) in air (Birnbaum et al, 1968) showed a particle distribution of 85% of particles less than 1µm diameter and 99% less than 2µm. Analysis of the breakdown products showed many species including carbonyl fluoride and COFCl and COCl containing groups.



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Polytetrafluoroethylene

Polymeric structure, $-(CF_2-CF_2)_n-$

The melting point of PTFE is 327°C. Decomposition begins at around 230°C (Kirk-Othmer Encyclopedia of Chemical Technology) and it is reported that polymer fume fever may result when even trace amounts of PTFE heated in the range 315 to 375°C are inhaled (Patty's Industrial Hygiene and Toxicology).

When heated to temperatures below 500°C it is reported that particulate is generated with possible absorbed substances such as fluorinated acids and olefins (Patty's Industrial Hygiene and Toxicology).

Tetrafluoroethylene monomer has been detected from PTFE heated to 440°C and perfluoroisobutylene (highly toxic) at 475°C. Hexafluoroethane, hexafluoropropylene and octafluorocyclobutane have also been identified as pyrolysis products (Zapp et al, 1959). It is thought that the main PTFE polymer is cleaved into smaller chains as a result of heat, not necessarily in the presence of oxygen. Further cleavage gives the fragment difluorocarbene, $CF_2:$, and these combine to form tetrafluoroethylene $CF_2=CF_2$. Further reactions of the monomer with $CF_2:$ would then give hexafluoroethane and perfluoroisobutylene. Octafluorocyclobutane could be formed by the dimerisation of tetrafluoroethylene (Waritz and Kwon, 1968).

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At heating temperatures in the range 500 to 650°C carbonyl fluoride has been found to be predominant and above 650°C carbon tetrafluoride and carbon dioxide were the major products (Coleman et al, 1968). Other species detected include hydrogen fluoride, trifluoroacetyl fluoride (from the oxidation of the free radical CF₃CF₂) and trifluoroacetic acid (from trifluoroacetyl fluoride in the presence of water vapour) (Arito and Soda, 1977). These products result from competing reactions which can occur in the presence of air. The end groups of the cleaved fragments can react to give carboxylic acid fluoride end groups which can then hydrolyse to carboxylic acids and HF. Difluorocarbene, CF₂, can react in a similar manner to give carbonyl fluoride which at high temperatures can form carbon tetrafluoride or hydrolyse in the presence of water vapour to form HF and CO₂.

Carbonyl fluoride is reported as the dominant vapour-phase product of PTFE degradation under oxidative conditions whereas perfluoroisobutylene is the major product in the absence of oxygen (Shusterman, 1993). Oxidation is not necessary to produce the toxic effect from fluoropolymer degradation (Seidel et al, 1991).

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In our studies with a new form of acid scavenger called STF-1 and the series of STF fluoride scavengers tailored for levels of HF formed by the fluoropolymer we find total mediation of the corrosive hydrofluoric acid and levels of other species mediated to the extent that loss of weight is controlled at levels from 1 to 3% active of the neat additive during processing in humid air environment.

In the case of FEP the level of hydrogen fluoride produced was found to range from 0.98-1.2 mg/m³. With addition of 2% STF-1 total elimination of hydrogen fluoride and 98% retention of weight at processing temperatures of 280-300C. No carbonyl fluoride was detected while the control showed levels in excess of 40 mg/m³.

In the case of ECTFE the level of hydrogen fluoride produced ranged from 2 to 25 mg/m³. With addition of 2% STF-1 total elimination of hydrogen fluoride and 97% retention of weight loss at process temperatures of 250 to 300C. No carbonyl fluoride was detected while the control showed levels in excess of 8 mg/m³.



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Control of VOC (volatile organic compounds):

In addition to HF formation other semi-volatile compounds were detected by GCMS which included toluene, chlorinated hydrocarbons, benzene, octadecyl chloride and acetates, cyclohexane, methyl styrene, butyl alcohol, acetic acid, benzaldehyde, phthalates and traces of benzene; etc. Control and or total elimination of these VOC type compounds is controlled by the addition of STF-2 which contains a clathrate structure found to capture VOC and HAP (Hazardous airborne pollutants).

Recommendation:

Clearly the optimal level of the fluoride scavenger is up to the user. We recommend starting with 3-5% levels and working down to lower levels to optimize weight loss and corrosion.

The additive is extremely thermally stable and does not contribute to antagonisms with other additives nor cause major discoloration due to breakdown in the polymer. The product selectively and chemically reacts in-situ with acidic HF and other fluoride species while trapping these transformation products before they can function in side reactions to destroy the polymer.

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The additive and its series of analogs are all TOSCA and EINECS registered and GRAS approved. The proprietary nature of the additive and its analogs does not limit the use of these products in non fluorinated polymers including chlorinated resins prone to formation of hydrogen chloride.