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Additives in Plastics

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The polymers used in plastics are generally harmless. However, they are rarely used in pure form. In almost all commercial plastics, they are "compounded" with monomeric ingredients to improve their processing and end-use performance. In order of total volume used, these monomeric additives may be classified as follows: reinforcing fibers, fillers, and coupling agents; plasticizers; colorants; stabilizers (halogen stabilizers, antioxidants, ultraviolet absorbers, and biological preservatives); processing aids (lubricants, others, and flow controls); flame retardants; peroxides; and antistats. Some information is already available, and much more is needed, on potential toxicity and safe handling of these additives during processing and manufacture of plastics products.

The polymers used in plastics are generally harmless. However, they are rarely used in pure form. In almost all commercial plastics, they are "compounded" with monomeric additives to improve their processabilty and to modify their end-use properties and product performance. Some limited information is already available on the health hazards which may be involved in their use. Much more information is needed to insure worker safety in manufacturing operations. As a guide to industrial health scientists working in this field, the monomeric additives used in plastics manufacturing are classified here, in approximate order of total volume now in use in the United States.

Fillers and Reinforcements

Fibers

Fibers are frequently added to plastic materials to improve their rigidity, strength, toughness, and dimensional stability (*1, 2*). These so-called "reinforced plastics" totalled 1.2 billion pounds in 1972.

Glass: The most common reinforcement in plastics is glass fibers, generally used at 10-50% of the total composition by weight. Some are woven, but most are chopped to 2 in. or shorter, and some are actually chopped and sprayed in a single operation. The use of glass fiber involves considerable direct manual labor. Since glass fiber is frequently irritating, the use of gloves, ointments, and masks is fairly common.

Asbestos: Asbestos fibers offer the advantages of low cost plus heat and flame resistance. They are most commonly used in vinyl flooring, where the weight of asbestos can greatly exceed the weight of vinyl resin. They also find increasing use in flame-retardant polypropylene and in other special high-temperature plastic products. In recent years they have been recognized as a serious lung hazard, and the industry is currently working on improving health safeguards in manufacturing. Once incorporated in the plastic, they are believed to be harmless.

Wood Flour: The oldest reinforcing fiber in the plastics industry is finely powdered wood flour, used in phenolic plastics since 1908. Safety should be similar to that of sawdust in carpentry, and no problems appear to arise from its use.

Future Developments: Increasing use of glass fiber in reinforced thermoplastics, which can be reground and remolded, may bring new hazards and require new precautions as this portion of the industry reaches its major

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growth stage. New reinforcements, such as carbon fibers and later whiskers, should be examined to determine worker safety in their use.

Fillers

Fillers are primarily common inorganic mineral powders, added to improve processing, rigidity, dimensional stability, hiding power, and costs (*1,2*). As common natural powders, they do not bring any new health hazards into the plastics industry. Most common are calcium carbonate, clays, and silicates, often used in quantities exceeding the polymers themselves. The largest use is in vinyls, with smaller amounts in polyesters and other plastics families.

Coupling Agents

Since inorganic fibers and fillers are so different from organic polymers, it is often beneficial to apply a surface treatment to bond them more firmly together and thus improve strength and water resistance. The most common are reactive organosilanes, such as vinyl or aminoalkyl triethoxysilanes. Another type often used is methacrylatochromic chloride. While they are usually applied to the inorganic surface before compounding, they are sometimes added directly during compounding. Concentrations are generally small.

Plasticizers

Plasticizers (*2–4*) are high-molecular-weight monomeric liquids of high boiling point, added to vinyl and cellulosic plastics to improve their processability, and particularly their flexibility and softness. They are generally used in concentrations of 20–50% or more of the total plastic composition. During processing they volatilize slightly, so that most plants provide some types of ventilation for worker protection. Some have general or limited FDA approval, others do not.

Phthalates

The most common are dialkyl esters of *o*-phthalic acid, primarily the octyl esters—2-ethylhexyl, "iso-octyl," and more recently *n*-octyl, generally referred to as general-purpose plasticizers. Others run from dimethyl up to ditridecyl, generally chosen to balance compatibility and softness against low volatility. While generally considered harmless, there has been some recent concern in specialized applications such as blood bags, so the general safety of their use in manufacture may require more careful study of ventilation standards.

Phosphates

Organic phosphate esters, such as cresyl, phenyl, and octyl, are often used for flame retardance and heat resistance. While food contact caused some cases of poisoning a generation ago, recent practice has improved to the point that some are considered quite harmless.

Epoxidized Esters

Epoxidized soybean oil, as well as tall oil and oleic esters, are frequently used in vinyls, at concentrations of about 5 phr (parts per hundred of resin), as combined plasticizers and stabilizers. Some of these are acceptable to FDA.

Linear Aliphatic Esters

Dialkyl esters of adipic, azelaic, and sebacic acid are frequently used for low-temperature flexibility. They have not brought any health problems.

Polyesters

Linear polyesters of 1000–5000 molecular weight are viscous liquids and can be fairly effective as plasticizers. Their high molecular weight makes them more permanent, which is the reason for their use. Thus they should be safer to handle as well. This would have to be weighed against their low efficiency as plasticizers.

Colorants

Whereas conventional materials are post-colored on their surface, plastics are generally integrally colored throughout. Large quantities of colorants are therefore used for their decorative value in plastic products (*3,4*).

Inorganics

Most colorants are inorganic pigments. Titanium dioxide is by far the most common, used for its high whiteness and hiding power. Iron oxides are second most common. More specialized pigments based on cadmium, chromium, and molybdenum are coming under increasing critical scrutiny for toxicity, in both FDA and toy applications.

Organics

A wide variety of organic colors, both incompatible pigments and compatible dyes, are used in plastics; their use is increasing, to replace the suspect inorganics mentioned above. Some of these organics have received FDA approval, others have not.

Stabilizers

Organic polymers are not generally stable enough for satisfactory processing and long-term use. Almost all of them are improved by the addition of small quantities of stabilizers, generally 0.1 to 10.0% (*2–4*). There are several major classes.

Halogen Stabilizers

Poly(vinyl chloride) tends to lose HCl during hot processing and also during long-term use. This can be retarded successfully by any of several families of thermal stabilizers.

Barium-Cadmium-Zinc-Epoxy-Phosphite: The most common stabilizer system for vinyls is a complex synergistic mixture of barium soap, cadmium soap, zinc soap, epoxidized fatty ester, and organic phosphite ester. The metal soaps are based on naphthoic, ethylhexoic, lauric, or stearic acids or on phenols. While zinc is generally safe and barium fairly so, cadmium is under scrutiny for its toxicity. Since cadmium is the most powerful part of the stabilizer system, its loss would be a major problem. The epoxidized fatty esters have already been described above. The organic phosphite esters may be alkyl, aryl, or mixed alkylaryl; some have FDA approval. Concentrations are about 1 phr of each ingredient.

For FDA applications, calcium soap is used in place of barium and cadmium but produces much weaker stabilization.

Lead Compounds: Lead compounds provide a strong stabilizing effect and also improve electrical insulation. They may be either neutral or basic salts of inorganic acids such as silicates and sulfates, or of organic acids such as maleic and stearic. They are generally used at 3–8 phr in wire and cable insulation and in flooring. With recent concern over lead in paint and gasoline, there may be increasing concern with these lead stabilizers even in processing.

Organotin Compounds: The most powerful stabilizers for vinyls are the dialkyltin diesters such as maleate and laurate, and the dialkyltin mercaptides such as the octyl thioglycollate. The two alkyl groups are most often butyl, more recently octyl for FDA approval, and most recently methyl for economy. Concentrations are generally 1–3 phr. Because of their high cost, use is restricted largely to rigid vinyls, where the need is greatest.

Antioxidants

Most organic polymers are subject to atmospheric oxidation, particularly during hot processing. They are most often stabilized by additives which retard the oxidative reactions. Most common is butylated hydroxytoluene (BHT), first used as a food preservative. Many other hindered phenols and their sulfide dimers are also in use. Some have FDA approval. Less common are aromatic amines, generally less acceptable to FDA. The polymers which require most of these antioxidants are the polyolefins, rubber, and rubber-containing plastics such as impact styrene and ABS.

In addition to the hindered phenols, several other classes of stabilizers are added as synergists: dilauryl and distearyl thiodipropionates, organic phosphite esters such as tris(nonylphenyl) phosphite—some of them acceptable to FDA—and metal deactivators such as hydrazides and triazoles for use in insulating copper wire.

Concentrations run from tenths of a percent up to 1% or more.

Ultraviolet Absorbers

Atmospheric oxidation of most polymers is accelerated by ultraviolet light from the sun.

Therefore plastics for outdoor use are frequently stabilized against ultraviolet light specifically. The most common stabilizers are ultraviolet absorbers such as *o*-hydroxy benzophenones and *o*-hydroxyphenyl benzotriazoles. Since these are very expensive, they are rarely used in concentrations over a few tenths of 1%. Salicyclic esters, though much weaker, are sometimes used because they are cheaper. Organonickel synergists are sometimes added, particularly in polyolefins. Carbon black is particularly effective where opaque black products are acceptable. The greatest use is in polyolefins.

Biological Preservatives

Mold and fungus can make some plastics unsightly, and even deteriorate properties, particularly where there are monomeric ingredients such as plasticizers for them to feed on. There are a variety of additives which may prevent such attack. Copper quinolinate, trichloromethyl phthalimide, and quaternary ammonium compounds are typical. Organomercurials are in disfavor because of toxicity to humans. Tributyltin oxide is useful but causes odor in processing. Diphenyltin diethylhexoate has received EPA approval for baby pants and mattress covers.

Processing Aids

A great variety of materials are added in small amounts to improve processing. Concentrations may range from a few tenths of a per cent up to several per cent in different systems (*3,4*).

Lubricants

Lubricants improve melt flow either by lowering melt viscosity or by reducing adhesion of the plastic melt to the metal surface past which it is flowing. Both ways they give faster, more economical processing. Calcium, zinc, and lead stearates, petroleum and polyethylene waxes, and fatty esters and amides are the most common types. The lead stearate should obviously be used with caution; the others are not known to present problems.

Other Processing Aids

Plastisol viscosity depressants are frequently ethoxylated fatty acids.

Mold release agents are used in trace amounts to reduce sticking of the finished molding in the mold. Most common types are waxes, silicones, fluorocarbons (powdered polytetrafluoroethylene dispersions), metal stearates, powdered polyethylene, mica, and talc.

Emulsifiers generally remain in polymers made in emulsion and are also added to latexes for stability during processing. These come in a tremendous variety of types—anionic, nonionic, and cationic.

Antiblocking (slip) agents keep film from sticking during processing. Some fatty esters have FDA approval. Waxes, metal soaps, poly(vinyl alcohol), polyethylene, polyamides, silicones, fluorocarbon polymers, and inorganic silicates and silica may also be used.

Antifog agents are actually added to film and sheet to reduce fogging by water vapor. They are often modified fatty esters.

Flow Controls

In formulating plastisols, rheology is often very important, for example, in cloth coating and foaming. Viscosity can be increased by gellants such as modified clays (montmorillonite), metallic soaps (calcium), and quaternary ammonium compounds.

Flame Retardants

Flammability of organic polymers can be reduced by organophosphorus compounds and especially their halogenated esters, heavily brominated or chlorinated organic compounds, and antimony oxide acting as a synergist for the halogens (*3–6*). Concentrations are often 10–20%. Use is expected to increase rapidly due to increased concern with product safety.

Peroxides

Peroxides are used mainly for cure of glass-reinforced polyesters, for specialty elastomers such as EPR and silicone rubber, and for cross-linking of polyethylene as in wire and cable insulation. Benzoyl peroxide and methyl ethyl ketone peroxide are most common, with a wide variety of others used in small amounts. Peroxides are often used in conjunction with amines, cobalt naphthenate, and similar compounds as accelerators. Peroxide concentrations may run from tenths of a per cent up to several per cent. While their long-term toxicity has not been discussed, immediate hazards such as fire and explosion have caused a few industrial accidents, and cautious handling has always been recommended. In view of the number of small operators in polyester processing and manufacture, the safety record is gratifying.

Antistats

Since plastics are electrical insulators, they tend to hold any charge which builds up on them accidentally. During processing this can cause annoying clinging and even dangerous sparking. During use it can cause accumulation of dust. To reduce such static build-up, antistatic agents are often added. Most common types are amines, quaternary ammonium compounds, organic phosphates, and polyoxyethylene glycol esters. Some have FDA approval.

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