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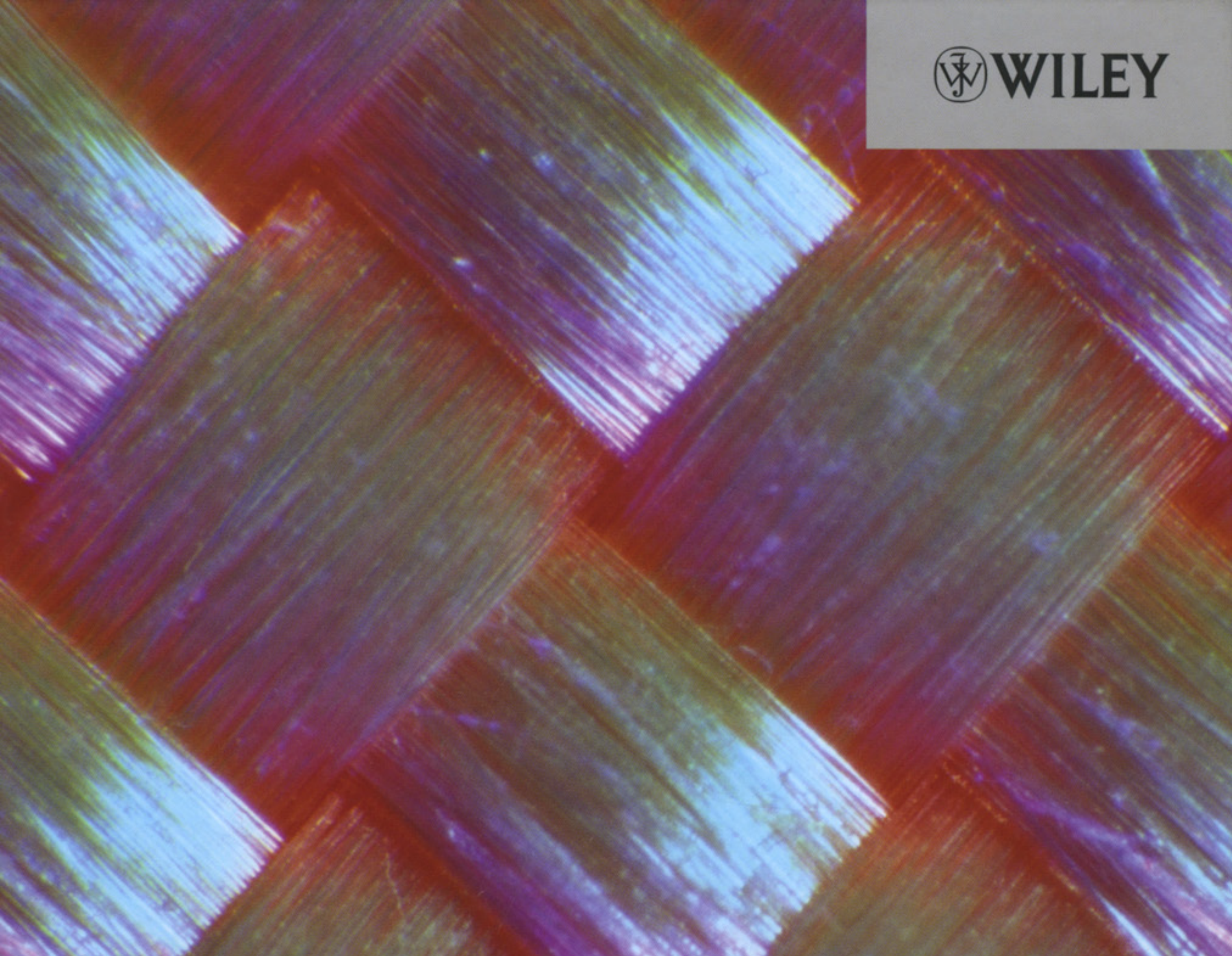

Processing and Finishing *of* Polymeric Materials

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Processing and Finishing of Polymeric Materials

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PREFACE

Owing to their versatility and wide range of applications, polymeric materials are of great commercial importance. Manufacturing processes of commercial products are designed to meet the requirements of the final product and are influenced by the physical and chemical properties of the polymeric material used.

The two-volume set **Processing and Finishing of Polymeric Materials** offers over 45 self-contained articles written by prominent scholars from around the world. The articles provide comprehensive, up-to-date information on key manufacturing technologies, including blending, compounding, extrusion, molding, coating, and more.

Containing carefully selected reprints from Wiley's renowned *Encyclopedia of Polymer Science and Technology* and additional sources that also appear online, as well as new contributions, this reference features the same breadth and quality of coverage and clarity of presentation found in the original. This reliable reference will be of particular interest to polymer and materials scientists, chemists, chemical engineers, process engineers, students, researchers, and educators in related fields, and consultants and suppliers in the plastic and related industries.

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ADDITIVES

Introduction

Additives for plastics are typically organic molecules that are added to polymers in small amounts (typically 0.05 to 5.0 wt.%) during the manufacture, melt processing, or converting operations so as to improve the inherent properties of the polymeric material. Additives can be categorized in three major segments: polymer modifiers, performance enhancers, and processing aids. Pigments and Colorants are not covered in this review. Additives used exclusively in elastomers are also excluded (Antiozonants, curing accelerators, and vulcanizing agents). The global market for plastics additives in 2007–2008 timeframe was estimated in the order of $ 32 billion in value and over 12 million tons in volume when plasticizers are included (1). When the commodity plasticizers (ca. 50% of additives volume) are omitted, then global consumption was about 4.7–5.5 million tons with value ranging from $16–19 billion (2). Poly(vinyl chloride) (PVC) by far is the largest consumer of additives (the combined volume of plasticizers and property modifiers account for 74% of global plastic additives). Polyolefins and styrenics together are the second largest volume consuming group. Global additives market growth rates for the time-period 2004–2009 were forecasted to be 4–5% annually, with China growing at 10% per year and the group of North America, Europe, and Asia (ex-China) growing at 3% each annually. The future growth of plastic additives depends on the growth of the various plastics resins and in turn on the market segments consuming plastics (mainly packaging, automotive and construction). (3).

Polymer modifiers are used primarily to alter the physical or mechanical properties of the plastic. These include plasticizers, foaming (blowing) agents, coupling agents, impact modifiers, organic peroxides, and nucleating/clarifying agents. Polymer modifiers continue to account for about 11% of the total volume in 2004 of all additive classes.

Performance enhancers are added to plastics to provide functionality not inherent to the polymer itself. These include Flame Retardants (FRs), Heat Stabilizers for PVC, Antioxidants, Light Stabilizers/light-filters, Biocides, and Antistatic Agents. A newer additive family includes conductive carbon black and carbon nanotubes, graphenes, & organic conducting polymers to impart an antistatic, electromagnetic shielding or a conductive effect to plastics or paints/coatings. Performance enhancers account for 24% of the total global additives market (3) and are led by FR's with an approximate value of $827 million in the United States with 3% annual growth rate through 2011 (4).

Processing aids are typically surface-active agents that are added into plastics converter operations to improve throughput and alter the surface properties of the finished article. Additives in this class include lubricants, slip agents, antiblocks, and mold-release agents. In 2005 this class accounted for 7% of global additives volume.

A key driver of change and new product development in the plastics additives markets is a variety of environmental concerns. This has been seen most dramatically in PVC where concerns over the use of heavy-metal heat stabilizers based on lead have motivated a widespread conversion to tin-based materials and even to nonmetallic stabilizers. The widely used phthalate-based Plasticizers for flexible PVC have come under scientific and regulatory scrutiny because of concerns over their potential adverse effects on the human reproductive systems. Concerns over the potential for certain brominated FRs to form dioxins are driving the development of new halogen-free systems.

Furthermore in very recent years there are growing concerns over the environmental sustainability of plastics driven both by high crude oil prices *(affecting raw material costs of monomer feedstreams for plastics manufacture)*, high consumer demand for plastics *(e.g. beverage packaging)*, and environmental impacts associated with accumulation of plastics in the environment. In response major end-users and brand owner corporations are being challenged, and in turn are challenging the plastics industry value-chain participants to develop strategies and technologies for the enhanced recycling and reuse of plastics. One example is a so-called "Wal-Mart effect" where this major global retailer developed a scorecard for suppliers to document their efforts to satisfy sustainability goals such as energy usage, material efficiency, and natural resources (5,6). For plastics additives producers this has created renewed interest in additives that enable the reuse of post-consumer recycled (PCR) plastics into new or higher-valued applications. Examples include the recycling of used polyester (PET) carpeting into new beverage bottles, or sanitizing and upgrading of post-consumer PET bottles to allow new bottles to be molded using a portion of recycled PET content (7).

Plastics additives are used extensively in food packaging and as such are regulated by the U.S. Food and Drug Administration (FDA) (and related international agencies) as indirect food additives. Regulation by the FDA of a new additive requires submission of toxicity as well as migration data from the polymer in question into a variety of food simulants so as to calculate estimated daily intake. The level of migration and anticipated annual usage determines the extent of toxicity testing that is required. Information on the petition process for obtaining regulations as well as a directory of all indirect food additives can be obtained through the FDA website www.fda.gov.

Additives are incorporated into polymer matrices by a variety of methods and at various points in the manufacturing process. Polymer producers typically incorporate additives as single components or as blends of two or more additives during the polymer pelletization/isolation step. Converters and transformers often introduce additives as a concentrate or master batch or liquid dispersion. A *concentrate* is a mixture of an additive dissolved in a polymer resin carrier at fairly high (10 – 30%) concentrations. A *master batch* is a blend of additives and often pigments in a resin carrier designed for a specific end-use application. In a *liquid dispersion* additives or colorants are dispersed or suspended in an inert or reactive liquid carrier such as a mineral oil, aliphatic glycols or alkylene esters along with proprietary dispersants. Such liquid systems are directly injected into converting machinery via a peristaltic metering pump.

Modifiers

Plasticizers. Plasticizers, through their use in flexible PVC, are the largest volume polymer additives used in plastics. Flexible PVC accounts for nearly 90% of the volume of plasticizers used in plastics. Plasticizers are added at very high loadings (up to 80%) depending on the degree of flexibility required. Plasticizers are added to inherently hard thermoplastics to increase the flexibility, softness and/or extensibility. In addition, secondary benefits of improved processability, greater impact resistance, and higher ductility can often be achieved.

Plasticizers are often used as carriers for pigments and are the liquid vehicle for PVC plastisols. Plasticizers are predominately esters produced through the reaction of an acid or anhydride with a linear or branched alcohol (8). Typical examples are di- or tri-substituted esters produced by the reaction of phthalic anhydride [88-44-9] with linear or branched alcohols varying in chain length from C_4 to C_{11} such as with 1-butanol [71-36-3], 2-ethyl-1-hexanol [104-76-7] and 1-octanol [111-87-5]. While somewhat interchangeable, performance properties such as low temperature flexibility, volatility, processability, and extractability are governed by chain length and degree of branching. For example in interior automotive PVC applications, the octyl phthalates have been replaced by isodecyl phthalates because of their lower volatility and thereby enhanced fogging resistance.

The remaining plasticizers are more specialty in nature. Aliphatics are typically 2-ethylhexyl esters of dibasic acids, such as glutarates, adipates, or sebacates. The primary use of aliphatics is when low temperature flexibility and crack resistance are required. When very low volatility and low migration is required, the plasticizers of choice are based on esters of trimellitic anhydride [552-30-7]. A typical application for mellitates is in PVC wire and cable jacketing or automotive interiors which require excellent long-term heat aging properties and extraction resistance. In these applications lower volatility plasticizers such as diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP) are replacing dioctyl phthalate (DOP) plasticizers. For particularly demanding performance applications, dibasic acids are polymerized with diols to produce low molecular weight polymeric plasticizers. Esters of phosphorus oxychloride [10026-87-3], the phosphate esters, are typically used as FRs and also impart plasticizing properties. A final class are the epoxies, with epoxidized soybean oil [8013-07-8] (ESBO) being the most common (epoxies based on tall oils and linseed oil are also available). While primarily added as secondary thermal stabilizers in PVC because of their ability to scavenge HCL generated during processing, as plasticizers they exhibit excellent extraction resistance and low migration.

Market drivers for plasticizers today and near future include strong consumptive growth of PVC in the China, continued global consumption of PVC in construction and automotive markets, and ongoing concern in North America and Europe over toxicological implications of DOP plasticizers, the latter driving commercialization of aforementioned non phthalate plasticizers (DIDP, DINP). Polymer processors are switching to DOP alternatives, in the short term are 2-ethylhexyl phthalates and longer term new products such as diisononyl cyclohexane-1,2 dicarboxylate (DINCH) [474919-59-0], (9).

Typically the large producers of plasticizers are backward integrated into either alcohol and phthalate anhydride or both. The key suppliers of the commodity plasticizers in North America are BASF (Palatnol®, Hexamoll®), Eastman (Eastman), and ExxonMobil (Jayflex). Worldwide consumption of plasticizers is about 6 million tons/year. The Chinese market is the highest global volume consumer of plasticizers (34%) followed by Asia (22%), Europe (18%), North America (15%) (10).

Foaming (Blowing) Agents. *Chemical blowing agents* are inorganic or organic additives that produce a foamed structure. They are used extensively in PVC but also in polyethylene (PE), polypropylene (PP), and polystyrene (PS) to improve properties and appearance (insulation against heat and noise, better stiffness, removal of sink marks in injection-molded parts, and improved electrical properties) as well as to reduce parts weight. Chemical-blowing agents can be classified as either physical or chemical. They are typically added via a concentrate or master batch (11). The total market for blowing agents in North America is near 10 kilotons and near 200 kilotons worldwide with China consuming 50% volume. In North America, volume growth is anticipated to move with the construction market segments including foamed plastic-wood composite decking, windows and doors, and composite fence materials (12).

Physical blowing agents are volatile liquids or compressed gasses that are dissolved in the polymer and change state during processing to form a cellular structure. *Chemical blowing agents* (CBAs) decompose thermally during processing to liberate gasses that form a foamed product. Organic CBAs typically are solid hydrazine derivatives that generate nitrogen in an *exothermic* reaction. Most common is azodicarbonamide [123-77-3], which in pure or modified form accounts for up to 80% of all CBAs. It beings to compose at 390°F. However this product was recently banned in Europe with North America to follow, for use in gaskets that are in contact with food substances, to be replaced by alternative *endothermic* blowing agents (12). Other types are the sulfonyl hydrazides {most common is 4,4′-oxybis(benzenesulfonyl hydrazide) [80-51-3] which is used for low temperature applications} and p-toluene semicarbazides {most common is p-toluenesulfonyl semicarbazide [10396-10-8] which is used in high temperature applications such as acrylonitrile-butadiene-styrene (ABS), poly(phenylene oxide) (PPO), nylon, and high impact polystyrene (HIPS)}. High gas yields and pressures for *exothermic* CBAs make them useful in applications such as crosslinked PE and extruded products. Chemtura and Lanxess are the leading producers of these products in North America. *Endothermic* CBAs are based on blends of inorganic carbonates and polycarbonic acids both emitting carbon dioxide. Proper combination of these materials allows for operating temperature ranges of 150–300°C. A common commercial system is based on citric acid [77-92-9] and sodium bicarbonate [144-55-8]. Endothermic CBAs generally produce a lower gas yield providing foams with smaller cell structure than do exothermic CBAs.

Coupling Agents. Coupling agents promote adhesion between polymers and inorganic fillers by forming stable chemical bonds between the organic matrix and the surface of the filler. The highest usage of coupling agents is in the treatment of glass fibers for use in thermosets such as epoxies and polyesters. Other fillers include clay, silica, mica, wollastonite, calcium carbonate and aluminum trihydrate (ATH).

The most common type of coupling agent is the organosilanes. Silanes have the general structure RSi(OR')3, where R is a functionalized organic group that binds to the polymer matrix (i.e., amino, epoxy, acrylate, or vinyl) and R' is typically methyl or ethyl. The methoxy or ethoxy groups hydrolyze to silanols which react with surface hydroxyl groups on the inorganic fillers to form oxane bonds. The result is improved mechanical or electrical properties. Amino silanes are typically used for epoxy and phenolic rsins, epoxy silanes for epoxy resins, and methacrylate silanes with unsaturated polyesters. Fillers are typically pretreated with an aqueous dispersion of silane at levels of 0.2–0.75%. The treated fillers are then reacted with the polymer matrix during compounding. The silane improves wetting during the compounding process thereby reducing the surface tension of the organic-inorganic interface for better dispersion. Evonik and Momentive are major suppliers of silanes in North America.

In addition to silanes, a variety of organometallics (primarily titanates but also zirconates, aluminates, and zircoaluminates) area used as coupling agents, although in significantly lower volumes. While mechanistically similar, titanates are more versatile than silanes because they can react with a broader range of fillers (i.e., calcium carbonate). However they are more susceptible to hydrolysis. Titanates are often used as dispersing agents for fillers in polyolefins by reducing the surface energy of the filler, resulting in better impact strength, lower melt viscosity, and better aged mechanical properties. In North America DuPont and Kenrich are the primary suppliers of organometallics.

A specialty class of coupling agent are the maleated polyolefins (13). The pendant maleic anhydride unit reacts with surface hydroxyl groups (or siloxy group in the case of pretreated fillers) while the polymeric portion cocrystallizes with the polymer matrix. Their main applications are in glass-filled PP composites and in non-halogenated FR wire and cable applications. The addition of 1–2% maleated PP can improve the tensile strength of a 30% glass-filled PP by up to 40%. In FR applications, 4% maleated PE in a PE/EVA (polyethylene/ethylene-co-vinylacetate) blend containing 65% ATH gives up to three times improvement in elongation. The maleic anhydride reacts with the basic inorganic FR, fillers, ATH, and magnesium hydroxide (14). Maleated polyolefins are marketed in North America by Chemtura, DuPont, Eastman and ExxonMobil as major suppliers.

A relatively new class of property modifiers are chain extenders additives. These function to increase polymer molecular weight by reactively combining polymer endgroups. Some chain extenders can be used to produce alloys of two dissimilar polymers through reactive coupling. Renewed interest in these additive technologies has arisen in part to public and industry interest in improving the sustainability of plastics, in particular by improving the quality and properties of recycled polyesters and polyamides (7). Recycled PET and PA can be reused into higher valued articles such as fiber or incorporating a portion of PET recyclate into beverage bottle manufacture (15–17). Suppliers of these chain extenders include BASF (Joncryl®), DSM (ALLINCO).

Organic Peroxides. Organic peroxides are used in the plastics industry to catalyze polymerization reactions or to modify the properties of polymers (18,19). On the polymerization side, peroxides are used as initiators for PVC, low density polyethylene (LDPE), polystyrene (PS), and acrylics. As modifiers for existing polymers, peroxides are used for the curing of unsaturated polyester resins, as cross-linkers of PE silicones, and a variety of ethylene-based elastomers and to break down the molecular weight of polypropylene in a process known as *visbreaking* or *controlled rheology* (20). Peroxides function through the thermal decomposition of the unstable peroxide bond to generate two free radicals. The reactivity of the peroxide is modified by altering the organic substituents attached to the peroxide or through the use of coadditive promoters. The reactivity of the peroxide is defined by the *ten-hour half-life temperature*, or the temperature at which one-half of the peroxide decomposes in a 10-h period. The lower the 10-h half-life temperature, the more reactive is the peroxide. Organic peroxides fall into seven basic groupings depending on the organic substituent. These are dialkyl peroxides, diacyl peroxides, hydroperoxides, ketone peroxides, peroxydicarbonates, peroxyesters, and peroxyketals (21).

The choice of organic peroxide used for initiating polymerizations is dictated by the polymerization temperature used to produce the polymer. The low temperatures used for PVC polymerization, for example, dictate the use of organic peroxides with low 10-h half-life temperatures. For the higher polymerization temperatures used for LDPE, an organic peroxide with a higher 10-h half-life temperature may be used. When used as polymerization catalysts, organic peroxides are typically used in the 0.1–0.5% range. Approximately half of all organic peroxides by volume are used in the various polymerization processes.

Unsaturated polyesters are produced through the cross-linking of low molecular weight polyester resins and comonomers such as styrene present at 1.0–2.5% based on resin weight. Fillers, pigments, and reinforcements such as glass fiber are often added. Depending on the cure temperature, co-catalyst promoters are often used. For room-temperature cures and resin-transfer molding, organic cobalt and copper promoters are added to the ketone peroxides, which are typically used. Unsaturated polyester resin production is the largest single application of organic peroxides, accounting for 30–40% of total consumption.

For the cross-linking of ethylene-based polymers for applications such as wire and cable jacketing and tubings, peroxides are added during compounding/processing at levels of 0.2–0.4%. In the visbreaking of controlled-rheology PP similar levels are used, to reduce the molecular weight and melt viscosity of the polymer. Controlled-rheology PP is particularly common for fiber and extrusion grades. When peroxides are used together with other additives, particularly antioxidants, a careful balance of concentrations must be chosen since the radicals formed during thermal decomposition can react with the other additives, lowering the effective concentrations of each (19).

A new specialty technology for the vis-breaking of PP utilizes a hydroxylamine ester as an alternative to organic peroxides. The additive is incorporated into the extruder of a meltblown nonwoven fiber line where a controlled visbreaking occurs to produce PP of high melt flow rate. Reported advantages are the production of non-wovens exhibiting improved air permeability and thermal stability (22,23). Key suppliers of organic peroxides in North America include

Akzo Nobel (Trigonox, Perkadox) and Arkema (Luperox). The supplier of hydroxylamine ester is BASF (Irgatec® CR).

Impact Modifiers. Impact modifiers function by absorbing the impact energy and dissipating it in a nondestructive manner. Typically impact modifiers are elastomer materials and are added to a wide range of thermoplastic materials at levels up to 20%. The major types of impact modifiers are acrylics, styrenics including methacrylate-butadiene-styrene (MBS) copolymers and acrylonitrile-butadiene-styrene copolymers, chlorinated polyethylene (CPE), EVA copolymers, and the ethylene-propylene copolymers and terpolymers. The major market for impact modifiers is in PVC, although they are used in a wide range of other polymers such as polyolefins and engineering polymers.

MBS is the highest volume of the styrenic types. These terpolymers consist of an elastomeric core with a hard outer shell, which provide good impact resistance together with excellent processibility. Typically used in transparent PVC packaging because of its good clarity, its market growth has slowed as PET and polyolefins have replaced PVC in packaging applications. Because of poor weatherability owing to the butadiene component, outdoor applications are limited. Kaneka and Rohm and Haas are the major producers.

ABS is used in a variety of resins with PVC again being the major market. Similar to MBS, ABS suffers from poor weatherability and is therefore useful in outdoor applications only when a uv-resistant capstock is applied.

Acrylics are the fastest growing impact modifiers because of their usage in exterior PVC siding and profile. While they function in the same way as MBS and ABS, the graft phase is based on butyl or ethylhexyl acrylates which are far more uv-stable than butadiene. Arkema, Kaneka, and Rohm and Haas are the major producers in North America.

EPDM and EPR are used to modify polyolefins, primarily in the automotive industry. The largest volume is in automotive PP bumpers. This application is being replaced by impact-resistant polymer produced by metallocene technology, providing better performance and economics. Dow, Dupont, and Exxon are leading producers in North America. When used with plastics such as nylon, PET, and PBT, the EPDM and EPR are often modified with a functionalized monomer to allow them to react with these plastics. Additionally, the shell of a core-shell modifier can be modified to include a reactive group.

CPE is most widely used in PVC, although it does find applications in polyolefins. It can only be used in opaque applications but it does have excellent weatherability, making it useful for PVC pipe, siding, and profiles. Dow is the leading producer in North America.

Nucleating/Clarifying Agents. Materials added to semicrystalline plastics prior to processing and fabrication, which affect the rate of crystallization and spherulite size, are referred to as *nucleating agents*. These are typically insoluble or immiscible materials which provide sites for crystal formation. The main benefit for the addition of nucleating agents is improved cycle time during injection molding. When the addition of nucleators decreases the size of the crystallites to less than the wavelength of visible light, these agents are referred to as *clarifying agents* because they reduce haze and improve transparency (25).

For nucleation of nylon and PP, sodium benzoate [532-32-1] is the traditional material of choice. Use levels are on the order of 0.1% with injection-molded packaging closures being a major application. Sodium benzoate does not impart any improvement in optical properties. Low molecular weight polyolefins, ionomers, as well as plasticizers such as ESBO are used for nucleation of semicrystalline plastics such as PET. Modified benzylidene sorbitols dominate the market for nucleation and clarification of PP. They are used at 0.1–0.3% levels in both homopolymer and copolymers, with injection-molded housewares, medical devices such as syringes, and other packaging being the major applications. Metal salts of organic phosphates have been introduced for nucleation/clarification of PP as well as newer non-sorbitol technology (26,27).

Talc and other minerals are often used as nucleators. In North America, Amfine (AdekaStab North America), BASF (Irgaclear®), and Milliken (Millad) are key suppliers.

Property Extenders

Antimicrobials/Biocides. Biocides are used to provide protection against mold, mildew, fungi, and bacterial growth on the surface of polymers. Left unchecked, these organisms can grow on plastic surfaces resulting in discoloration, odor, and parts failure. Since they function by being toxic to the microorganisms which cause growth, biocides are considered as pesticides under the Federal Insecticide, Fungacide and Rodenticide Act and as such are carefully regulated by the U.S. EPA (and in Europe under the Biocides Product Directive (BPD)). All end-use applications and related performance claims must be registered through the EPA and supported with toxicity, safety, handling, environmental, as well as efficacy data. Since microorganisms grow at the surface of plastics, in order to be effective biocides must migrate. Their rate of migration is closely related to their efficacy (28).

The primary use of biocide additives is for flexible PVC which has dropped from 70 to about 60% of total demand in the past decade as other plastics applications are developing or replacing PVC. While PVC is inherently resistant to microbial attack, the phthalate plasticizers are quite susceptible. Moisture contact and external factors such as uv-exposure can increase susceptibility by providing surface crazing/defects as sites for growth. Typical applications for biocide use in PVC are pool and pond liners, outdoor furniture, marine upholstery, roofing membranes, garden hoses, shower curtains, and wire and cable jacketing. Use of biocides in polyolefins is growing with applications such as children's toys and furniture, kitchen utensils, cutting boards, and trash bins. Biocides are also used in a variety of engineering polymers (PET, PA), and in PUR foams.

A variety of organic and inorganic biocides have been developed for use in plastics, including arsines, isothiazolinones, chlorinated phenols, silver, and zinc compounds. Among the arsines, 10,10′-oxybisphenoxyarsine (OBPA) [58-36-6] is the most common and is used at an active level of 0.02–0.05%. A typical isothiazolone is 2-n-octyl-4-isothiazolin-3-one (OIT) [26530-20-1]. These are used at levels of 0.1–0.15% and are available as a concentrate in a plasticizer (either dialkylphthalate or ESBO). Zinc-2-pyridinethianol-1-oxide [13463-41-7] (commonly known as omacide or zinc omadine) and trichlorophenoxyphenol [3980-34-5] (Triclosan) are other common biocides. A variety of silver based biocide products have emerged, functioning primarily as bactericides. They have comparatively safe toxicological profiles, and in some cases are approved for food or water-contact applications or for medical applications. Well over 20 producers of biocide additives and formulated products exist. Due to the costs and risks to develop and register formulated biocide products, typically the producers of biocide compounds do not provide formulated products. In North America, some biocide producers & formulators include Akros Chemicals, Arch Chemicals, BASF, Ferro, and Rohm and Haas. The global market for biocides used in plastics is about 15 kilotons.

Antioxidants. Polymers may become oxidized during melt processing and fabrication, and end use resulting in loss of aesthetic and mechanical properties. This thermally induced autooxidation results in the formation of free radicals which will react with oxygen to form hydroperoxides. These hydroperoxides are themselves thermally unstable and their ensuing decomposition results in polymer chain scission, cross-linking, and the formation of color chromophores. The extent of these decomposition processes depend on the particular polymer and the exposure environment. In order to inhibit the initiation of polymer oxidation and to retard the resulting destructive chemical processes, antioxidants are added during the manufacture, processing, and/or during fabrication of plastic articles (29,30). The global market for antioxidants in 2004 was estimated to be 700 million pounds or $750 million, the largest volume region being Asia-Pacific (excl. China) at 34% with Europe and North America at 25% each (31).

Traditional antioxidants are classified as either primary or secondary types depending on their mode of action. Primary antioxidants act by trapping free radicals, usually hydroperoxy radicals, through donation of a labile hydrogen to the radical species. Secondary antioxidants interfere with the propagation steps of autooxidation by decomposing hydroperoxides to form stable, nonradical species. It is quite common for a combination of primary and secondary antioxidants to be used to provide the maximum stabilization of a plastic. Use of antioxidants in plastics is ubiquitous, since nearly all polymer types require some form of stabilization in order to provide useful and durable materials.

The two most common classes of primary antioxidants are the aromatic amines and hindered phenols. Aromatic amines, such as substituted diphenylamines are extremely effective, acting as both radical chain terminators and peroxide decomposers. A major drawback of aromatic amines is their tendency to form highly discolored oxidation products during use (hence sometimes called staining antioxidants) (32). As a result their use is restricted to applications where discoloration is not an issue, such as carbon black filled or pigmented systems. As such their major usage is in the rubber industry. In plastics a major application is black wire and cable jacketing. Chemtura (Naugard), Eliochem (Wingstay), Lanxess (Vulkanox) are among the leading suppliers of aromatic amines. For stabilizing end-use articles, relatively high levels of amine are used – typically 0.5–1.0 wt%. When used as a storage stabilizer for polyols which in turn are used in polyurethane (PUR) manufacture, lower levels (typically 500–2000 ppm) are used. The standard primary antioxidants used in plastics are based on hindered phenols which in turn are usually based on derivatives of 2,6-di-*t*-butylphenol [128-39-2] (BHT). While highly effective, BHT is volatile and is susceptible to discoloration upon oxidation. In order to improve on the properties of BHT, a host of analogues have been developed. These modifications generally involve either altering the hindering alkyl groups or changing the substituent in the 4-ring position. In order to improve on the volatility of BHT, antioxidants with two, three, and four hindered phenols linked together are available and commonly used. Hindered phenols are effective both during polymer processing and during end use. Typically they are used in combination with a secondary antioxidant to maximize their effectiveness during high temperature processing and to minimize color formation resulting from the over-oxidation of the phenol. Use levels of 0.1–0.5% are common. Hindered phenols are available from a number of producers, with BASF (Irganox®) and Chemtura (Anox, Lowinox) are the two leading volume producers in North America and globally. Non-traditional antioxidant compounds are used in niche applications. Vitamin E (α-tocopherol) [10191-41-0], a high molecular weight but extremely reactive phenol has found use primarily in food-contact packaging applications because of its effectiveness at low levels (100–200 ppm) and its 'green' image. Its major limitation is its tendency to form highly discoloring chromophores upon oxidation. Another stabilizer class, the hindered-amine light stabilizers (HALS) can be used as antioxidants when use temperatures are below 135°C, primarily in polyolefins (33). The primary benefit of using a HALS as an antioxidant their oxidation products are colorless unlike aromatic amines or hindered phenols. Since HALS do not provide higher temperature stability they must be used in conjunction with a melt-processing stabilizer such as phosphites.

Secondary antioxidants generally fall into two classes: the organophosphites and thioesters. Organophosphites are typically trivalent arylphosphites which react with hydroperoxides in the polymer to generate a pentavalent phosphate and a nonreactive alcohol. Phosphites are effective at the high temperatures used in polymer processing but do not provide any stabilization during end-use. As such they are nearly always used with hindered phenols in practical applications. Tris-nonylphenylphosphite [26523-78-4] has been commonly used ranging from 500–1500 ppm, but is being replaced in some cases by more complex arylphosphites with improved hydrolytic stability. There is also increasing scrutiny about the health effects of nonylphenol that can be produced via hydrolysis of the phosphite). BASF (Irgafos®), Chemtura (Ultranox) and Clariant (Sandostab) are major suppliers. Thioesters are derivatives of 2,2′-thiobispropionic acid [5811-50-7], the most common being the lauryl esters, dilaurylthiodipropionate [128-28-4], and stearyl esters, distearylthiodipropionate [693-36-7]. In contrast to the arylphosphites, thioesters are active at the lower end-use temperature range 125–150° C and are often used in combination with hindered phenols to stabilize polyolefins for under-the-hood automotive applications. They are not active as melt-processing stabilizers. The primary drawback of thioesters is poor organoleptic properties, which limit their use in food-contact applications. Typical use levels are in the range of 1.0–1.5%. BASF (Irganox), Cytec (Cyanox) and Chemtura (Argus) are major suppliers in North America.

Alternative antioxidant systems (34–36) include higher performing stabilizers which can be used at low levels with enhanced ancillary properties such as low color and odor. Dialkylhydroxylamines used in combination with HALS provide an excellent, low color stabilization system for PP fiber.

Antistats. Due to their low low electrical conductivity (surface resistivity in the order of 10^{15}–10^{17} ohm/sq), plastics are known for their ability to accumulate electrostatic charges. The static charge can be generated during processing, transportation, handling, or final use, and typically occurs because of friction between the plastic and another material. The build up of static charge leads to a number of undesirable properties such as dust/dirt buildup, solids buildup on walls of plastic containers during filling, clinging effects during fabrication or conversion of films, destruction of electronic parts packaged in plastic materials, and ignition of vapors or particulates. A number of approaches have been developed to address these problems including topically applied antistatic additives, carbon black and other conductive fillers, intrinsically conductive polymers, and the classical migratory additives such as ethoxylated amines and glycerol monostearates (37). The total market for antistats in North America is estimated to be $ 30 million. Polyolefins, styrenics, and PVC consume the majority of antistatic agents.

For nondurable applications, topical, external antistats can be applied to the finished plastic article through dipping or spraying of the part. The most common type is the quaternary ammonium salts or "quats", which are typically applied as a water or alcohol solution. Since these materials are easily removed during handling or use, they are only effective for relatively short duration (<1 year). For more durable applications, internal antistats added during compounding have been developed. The classical systems have a lipophilic tail which remains in the bulk phase of the polymer while a hydrophobic head migrates to the polymer surface to form a moisture-absorbing layer allowing for static dissipation. These systems rely on migration of the additive and sufficient humidity to form the moisture layer. The most common type of migratory antistat is the nonionics, essentially surfactants. This class is dominated by the ethoxylated alkylamines and alkylamides, and fatty acid esters like glycerol monostearate. In the ionic antistat family examples are metal salts of alkylsulfonates and alkylphosphates. These antistats are effective a lower loadings (<2%), require at least 50% relative humidity, have an induction time before being active, can ultimately be wiped or washed from the surface compromising their permanence, and can have adverse surface effects such as plate-out and poor printability. To achieve the optimum blend of performance characteristics (permanence versus fast induction time) a blend of fast and slow migrators can be used (38). Key suppliers of migratory antistats in North America are Akzo (Armostat), BASF (Laurostat), Croda (Atmer).

In order to improve on the performance of the classical migratory antistats with respect to permanence and humidity sensitivity, newer approaches have been developed. These include inherently conductive polymers (ICP), conductive fillers, and hydrophilic polymers. The most common ICPs are based on polyaniline, a highly conjugated polymer which is converted to a cationic salt with an organic acid. The relatively high cost has relegated these materials to niche, albeit high value applications (39).

Fillers such as carbon black and nickel-coated graphite have good permanence but can affect mechanical properties and are highly colored. The hydrophilic polymers also known as static dissipative additives, have experienced good growth rate over the past decade as permanent antistat technologies. These are based typically on segmented copolymers of polyether and either polyamide or polyester blocks. They develop a conductive network in the host plastic when used at 10–30% loadings. These types of permanent antistats are available in North America from Arkema (Pebax), BASF (Irgastat®), DuPont (Entira). Typical applications are to dissipate static electricity buildup in business machines such as fax and copier parts in typically HIPS and ABS plastics, electronic parts packaging transport trays in HIPS and polyesters.

Starting in the mid 1990's new electrostatic dissipative additives based on conductive carbon nanotubes (CNTs) moved from research to commercial products. Carbon nanotubes have a very high aspect ratio (long length to small diameter particles). What once were research curiosities have become commercial products as the production optimization has improved the yield, quality and purity and prices are now in the range of $100/pound or lower (40,41). A desirably low surface or volume resistivity can be achieved with low concentrations of CNTs (2–5%) allowing a low percolation threshold where a conductive network is formed. At such low loadings the bulk mechanical properties of the host plastic are not compromised as sometimes occurs with static dissipated polymers discussed earlier. Disadvantages of CNTs are their black color which affects the transparency and coloration when used in plastics. Also their dosage into host polymers must be carefully controlled to achieve sometimes narrow static dissipation target values. Masterbatch forms of CNTs are available from some suppliers to facilitate proper letdown into the host plastic, yet again careful attention to proper extrusion or injection molding parameters is required to ensure adequate dispersion of CNTs occur for optimum static dissipative performance. Major suppliers of CNTs include Arkema (Graphistrength), Bayer (Baytubes), Hyperion Catalysis (FIBRIL), Nanocyl.

Flame Retardants. Worldwide consumption of flame retardants for plastics was nearly 1.7 million tons in volume and $4.2 billion in 2007 (excluding textiles & rubber applications). North America had the largest volume share of FRs (30%) share followed by Europe and Asia (ex-China) about 25% each and China at 17%. In North America ATH was the single largest FR class in volume due to its comparatively low cost, with brominated products next at 16% volume, followed by phosphate esters (1). These chemical additives in plastics inhibit ignition and retard the spread of flame. Flame retardants (FR) can be categorized as one of the following families by their mechanistic function (42,43):

(1) **Char Formers**: Typically phosphorus-based organic compounds which when burned provide a physical and insulating barrier between the flame and the fuel or polymer.

(2) **Heat Absorbers**: Examples include aluminum trihydrate (ATH) or magnesium hydroxide which decompose at high temperatures to generate water and in turn removes heat from the system through evaporation. Additionally they form glassy oxide barrier layers.

(3) **Radical Sources**: Typical are brominated or chlorinated hydrocarbons. They act by interfering with the radical-chain mechanism occurring in the gas phase. High energy hydroxyl and oxygen radicals formed during the chain-branching phase of combustion are trapped in the gas phase and are

replaced by much lower energy halogen radicals. A new niche subset of organic latent radical sources are non-halogenated compounds capable of producing carbon or oxygen free radicals that interfere with the mechanisms of polymer decomposition and fire production. Efficacious in some polyolefin applications as flame retardants are novel chemistry families such as N-alkoxy-substituted piperidines, or bis-alkylidene azo compounds (44–46).

(4) **Synergists with Antimony Oxides**: Antimony trioxide [1309-64-4] which shows no FR activity on its own, synergizes with halogen-containing compounds through the formation of antimony halides which have lower volatility and longer persistence in the gas phase.

By chemical class, FRs can be categorized as follows:

Brominated Hydrocarbons. Accounting for the highest dollar value, these consist of additives such as decabromodiphenyloxide [1163-19-5] and tetrabromo bisphenol A [79-94-7] and like derivatives. These products are used in engineering resins primarily (HIPS, ABS, PC) for the business machine and television cabinet markets. Typically they are used with antimony oxide [1309-64-4] as a synergist in approximate ratio of 3:1 respectively. Major global suppliers of brominated FRs are Albemarle, Chemtura, and ICL Industrial Products.

Chlorinated Hydrocarbons. The chlorinated paraffins are used as FR's and plasticizers for PVC and in certain elastomeric materials. Dover Chemicals (Chlorez) is the major U.S. supplier. Declorane Plus [13560-89-9] (Occidental) has its main application in nylon and polyolefin wire and cable jacketing. Often the chlorinated FR compounds are used with antimony synergists.

Phosphate Esters. The phosphate esters can be subdivided into halogenated and non-halogenated versions. Halogenated phosphate esters are used almost exclusively in PUR foams. Albemarle (Antiblaze), Chemtura (Firemaster), and Supresta (Fyrol), and are key suppliers. The non-halogenated phosphate esters are primarily aryl esters and are used in engineering plastics (PET, PBT, PC, nylons). They are widely used in lubricants and as plasticizers in PVC. Chemtura, Clariant (Exolit), and Supresta (part of ICL) are the key producers.

Antimony. Antimony trioxide (ATO) is the primary product yet antimony pentoxide is also used to a lesser extent. Antimony compounds are used as synergists with halogenated FRs, with Chemtura (Fireshield) and China Minmetals as major producers/distributors. China produces about 90% of global ATO.

Aluminum Trihydrate. Since aluminum trihydrate (ATH) [21645-51-2] begins to decompose at relatively low temperature, it can only be used in polymers which can be processed at temperatures not exceeding 200° for long periods of time (polyolefins, acrylics, unsaturated phosphate esters, and PVC). When higher temperature processing is required, magnesium hydroxide can be substituted. It is used at very high loading levels (60 wt% or greater). ATH is used in significant quantities in household cabinetry tabletops in polyester or acrylic resins, as well as an FR in elastomeric latex carpet backings. (42). These high loadings can have a detrimental effect on physical properties. There are numerous global distributors.

Heat Stabilizers. Chlorinated polymers, primarily PVC, decompose during processing to liberate HCl via dehydrochlorination reactions. The liberated

HCl catalyzes the dehydrochlorination leading to rapid discoloration, embrittlement, and loss of mechanical properties. Since the decomposition is not free radical chain mechanisms, the traditional antioxidant stabilizers are not effective as heat stabilizers. The Primary Heat Stabilizers act by trapping the liberated HCl and also by reacting with labile chlorines on the polymer chain formed during polymerization (e.g., allylic chlorines) (47). There are three major types of primary heat stabilizers: lead compounds, mixed metal salts, and organotins. Major producers in North America include Arkema (Thermlite), Chemtura (Mark), Ferro (Therm-chek), and Rohm and Haas (ADVASTAB). In 2007 the total market in North America was over 79 kilotons and value just below $400 million. Globally the heat stabilizer market was valued in 2003 at about 1.2 billion pounds (about $1.8 billion) (48).

Lead Compounds. These may be either organic or inorganic with dibasic lead stearates and phthalates, tribasic lead sulfate, and dibasic lead phosphite and carbonate, as examples. Their primary usage is in wire and cable insulation because of their nonconductive properties due to the water insolubility of the lead chloride which is produced in thermal processing in the case of PVC. Once extensively used in a wide variety of applications, they have largely been replaced by mixdd metals and tins because of intense regulatory pressure. Only in wire and cable have lead compounds persisted since no suitable technical replacement is available despite significant R&D activity.

Mixed Metal Salts (or Soaps). These consist of Ba/Cd, Ba/Zn, and Ca/Zn salts. The Ba/Cd salts were very effective but now largely replaced by noncadmiums in Western countries owing to regulatory pressure). The efficacy of these 'mixed metal salts' as thermal stabilizers follows that order. Mainly used in flexible or semirigid PVC, they are available in solid and liquid versions. Solids are typically salts of fatty acids such as stearates and laurates while liquid versions are octoate, phenolate, and neodecanoate salts. Mixed metal salts are almost always used in the presence of secondary stabilizers such as organophosphites, epoxies (e.g., epoxidized soybean oil), and β-diketones. This is particularly the case for the less active Ba and Ca/Zn. The ratio of metal salt to secondary stabilizer is typically 4:1. Mixed metal salts or soaps are available in North America from Baerlocher, Chemtura, Ferro, and Rohm and Haas.

Organotins. Primarily used in rigid PVC, the most widely used types are the dibutyl and octyltin mercaptides. While excellent stabilizers, they suffer from odor, staining, and poor uv-stability. Sulfur-free ortanotins which include the dibutyltin maleates are useful in applications requiring good weatherability such as extruded siding and profile. Methyl tins are the most active (particularly at high temperature and shear) and are favored from a toxicity and regulatory perspective. Arkema, Chemtura, and Rohm and Haas are the leading suppliers in North America.

Light Stabilizers. Most polymers degrade as a result of photo-induced oxidation so that for durable applications requiring weatherability it is necessary to add light stabilizers. Ultraviolet induced degradation results in the loss of both aesthetic (color, gloss, clarity) as well as mechanical properties. The uv-portion of sunlight has sufficient energy to break chemical bonds in polymers resulting in the formation of free radicals. Light stabilizers interfere with these processes, slowing the harmful effects of uv-radiation (49).

Light stabilizers fall into three general categories: ultraviolet absorbers (UVAs), hindered amine light stabilizers (HALS), and nickel quenchers. While the largest consumption of light stabilizers is in polyolefins, there are significant usages in engineering resins, styrenics, PURs, and in coatings. HALS account for approximately half of the sales of light stabilizers and has approximately double the growth rates of UVAs in total. The North American light stabilizer market is valued about $150 million.

UVAs are organic molecules that preferentially absorb uv-radiation and dissipate it in the form of heat. They are transparent in the visible region so as not to timprt color and are hightly photostable in order to provide long-term protection. UVAs are added to polymers at levels of 0.2–0.5%, depending on the type of polymer and the weatherability requirements of the end use application. UVAs fall into two major classes: 2-hydroxy-4-alkoxybenzophenones and substituted 2-hydroxy-benzotriazoles. A wide variety of modifications have been made to these basic types to provide for enhanced ancillary properties such as reduced volatility, better polymer compatibility, and enhanced photostability. Benzophenones are widely used in PVC and polyolefins. Because of their superior performance, benzotriazoles are used in high performance resins such as PC, nylon, and acrylics. Other minor types include benzoates, salicylates, and diphenyl acrylates. The most recent class of high performance UVAs are based on 2-(2-hydroxyphenyl)-1,3,5-triazines. These products have superior inherent photostability compared to the standard UVA types making them suitable for applications such as automotive and construction having high weatherability requirements.

The other important class of light stabilizers, the HALS, are based on substituted 2,2,4,4-tetramethylpiperidines. During light exposure, HALS are converted to nitroxyl radicals which are effective scavengers of the free radicals formed as a result of photolysis or photo-oxidation during weathering. A wide range of variations of HALS are available to optimize volatility and migration and to minimize interaction with other additives. For example, high molecular weight HALS have been developed to minimize volatility from high surface are PP fibers or polyolefin thin films. Other developments involve modifying the piperidine nitrogen with alkyl or alkoxy groups to reduce basicity, and hence interaction with other additives such as FRs, thioester antioxidants, and environmental agents such as pesticides and acid rain. The HALS major application is in polyolefins but they are also used extensively in styrenics, acrylics, and PVC. Typical use levels are from 0.15–0.3%. For the combined light stabilizers (UVAs and HALS together), the acquisition of BASF in 2009 by BASF (Tinuvin®, Uvinul®) created the volume leader globally, followed by the cluster of Cytec (Cyasorb), Adeka, Chemtura, and Clariant (Sanduvor). In 2007 the global volume of combined light stabilizers was over 64 kilotons (50).

Because HALS and UVAs function via different stabilization mechanisms, they are often used together for synergistic performance and optimum weatherability.

Nickel quenchers such as nickel dibutyuldithiocarbamate [13927-77-0] and 2,2-thiobis-(4-octylphenolato)-*n*-butylamine nickel (II) [14516-71-3] deactivate excited chromophores which act as sensitizers for the photolysis of hydroperoxides (49). Once widely used in PP fibers they have been replaced almost entirely by HALS. Their usage is declining because of concerns over the toxicity of the nickel.

Processing Aids

Lubricants. Lubricants are added to polymers during processing to improve their flow characteristics. While primarily acting as processing aids to reduce energy consumption and enhance the surface properties of extruded articles, they provide additional benefits in terms of mold release, improved antistatic properties, and better pigment dispersion. These additives act either “internally” as friction modifiers between polymer chains to decrease melt viscosity or “externally” by coating or treating the metal surfaces of the processing equipment, thereby reducing the friction at the polymer-metla interface. A wide variety of chemical classes of lubricants are available, including metal stearates, fatty amides, fatty acid and glycerol esters, waxes of various types, and fluoropolymers. Depending on the application, many of these exhibit both external and internal lubricating properties (51).

Metal stearates including predominantly calcium stearate as well as zinc stearate, are the most widely used lubricants. In PVC calendaring and extrusion, the stearates provide heat stabilizing effects as well as act as an internal lubricant. In polyolefins stearates act as external lubricants as well as deactivators of catalyst residues. Baerlocher, Chemtura, and Ferro are the major producers of metal stearates in North America.

Fatty amides provide multifunctionality, acting both as external lubricants and as slip agents and antiblocks. Primary amides such as oleamide [301-0202], erucamide [112-84-5], and stearamide [1309-64-4] are primarily used as slip and mold-release agents for polyolefins. The higher molecular weight ethylene bisstearamide is used as a lubricant in both rigid and flexible PVC and in engineering polymers such as polyacetal, nylon, and ABS. Croda, Lonza and PMC Group are major suppliers of amides in North America.

Fatty alcohols are used primarily in rigid PVC where their excellent compatibility makes them useful where clarity is important. Fatty acids, represented by stearic acid, find some use in calendered and blow-molded PVC. Fatty esters, such as glycerolmonostearate [31566-31-1] function as either internal or external lubricants depending on molecular weight (compatibility). Again, PVC is the primary substrate but PC, PS, and PUR can be processed with these materials.

Polyethylene and paraffin waxes are used widely as external lubricants for PVC because of their high level of incompatibility. They are often used in combination with calcium stearate in unplasticized PVC pipe formulations. BASF, Clariant, and Ferro are leading North American suppliers of waxes.

Fluoropolymers, a small but high value (about $30/kilogram) type of external lubricant/processing aid, are based on tetrafluoroethylene (52–55). These fall in two classes, those that are used in spray-on mold release agent formulations, and in-polymer incorporated products act as lubricants or processing aids. These