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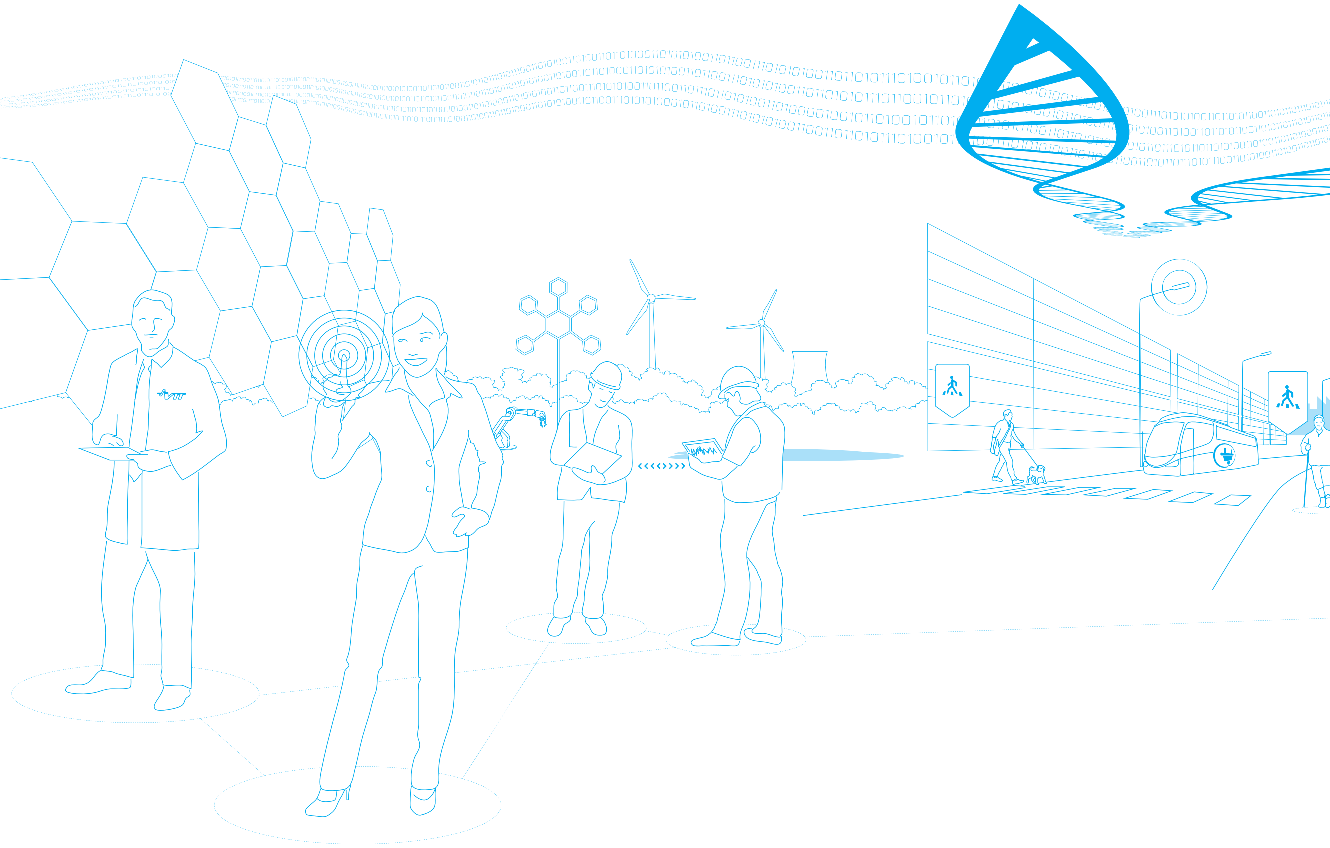
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Preface

This work was carried out as part of the OSER project (”Osaava energiantuotanto Keski-Suomessa”). The manuscript is based on three journal manuscripts prepared by Matti Ranta-Korpi of the Department of Chemistry, University of Jyväskylä (JYU). Pasi Vainikka from VTT and professor Jukka Konttinen from JYU worked in cooperation in this. Antti Saarimaa and Milena Rodriguez have edited the manuscript in the format of this report. Raili Taipale from VTT is also thanked for her contribution.

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Contents

List of symbols

ABS	Acrylonitrile-Butadiene-Styrene co-polymer
ACM	Acrylic Elastomers
ATH	Aluminum Trihydroxide = Alumina Trihydrate
ATO	Antimony Trioxide
BIIR	Bromobutyl Rubber
CFC	Chloroflourocarbon
CIIR	Chlorobutyl Rubber
CPE	Chlorinated Polyethylene
CR	Chloroprene Rubber
CSM	Chlorosulfonated polyethylene
CSM	Chlorosulfonated polyethylene
DAS	Diaminostilbene
DBDPE	Devabromodiphenyl ether
DMT	Dimethyl Terephthalate
DSBP	Distryryl Biphenyl
ECH	Polyepiclorohydrin
EPDM	Ethylene-propylene Diene Monomer
EPS	Expandable Polystyrene
FEP	Perfluorinated Ethylene-propylene
FWA	Fluorescent Whitening Agent
GWP	Global Warming Potential
HALS	Hindered Amine Stabilizers

HBCD	Hexabromocyclododecane
HBCD	Hexabromocyclododecane
HCFC	Hydrochlorofluorocarbon
HDPE	High-Density Polyethylene
HFC	Hydrofluorocarbon
HFP	Hexafluoropropylene
HIIR	Halobutyl Rubber
HIPS	High-Impact Polystyrene
IIR	Bytyl Rubber
LDPE	Low-Density Polyethylene
LLDPE	Linear Low-Density Polyethylene
MDH	Magnesium Dihydroxide
MSW	Municipal Solid Waste
NR	Natural Rubber
OBSH	Oxibis(benzenesulfonyl) Hydrazide
ODP	Ozone Depleting Potential
PA	Polyamide
PBCDD	Polychlorinated/brominated Dibenzo-p-dioxin
PBCDF	Polychlorinated/brominated Dibenzofuran
PBDE	Polybrominated Diphenyl Ether
PBT	Polybutylene Terephthalate
PC	Polycarbonate
PCDD	Polychlorinated Dibenzo-p-dioxin
PCDF	Polychlorinated Dibenzofuran
PE	Polyethylene
PES	Polyethersulfone
PET	Polyethylene Terephthalate
PFA	Perfluoroalkoxy
PP	Polypropylene
PPS	Poly(p-phenylene sulfide)

PPSF	Polyphenylenesulfone
PS	Polystyrene
PSF	Polysulfone
PSW	Plastic Solid Waste
PTFE	Polytetrafluoroethylene
PU	Polyurethane
PVC	Polyvinyl Chloride
PVCD	Polyvinylidene Chloride
PVDF	Polyvinylidene Fluoride
SAN	Styrene acrylonitrile co-polymer
SBR	Styrene-Butadiene Rubber
TBBA	Tetrabromobisphenol-A
TFE	Tetrafluoroethylene
TPA	Terephthalic Acid
TSH	p-Toluenesulfonyl Hydrazide
TSSC	p-Toluenesulfony Semicabazide
UVA	UV light Absorber
VDF	Vinylidene Fluoride
Z-N	Ziegler-Natta Catalyst system
ZB	Zinc Borate
ZHS	Zinc Hydroxy Stannate
ZnSt	Zinc Stearate
ZS	Zinc Stannate

1. Introduction

Plastics can be defined as a synthetic sub-class of polymers produced from monomers via a controlled polymerization reaction. Due to their unique properties such as light weight, good moldability, and good solvent and thermal resistance, their annual global consumption is huge; for instance in 2008 it was 245 million metric tons (Andrady and Neal, 2009). Plastics are used in all kind of applications, but one can still distinguish areas where the consumption is the most significant. Majority of the production, about 50 %, is consumed among packaging sector where plastic films, wraps and sheets are the main products. Another big consumption area is construction, in which plastics are used e.g. in pipes, cable coatings and building materials. The rest of the consumption is divided between areas such as electronic devices, furniture, sport goods, and vehicles (Andrady and Neal, 2009; Hopewell, 2009). Even though there are tens of different types of plastics on the market, only a handful can be described as commodity or mass consumption plastics in terms of their high production volume and economical price (Andrady and Neal, 2009). Low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), and polyethylene terephthalate (PET), account for the majority of global demand. Figure 1 illustrates the consumption of plastics and rubbers worldwide in year 2006 (in millions of metric tons).

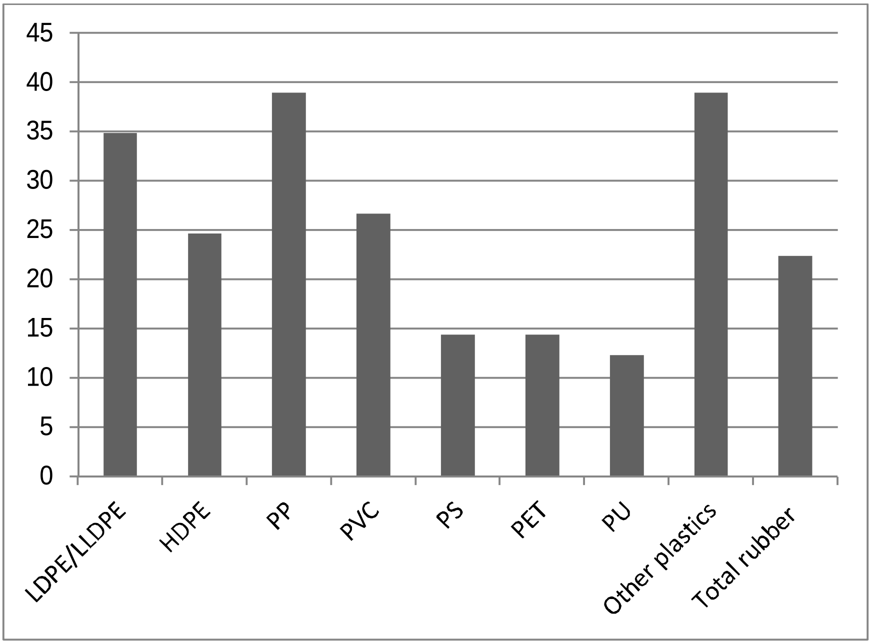


Figure 1. The consumption of plastics and rubbers in 2006 (PlasticsEurope, 2012; The Rubber Economist Ltd, 2008).

Due to the large consumption, plastic solid waste (PSW) constitutes today a significant proportion of total amount of municipal solid waste (MSW); for instance in EU area the share of PSW in MSW is around 10 wt-% (Al-Salem, Lettieri and Baeyens, 2009). The share will even increase in the future due to new plastic materials developed and greater amounts of commodity plastics used in new applications, for example in composites. Due to the new regulations set by the EU, the volume of waste going to landfills should be minimized, and this will bring a challenge for both MSW and PSW disposal. In PSW disposal, there are some alternative treatment methods such as re-use of plastics, as well as different recycling (primary, mechanical and chemical) techniques, and the use of PSW for energy recovery (Al-Salem, Lettieri and Baeyens, 2009). Even though recycling is the primary option due to the economic and environmental reasons, it may be challenging to carry out for mixed plastic waste consisting of numerous different polymer types (which is typical situation in MSW) or for plastic articles containing several different polymers grafted to each other. In this case the use of PSW for energy recovery can be preferred; in addition, the volume reduction (90–99 %) and the high calorific value of plastics speak for their energy use (Al-Salem, Lettieri and Baeyens, 2010).

However, there are also some challenges related to the combustion of plastics. Maybe the most problematic issue is the additive compounds used in plastics for various purposes. They may be used as fillers to reinforce plastic resin and to lower the price of final product by dilution, thermal stabilizers to improve the durability of plastic matrix at higher temperatures, UV/light stabilizers to prevent degradation of polymer resin, flame retardants to prevent ignition and burning, color pigments (inorganic or organic) to enhance the appearance and light durability of polymers, and antimicrobials to improve the resistance against bacteria and fungi (Andrady and Neil, 2009; Al-Salem, Lettieri and Baeyens, 2009). Plastics may also contain catalyst residues from the polymerization processes, fluorescent whitening agents (FWA) to brighten the color of plastics, and antistatic additives to dissipate static charges on the polymer. Majority of the additive compounds contain either metals (mainly lead, zinc, iron, titanium, antimony, aluminum, calcium, barium, copper and nickel) and/or sulfur, chlorine and bromine atoms, either in organic or inorganic form. Both the types and the concentration levels of additive compounds depend on the application; plastics used e.g. in chemically and mechanically challenging environments may require higher additive concentrations than plastics used e.g. in packaging applications.

When halogen (i.e. chlorine, bromine and fluorine) and sulfur containing fuel material is combusted, harmful and toxic gaseous emissions such as HCl, HBr, HF, metal or alkali metal halides and sulfur compounds such as SO_2 are formed (Liu *et al.*, 2006; Guo *et al.*, 2006; Vehlow, 2003; Vehlow, 2000; Zhang *et al.*, 2007). The emission of the hydrides is primarily an emission problem, and their release to air must be controlled by air pollution control devices (APC´s) that are standard technology in modern waste-to-energy units. Volatilized metal halides will condense on the heat exchange surfaces of boiler walls, which will finally lead to the corrosion of the tube/wall area (Grabke *et al.*, 1995; Bankiewicz *et al.*, 2009; Albina, 2005; Kawahara, 2001; Lehmusto *et al.*, 2012; Lehmusto *et al.*, 2011; Enestam *et al.*, 2013). The role of sulfur on the volatilization of the metals is also important, since the formation of metal sulfides or sulfates with rather low vapor pressures will decrease the volatilization of these metals present in the fuel, at least at lower temperatures (Zhang *et al.*, 2007; Verhulst and Buekens, 1996; Sorum, 2003; Sorum, 2004). Also some other inorganic compounds, such as silicates and oxides of aluminum and iron will have an important role on the volatilization behavior of other metals at higher temperatures; they will decrease the volatilization of zinc, cadmium and lead by forming durable and non-volatile metal compounds such as silicates, aluminates and ferrites (Verhulst and Buekens, 1996; Evans and Williams, 2000; Jakob *et al.*, 1995; Zhang *et al.*, 2008; Abanades, 2002). The categorization of metals according to their tendency to volatilize during the combustion under oxidizing atmosphere has been shown in Figure 2.

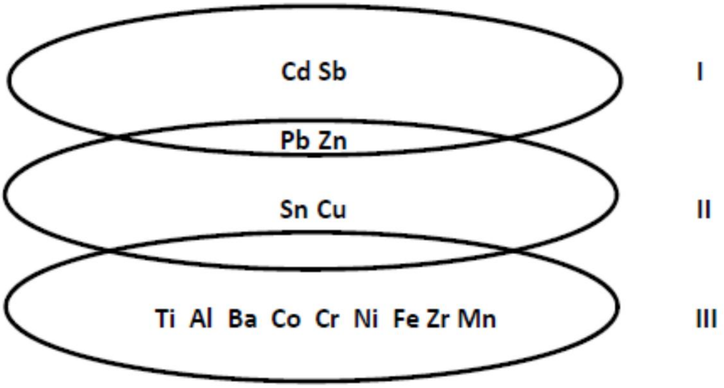


Figure 2. The volatilization tendency of metals typically present in MSW environment. I: Highly volatile metals, II: Semi-volatile metals, and III: Non-volatile metals. The information is obtained from references (Vehlow, 2003; Verhulst and Buekens, 1996; Sorum, 2003; Sorum, 2004; Abanades, 2002; Morf, 2000).

Besides the formation of metal halides, chlorine and bromine present in MSW promote the formation of polychlorinated/brominated dibenzo-p-dioxins (PCDD/PBCDD) and dibenzofurans (PCDF/PBCDF) at the cooler (250–400 °C) post-combustion zone (Tuppurainen *et al.*, 1998; Soderstrom and Marklund, 2002; Gordon, 2002). Some metal compounds, particularly copper chlorides (Halonen, 1997; Hatanaka, 2003; Hatanaka, 2002; Wang, 2002) will catalyze either the direct chlorination of dioxins/furans, or the formation of molecular chlorine Cl_2, which is an effective chlorinating agent in the formation of PCDD/Fs. Some other heavy metal compounds, such as oxides and chlorides of Co, Cr and Fe, may possess the opposite effect by degrading polyhalogenated aromatic compounds already formed and thus decrease the net formation of PCDD/Fs (Oberg, 2008; Oberg, 2007). Also sulfur in the form of SO_2 inhibits the formation of PCDD/Fs by reacting with Cl_2 in the presence of water (Xie *et al.*, 1999). Sulfur may also react with copper to form catalytically inactive $CuSO_4$, or form sulfonated phenolic precursors thus preventing chlorination, which will further prevent the formation of PCDD/Fs (Ruokojarvi, 1998).

Occasionally, if the concentration of some specific metal in ash fraction resulting from the combustion of MSW is too high, it will prevent its utilization due to the threshold concentration values set for harmful and toxic elements typically found in MSW ash. Particularly high concentrations of barium found in MSW bottom ash will restrain its use e.g. in concrete and road/building construction sectors (Korpijärvi *et al.*, 2009).

Considering the fact that all synthetic polymers may contain significant concentrations of halogen and sulfur containing species, as well as several metal compounds, their effect on the combustion process (i.e. emission formation and metal volatilization) may be greater than currently acknowledged. The aim of this study is to present a review on the halogen, sulfur and metal containing additive compounds used in different types of plastics and rubbers. In particular, the focus is on quantitative data on the concentrations of those elements and compounds in plastics that are relevant for ash chemistry during thermal conversion. The plastics include PVC, LDPE, LLDPE, HDPE, PP, PET, polybutylene terephthalate (PBT), PS and its derivatives, acrylonitrile-butadiene-styrene co-polymer (ABS), polyamide (PA), polycarbonate (PC), polyurethane (PU) and the most widely used rubber polymers such as natural rubber (NR), styrene-butadiene rubber (SBR), butyl rubber (IIR), nitrile rubber (NBR) and ethylene-propylene rubber (EPDM).

The study has been divided to four separate chapters. In the second chapter, after introduction, the most important metal compounds used in plastics and rubbers have been reviewed. The metals present in the second chapter are lead, aluminum, antimony, titanium, tin, zinc, iron, nickel, copper, cadmium, chromium, cobalt and manganese, and also silver and zirconium in some particular cases. In this chapter, the metals, their use and their typical structure types in different plastic and rubber polymers are introduced separately. Finally, the elemental concentrations of these metals in polymers are presented. When the elemental metal concentration has been calculated, the following equation has been used

$$c(M_i) = \frac{MW_{Mi}}{MW_{comp.}} \cdot c_{comp.}, \qquad (1)$$

where

MW_{Mi} = the molecular weight of the metal at issue (g/mol)

$MW_{comp.}$ = the molecular weight of the metal compound (g/mol)

$c_{comp.}$ = the concentration of the metal compound in the polymer (wt-%).

The concentration values of metal compounds have been obtained from the literature.

Third chapter will present halogen compounds used in plastics and rubbers as well as halogen containing additives used in plastic/rubber polymers. In particular, the focus is on quantitative data on the concentrations of those elements and compounds in plastics that are relevant for ash chemistry during thermal conversion. The polymers include PVC, LDPE, linear low-density polyethylene (LLDPE), HDPE, PP, PET, polybutylene terephthalate (PBT), PS and its derivatives, acrylonitrile-butadiene-styrene co-polymer (ABS), polyamide (PA), polycarbonate (PC), polyurethane (PU), and the most important fluorine containing polymers. In the chapter, the additive compounds are characterized starting from the chemical formula and the composition of the compound. Also the concentrations of the additive compounds in the polymers are estimated.

Fourth chapter will cover sulfur and alkaline earth metal compounds as well as sulfur/alkaline earth metal containing additives used in plastic/rubber polymers. In particular, the focus is on quantitative data on the concentrations of those elements and compounds in plastics that are relevant for ash chemistry during thermal conversion. The polymers include PVC, low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), PP, polyethylene terephthalate (PET), polybutylene terephthalate (PBT), PS and its derivatives, acrylonitrile-butadiene-styrene co-polymer (ABS), polyamide (PA), polycarbonate (PC), polyurethane (PU), and the most important rubber polymers. In the paper, the additive compounds are characterized starting from the chemical formula and the composition of the compound. Also the concentrations of the additive compounds in the polymers are estimated.

2. Metal containing additives

2.1 Lead compounds in plastics

Lead has a significant role in PVC, since several lead compounds can be used as heat stabilizers in various PVC applications. In addition, lead can be a part of inorganic metal compounds used as yellow and orange pigments widely applicable to the plastics. The use of lead has been declining due to the environmental issues linked to its toxicity, but the usage level particularly in heat stabilizers is still significant; in Europe the share of lead stabilizers was over 50 % of total consumption of heat stabilizers in 2007 (Sauerwein, 2009). However, lead stabilizers are not allowed in packaging applications, where Sn and mixed metal Ca/Zn stabilizers are the preferred options (Jacquinot *et al.*, 2000).

2.1.1 Lead in PVC heat stabilizers

Divalent lead has the ability of forming complexes, which is very useful for the substitution of labile chlorine atoms (which are the sites where the degradation of PVC typically starts) (Jennings and Starnes, 2005; Starnes and Jennings, 2009; Andreas, 1993). Additionally, lead chloride has no destabilizing effect on PVC, unlike e.g. zinc and cadmium chlorides with strong Lewis acid nature, which tend to accelerate the dehydrogenation in PVC (Jennings and Starnes, 2005; Thacker *et al.*, 2007). Since lead stabilizers do not increase the conductivity of PVC, electrical cable insulation is a major area of application (Jennings and Starnes, 2005; Starnes and Jennings, 2009; Summers, 1997; Carr *et al.*, 1995). The most important lead compounds used as heat stabilizers are tribasic lead sulfate, dibasic lead phosphite, dibasic lead phthalate, dibasic lead stearate and normal lead stearate. The usage level of these compounds depends on the application concerned, but rough estimations can be made. Typically, lead concentration in PVC resin stabilized by lead compounds ranges from 1 % up to 4 % by weight of PVC polymer (Jennings and Starnes, 2005; Starnes and Jennings, 2009; Thacker *et al.*, 2007).

The most important lead compound is tribasic lead sulfate with the chemical formula $3PbO{\cdot}PbSO_4{\cdot}H_2O$. It is used both in flexible and rigid PVC applications such as wire insulation compounds, rigid and flexible PVC foams, rigid vinyl pipe and profile applications, and PVC plastisols (Jennings and Starnes, 2005; Starnes and Jennings, 2009; Thacker *et al.,* 2007; Carr *et al.*, 1995; Dworkin, 1989). It is normally used in combination with dibasic lead stearate in order to obtain complementary lubricant effect, and with dibasic lead phosphite due to its antioxidant nature (Jennings and Starnes, 2005).

Dibasic lead phosphite (chemical formula $2PbO{\cdot}PbHPO_3{\cdot}2H_2O$) imparts both heat and light stabilizing effect in PVC (Thacker *et al.*, 2007). Therefore it is used e.g. in PVC roofing and garden hoses, flexible and rigid vinyl foams and extruded profiles for outdoor use (Thacker *et al.*, 2007; Carr *et al.*, 1995).

Dibasic lead phthalate (chemical formula $2PbO{\cdot}Pb[(OOC)_2C_6H_4)$ is the most versatile of lead stabilizers due to its good solubility in a variety of polymers; therefore it is commonly used in PVC blends and flexible PVC applications, such as wire and cable (Starnes and Jennings, 2009; Thacker *et al.*, 2007). Because of its structure (it does not contain long fatty acid chains) lead phthalate does not impart a lubricating effect, and therefore it can be complemented by the addition of lead stearates. Besides that, the addition of lead phosphite increases the light stability of the stabilizer system (Jennings and Starnes, 2005).

Normal lead stearate (chemical formula $Pb(OOCC_{17}H_{35})_2$) is mainly used only as an external lubricant with primary lead stabilizers (Thacker *et al.*, 2007; Dworkin, 1989), whereas dibasic lead stearate (chemical formula $2PbO{\cdot}Pb(OOCC_{17}H_{35})_2$) has both (internal) lubricating and stabilizing ability. It is typically used in combination with tribasic lead sulfate/phosphite both in flexible and rigid PVC applications. Table 1 presents some typical mixtures of lead stabilizers used in different kinds of applications and the lead concentration in the final PVC polymer.

Table 1. Lead based stabilizer compounds and lead content in PVC (Jennings and Starnes, 2005; Starnes and Jennings, 2009; Berard, 2005; Robinson *et al.*, 2007; Baerlocher, 2011).

Application	Pipe	Fittings	Window profile	Wire cable	Roofing
Lead Compounds	tribasic lead sulfate dibasic lead stearate neutral lead stearate	tribasic lead sulfate dibasic lead stearate neutral lead stearate	tribasic lead sulfate dibasic lead phosphite dibasic lead stearate neutral lead stearate	dibasic lead phthalate dibasic lead stearate	tribasic lead sulfate dibasic lead phosphite dibasic lead stearate
Pb content in PVC (mg/kg)	4500–9000	10000-14000	12500–17000	15500–27000	24000–33000

2.1.2 Lead in pigments

Inorganic pigments based on lead can be used when yellow, orange and red plastic articles are manufactured. There are a couple of possible options. For yellow color a pigment based on pure lead chromate or the mixture of lead chromate and lead sulfate ($Pb(Cr,S)O_4$) (Damm and Herrmann, 1993; Buxbaum and Pfaff, 2005) can be used, and for orange/red, lead chromate molybdate sulfate $Pb(Cr,S,Mo)O_4$ (Sicomin Red L 2922, 2011). In the latter, molybdenum and sulfur are incorporated in the crystal lattice of lead chromate.

Lead containing pigments are mostly used in plastics such as polyolefins (the common name for PE and PP polymers) and flexible PVC applications, but after suitable surface treatment such as stabilization by silicate or alumina (resulting with improved light, heat and chemical stability of pigments), they are generally applicable in thermoplastics (Damm and Herrmann, 1993; Buxbaum and Pfaff, 2005; Scherrer and Sykes, 2009). The biggest disadvantage in the use of lead based pigments is their toxicity; this is why e.g. lead carbonate has been replaced by more effective and less toxic white pigment titanium oxide. Although the use of lead pigments has decreased in Northern Europe, they (i.e. lead sulfochromate and lead chromate molybdate sulfate) still are relatively widely used in Southern Europe, North America and the rest of the world.

The amount of inorganic pigment usually needed for a good color is quite large, about 1 wt-% (Vasile and Rusu, 2000). In general, the amount of pigment added depends on e.g. the depth of shade required, the opacity and the thickness of the article; the concentration of the pigment can sometimes be as low as 0.01 % of the polymer (Mathew and Grossman, 2007). Table 2 presents the most typical lead based pigments used in different plastics and the final lead content in plastic polymer. In the calculations it has been assumed that lead pigments are used with concentrations in the range of 0.05–0.5 wt-%.

Table 2. Lead based pigments and lead content in final polymer (Sicomin Red L 2922, 2011).

Lead compound	**Target of use**	**Chemical formula**	**Pb-% in compound**	**Pb content in polymer (mg/kg)**
Lead sulfochromate	PVC, LDPE, HDPE	$Pb(Cr, S)O_4$	59–63	300–3000
Lead chromate/ molybdate/sulfate	PVC, LDPE, HDPE	$Pb(Cr, S, Mo)O_4$	58–61	300–3000

2.2 Aluminum compounds in plastics and rubbers

Aluminum compounds can be utilized during each stage of plastic production; from the polymerization through the stabilization and finally in pigments and fillers. There are both organic and inorganic aluminum compounds.

2.2.1 Aluminum catalyst compounds

Organoaluminum compounds are used as co-catalysts within the Ziegler-Natta (Z-N) and metallocene processes, and also within the polymerization of polybutadiene rubber, an important impact modifier for HIPS and ABS. The aluminum compound for the Z-N system (and also for the polybutadiene) is typically trialkylaluminum such as triethylaluminum $(C_2H_5)_3Al$ or its halogenated modifications such as $(C_2H_5)_2AlCl$ (Kissin, 1996b). For the metallocene system methylaluminoxane $Al(CH_3)O$ is the preferred compound (Kissin, 1996b; Kaminsky 1998). Besides aluminum co-catalysts, the support material for the metallocene system may contain aluminum. The concentrations of organoaluminum compounds used vary according to the system, but usually the molar concentration of aluminum is some 50–500 times higher than the concentration of the main catalyst (metal) component. Thus aluminum residues left in the polymer are higher too; they may be in the range of 10–30 mg/kg for the metallocene system (Hoàng *et al.*, 2006; Hussain *et al.*, 2010), and even higher for the Z-N system (Hussain *et al.*, 2010).

2.2.2 Aluminum compounds as co-stabilizers/acid scavengers and flame retardants

Aluminum based minerals such as zeolites (combination of sodium oxide, aluminum oxide and silicate) and hydrotalcites (combination of magnesium oxide, aluminum oxide, water and carbonate) have occasionally been utilized as co-stabilizers within lead based stabilizer systems (Kalouskova *et al.*, 2004), but are mostly used in combination with tin and mixed metal heat stabilizers in PVC(Starnes and Jennings, 2009; Thacker *et al.*, 2007; Atakul *et al.*, 2005). Zeolites and hydrotalcites act as acid scavengers/neutralizers and they do not directly contribute to the stabilization. When they are used in combination with e.g. tin, Ca/Zn and Ba/Zn systems, lower amounts of primary stabilizers are required due to the synergist effect gained; they can reduce the amount of metal stabilizer used even to one half (Advera Specialty Zeolites, 2011). Usually the proportion of zeolite/hydrotalcite in the stabilizer mixture varies between 30–65 wt-%, and the total amount of stabilizer used is in the range of 0.5–2 % by weight of the PVC (Starnes and Jennings, 2009; Thacker et al., 2007).

Alumina trihydrate (ATH) with chemical formula $Al(OH)_3$, is a widely used flame retardant particularly in PVC (Ning and Guo, 2000). The flame retardant mechanism is based on the release of water by decomposition of $Al(OH)_3$ which consequently will lead to the dilution and cooling of the flame zone. Due to the mechanism, very high concentrations (20–70 %) of ATH are required to impart an efficient flame retardant effect. Another drawback is its rather low decomposition temperature (200 °C); thus the range of polymers suitable for ATH is limited (van Esch, 1997). In applications processed at higher temperatures, magnesium oxide (MDH), which is stable up to around 300 °C is used (Troitzsch, 1993; Beard, 2007). Besides PVC, the use of ATH in LDPE, HDPE and rubbers (especially for cable insulation), as well as in PS and PU is profitable (Vasile and Rusu, 2000; van Esch, 1997; Troitsch, 1993; Evans and Huber, 2001). When it is used in combination with synergists such as antimony trioxide (ATO), zinc hydroxy stannate (ZHS) or zinc borate (ZB), the concentrations of ATH required may be reduced even to one half (Cusack and Hornsby, 1999; Baggaley *et al.*, 1997; Thomas, 2003).

2.2.3 Aluminum based fillers/anti-blocking additives and pigments

When inorganic fillers or impact modifiers are incorporated in the plastic resin in order to gain both economical and reinforcement effect, the loadings of these additives are typically very high, up to several tens of percent of the plastic polymer. Since fillers typically consist of several different metal compounds, the elemental metal concentrations may also increase to significant levels. Aluminum containing fillers are e.g. glass fibers, mica and kaolin clay, and in them aluminum is usually in the form of silicates. The content of elemental aluminum in fillers ranges between 6–30 wt-%, thus (due to high loading volumes) aluminum residues in final polymer may be as high as several percent by weight of the polymer. Aluminum containing fillers can be added to almost every polymer, but usually mica is used in PP, PBT and PA, whereas kaolin clay finds most use in PVC, PE and rubber goods (Hohenberger, 2009; Rodgers *et al.*, 2000). Glass fibers are generally applicable in plastics. Besides being fillers, kaolin and mica (as well as zeolites) are also used as anti-blocking additives in order to reduce the adhesion between a two adjacent plastic film layers (Robinson *et al.*, 2007; Kromminga *et al.*, 2009). They are used in PVC, LLDPE and LDPE at a concentration range of 2000–6000 mg/kg.

Aluminum compounds have also found use as inorganic pigments in the coloration of plastics and rubbers. The oldest aluminum based pigments are ultramarine blue and violet pigments with chemical formula $Na_{6\text{-}8}Al_6Si_6O_{24}S_{2\text{-}4}$, suitable for the coloration of PVC, PS, LDPE, HDPE and rubbers (Buxbaum and Pfaff, 2005; Scherrer and Sykes, 2009; Beebe, 1993). Other aluminum compounds are blue pigments cobalt aluminate $CoAl_2O_4$ and cobalt chromium aluminate $Co(Al,Cr)_2O_4$, which are generally applicable (Buxbaum and Pfaff, 2005; Beebe, 1993). In the coloration, maybe the most important use for aluminum is as metallic pigments; aluminum metal flakes, either separately or in combination with organic pigments and dyes are the most widely used metallic pigments possible to be used also in transparent applications. Pearlescent pigments based on mica or aluminum oxide, which are coated by metal oxide with high refractive index such as TiO_2, can be used in practically all plastic applications due to their excellent heat resistance. Table 3 introduces aluminum compounds used in plastics and rubbers (including catalysts, co-stabilizers, fillers, anti-blocking additives and pigments), their targets of use and aluminum residues left in the polymer.

Table 3. Aluminum compounds used in polymers.

Name	Chemical formula	Application	Target of use	Al content in plastics (mg/kg)
Triethyl aluminum	$(C_2H_5)_3Al$	Catalyst	LLDPE, HDPE, PP	10–100
Diethyl aluminum chloride	$(C_2H_5)_2AlCl$	Catalyst	LLDPE, HDPE, PP	10–100
Methylaluminoxane	$Al(CH_3)O$	Catalyst	LLDPE, HDPE, PP	10–30
Zeolite	$Na_{12}(Al_{12}Si_{12}O_{48})\cdot 27H_2O$	Co-stabilizer/anti-blocking additive	PVC/LLDPE,LDPE,PVC	300–2700
Hydrotalcite	$Mg_6Al_2/CO_3)(OH)_{16}\cdot 4H_2O$	Co-stabilizer	PVC	300–1300
Glass fiber	$SiO_2/CaO/Al_2O_3/B_2O_3$	Filler	PVC, PE,PP, PS, PET, PA, ABS, PU	6300–28000
Kaolin clay	SiO_2/Al_2O_3	Filler	PVC,PE, rubber	15000–58000
Mica	$SiO_2/Al_2O_3/K_2O$	Filler/pigment/anti-blocking additive	PP, PBT, PA	6300–37000
Alumina trihydrate	$Al(OH)_3$	Flame retardant	PVC,PE,PS, PU, rubber	65000–200000
Ultramarine blue	$Na_{6-8}Al_6Si_6O_{24}S_{2-4}$	Pigment	PVC, PS, LDPE, HDPE, rubber	90–900
Cobalt aluminate	$CoAl_2O_4$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	100–1600
Cobalt chromium aluminate	$Co(Al,Cr)_2O_4$	Pigment	PVC,PS,PO,ABS,PA	100–1600
Metallic aluminum	Al in metallic form	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	500–50000

2.3 Antimony compounds in plastics

Antimony compounds can be utilized as catalysts e.g. in the polymerization of PET, as individual flame retardant in PVC and as a synergist for halogenated flame retardants. Besides that, antimony may be incorporated into the lattice of rutile in mixed metal oxide pigments. The usage levels, especially when antimony compounds are used as flame retardants, can amount to several weight percent.

2.3.1 Antimony compounds as catalysts

Antimony compounds, particularly antimony trioxide (ATO) with chemical formula Sb_2O_3, are typically used as a polycondensation catalyst both in the transesterification and direct esterification processes of PET polymerization (Trojan, 1999; Sublett, 1992; Russin *et al.*, 1976; Moore *et al.*, 1999; Nichols, 1991; Nichols and Mason, 1992; Thiele, 2001; Duh, 2002). The amount of antimony compounds used starts from 100 ppm and it can increase up to several hundreds of ppm, depending on the application (Thiele 2001; Duh, 2002). The use of antimony based catalysts in the polymerization of PET has come under increasing scrutiny; potential alternatives have been investigated by the manufacturers (Thiele, 2001). Because of the price and effectiveness of antimony catalysts they will be in use also in the future.

2.3.2 Antimony compounds as flame retardants

Some inorganic antimony compounds, especially ATO, are the most widely used synergist flame retardant compounds in halogen containing plastic applications. They cannot act as independent flame retardants, but after reacting with hydrogen halides they form volatile compounds such as antimony trichloride and various antimony oxychlorides, which act as radical interceptors in the gas phase thus suppressing flame propagation (van Esch, 1997; Troitzsch, 1993). They are used either in combination with mineral flame retardants such as ATH and MDH mainly in PVC, or with halogenated flame retardants such as brominated aromatic hydrocarbons mainly in polymers such as PVC, PE, PP, PS, polyesters, ABS and PA (Troitzsch, 1993; Cha, 2005). The usage levels of antimony compounds depend on the application and the polymer resin, but it is usually in the range of 2–5 % of the polymer (Ranken, 2009; Cusack, 1997). The antimony content in polymer resins may be as high as 4 wt-%. Besides ATO, also sodium antimonate $NaSbO_3$ has been used, especially in PET resin.

2.3.3 Antimony compounds as pigments

There are several heat, light and chemical resistant inorganic antimony containing pigments on the market. For instance, generally applicable pigments such as nickel titanium yellow $(Ti,Sb,Ni)O_2$, manganese titanium yellow $(Ti,Sb,Mn)O_2$ and chromium titanium yellow $(Ti,Sb,Cr)O_2$, contain about 6–12 wt-% of antimony (Sicotan Yellow K 1010, 2011, Sicotan Brown K 2611, 2011; C.I. Pigment Yellow 53, 2011). Table 4 introduces typical antimony compounds used in different applications, their usage levels and also the antimony content in the final polymer resin.

Table 4. Antimony compounds used in different applications.

Name	Antimony trioxide	Antimony trioxide	Nickel titanium yellow	Manganese titanium yellow	Chromium titanium yellow
Chemical formula	Sb_2O_3	Sb_2O_3	$(Ti,Sb,Ni)O_2$	$(Ti,Sb,Mn)O_2$	$(Ti,Sb,Cr)O_2$
Application	Catalyst	Flame retardant	Pigment	Pigment	Pigment
Target of use	PET	PVC, PE, PP, polyesters, PS, ABS, PA	PVC, PE,PP, PS, PET, PA, ABS, PU	PVC, PE,PP, PS, PET, PA, ABS, PU	PVC, PE,PP, PS, PET, PA, ABS, PU
Sb content in compound (%)	83–84	83–84	10–11	6	10–12
Usage level of compound (%)	–	0.5–5	0.05–0.5	0.05–0.5	0.05–0.5
Sb content in plastics (mg/kg)	100–300	4200–42000	50–550	30–300	50–600

2.4 Titanium compounds in plastics and rubbers

Besides zinc, calcium and aluminum, titanium is the most versatile metal used in plastics and rubbers. Organic and inorganic titanium compounds can be used as catalysts in the polymerization of polyolefins and polyesters, while inorganic titanium compounds can be used as fillers/opacifying agents or diluents in combination with other pigments, and titanium based rutile/spinel type compounds may be separately utilized as pigments. In addition organic titanium compounds may be used as coupling agents in filler modified plastics.

2.4.1 Titanium based catalyst compounds

Today there is a wide range of catalyst systems developed for polymerizing both olefins and linear esters. Most of these systems are based on titanium compounds, either organic or inorganic, used with or without catalyst support materials such as silica, magnesium chloride and aluminum oxide.

For polyolefins, there are two different catalyst systems essentially based on titanium compounds; the Z-N system for polymerization of LLDPE, HDPE and PP, and the metallocene catalyst system, which has mostly been utilized in the polymerization of LLDPE and PP. In the Z-N method, titanium compounds such as titanium chlorides and titanium alkoxides are used in combination with co-catalysts such as organoaluminum compounds to catalyze the polymerization reaction on the surface of porous support material, which can be e.g. magnesium chloride (Kissin, 1996a). Because of the effective support materials and catalyst compounds, the concentration of the metal catalyst used in the polymerization is nowadays so low that the catalyst can be left in the polymer without further purification. Usually the titanium residue level left in polymer is lower than 15 mg/kg (Bichinho *et al.*, 2005, Goodall *et al.*, 1983; Epacher *et al.*, 2000) of the polymer; it may be as high as 50 mg/kg, depending on the catalyst system used (Hussain *et al.*, 2010; Bichinho *et al.*, 2005). Metallocene catalyst systems contain two components, a metallocene complex of titanium (or zirconium), and an organoaluminum co-catalyst component such as methylaluminoxane in combination with support material such as silica (Kissin, 1996a; Nielsen 1993). They are even more active than the previous Z-N system; thus the metal catalyst can remain in the product, and its content is much lower than in the Z-N case. If polyolefins are produced in a catalyst system based on chromium compounds (Phillip's catalysts), the support material of the catalyst is occasionally a mixture of silica and titanium oxide containing 2–20 wt-% of titanium (Kissin, 1996a). Titanium may thus exist as a residue in these polymers also at levels as high as 10 mg/kg (Epacher et al., 2000).

Organotitanium compounds have also been utilized in the polymerization of PET and PBT. PET is mainly produced by antimony catalysts such as antimony trioxide, but because of its toxicity, it is being replaced by less toxic alternatives such as titanium compounds. A composition of titanates and some phosphorus containing compounds offers an active and stable catalyst system, where the concentration of elemental titanium may be as low as 10–20 mg/kg (MacDonald, 2002). Titanium compounds such as tetraalkyltitanates are mainly utilized in the polymerization of PBT. Typically the concentrations of the total catalyst system are in the range of 25–100 mg/kg of the polymer; thus the residue elemental titanium content is low (Tong *et al.*, 1988; Kim *et al.*, 1992).

2.4.2 Titanium compounds as pigments/fillers and coupling agents

White titanium dioxide TiO_2 is the most widely used pigment for plastics; in 2004 the total production of titanium dioxide was around 4.4 million metric tons, and over 20 % of that is consumed in plastic applications (Buxbaum and Pfaff, 2005; Swiler, 2000). TiO_2 finds use also in rubbers but with minor volumes compared to plastics (Buxbaum and Pfaff, 2005). TiO_2 can be used for several purposes: as a diluent of colored pigments, a widely suitable white pigment, and when the concentrations are high enough it can also be considered as filler. The usage levels are high, typically between 0.5–5 wt-%. There are two different mineral forms of TiO_2 pigments, rutile and anatase, in which rutile is the dominant due to its high refractive index, which helps to protect plastics from harmful radiation (Damm and Herrmann, 1993; Scherrer and Sykes, 2009; Beebe, 1993). Therefore its use has been recommended particularly for plastics planned for outdoor use, such as automobiles and packaging films. Anatase can be used in indoor applications where less abrasive nature of the pigment is preferred over the loss of UV protection ability of rutile.

Complex mixed metal pigments, where metals such as nickel, zinc and antimony are incorporated into the lattice of rutile, are nowadays favored for yellow and green coloring, particularly due to their high resistance against weather, temperature and chemicals, but also because they replace more toxic cadmium/lead based yellow pigments (Damm and Herrmann, 1993; Mathew and Grossman, 2007; Rangos, 2005). Also some titanate pigments, such as cobalt nickel zinc titanate $(Co,Ni,Zn)_2TiO_4$, are widely used. The titanium content in these pigments varies between 45–55 wt-% (Sicotan Brown K 2611, 2011; C.I. Pigment Brown 24, 2011), and usage levels are in the range of 0.05–0.5 wt-%.

Titanates or zirconates may be used as coupling agents in plastics either in order to modify filler surfaces to improve incorporation and distribution, or to bind two different molecules together (e.g. filler that is attached to the polymer resin) (Robinson *et al.*, 2008; Scherrer and Sykes, 2009; Hohenberger, 2009). There are several compounds that can be used, such as pyrophosphate titanates and benzene sulfonyl titanates. The recommended concentration range is between 0.2–2.0 % by weight of the filler, and thus the titanium residue in the polymer may be as high as 100 mg/kg, depending on the type and amount of the filler used. Table 5 introduces titanium catalysts, pigments and coupling agents used in plastics, their applications and usage levels and also titanium residue levels in the polymer.

Table 5. Titanium compounds used in different plastic and rubber applications.

Name	**Chemical formula**	**Application**	**Target of use**	**Usage level of compound (%)**	**Ti content in plastics (mg/kg)**
Tetrabutyl titanate	$C_{16}H_{36}O_4Ti$	Catalyst	PBT	0.01–0.1	10–70
Titanium chloride	$TiCl_4$	Catalyst	LLDPE, HDPE, PP	–	10–50
Titanium oxide	TiO_2	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU, rubber	0.5–5	3000–30000
Nickel titanium yellow	$(Ti,Sb,Ni)O_2$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	0.05–0.5	200–2700
Manganese titanium yellow	$(Ti,Sb,Mn)O_2$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	0.05–0.5	200–2700
Chromium titanium yellow	$(Ti,Sb,Cr)O_2$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	0.05–0.5	200–2700
Nickel niobium titanium	$(Ti,Nb,Ni)O_2$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	0.05–0.5	200–2700
Co/Ti/Ni/Zn-oxid	$(Co,Ni,Zn)_2TiO_4$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	0.05–0.5	100–1100

2.5 Tin compounds in plastics

Tin compounds have a significant role both in the polymerization of plastics and also as heat stabilizers for PVC. In addition, specific tin compounds can be used as flame retardants suitable for several different types of plastic. When tin compounds are utilized as heat stabilizers and flame retardants, the final tin content in polymer can be as high as several weight percent. The usage level of tin compounds is expected to grow, especially within heat stabilizers and flame retardants, mainly due to the replacement of more toxic compounds based on lead and antimony.

2.5.1 Tin compounds as heat stabilizers for PVC

Tin containing heat stabilizers, which are by far the most effective stabilizer compounds in PVC, have gained a high level of use particularly in the U.S, where lead stabilizers are only used for wire and cable insulation (Jennings and Starnes, 2005; Dworkin, 1989). Due to their efficiency, the concentrations of tin compounds needed for stabilization are significantly lower than e.g. in the case of lead stabilizers. Mono- and dialkyltin compounds with the general formula $RSnX_3$ and R_2SnX_2 are the most common stabilizer types; in these compounds the R-group can be methyl, n-butyl or n-octyl and the ligand X is typically carboxylate, mercaptoester or sulfide (Starnes and Jennings, 2009; Thacker *et al.*, 2007; Piver, 1973). Some examples of these comprise dibutyltin dilaurate, dibutyltin maleate and dibutyltin S,S-bis(isooctylthioglycolate). The tin content varies according to the type of the ligand and alkyl groups, and is usually 15–22 percent by weight of the stabilizer, but in some specific cases it may decrease to as low as 4–13 percent (so called reverse esters) (Jennings and Starnes, 2005; Thacker *et al.*, 2007; Dworkin, 1989). Mono- and dibutyltin sulfides are used when higher tin contents in stabilizer systems are required. The sulfur containing stabilizers are dominant; they cover about 90 % of the overall organotin stabilizer market (Jennings and Starnes, 2005; Dworkin, 1989). Organotin stabilizers are commonly used in rigid PVC and also in some flexible PVC applications, and they are also suitable for manufacturing transparent PVC articles (Jennings and Starnes, 2005, Starnes and Jennings, 2009; Andreas, 1993; Summers, 1997; Tin Compounds, 1997). In North America organotin stabilizers have been used largely in rigid pipe and profile applications, and some compounds such as octyl tins are also approved for food contact applications. By choosing suitable co-stabilizers and lubricants for tin compounds, it is possible to improve their performance significantly and thus reduce their usage levels even to one half. Such synergist compounds are calcium stearate, hydrotalcite and zeolites (Jennings and Starnes, 2005; Thacker *et al.*, 2007). In Table 6 there are some typical applications of tin stabilizers, and also estimates of the final tin content in PVC matrices.

Table 6. Typical organotin stabilizer/lubricant levels by application (Jennings and Starnes, 2005; Thacker *et al.*, 2007; Thermolite 161, 2011; Thermolite 176, 2011).

Application	Pipe	Fittings	Window profile	Bottles	Calendered sheet
Typical stabilizer usage level (%)	0.2–0.5	1–2	0.8–1.3	1–2	0.8–1.3
Sn content in polymer (mg/kg)	200–800	2000–4000	1000–3000	2000–4000	1000–3000

2.5.2 Tin compounds as catalysts

Tin and especially organotin compounds are used in various polymerization reactions. In plastics, they are used as catalysts in the polymerization of PBT and PU.

PBT polymers are commercially produced in a polycondensation reaction between 1,4-butanediol and terephthalic acid (TPA), or 1,4-butanediol and dimethyl terephthalate (DMT) in the presence of an esterification catalyst. The suitable polymerization catalyst in the process, where PBT is formed from TPA and 1,4-butanediol, is an organotin compound (e.g. trimethyltin/triethyltin hydroxide, tributyltin acetate, diphenyltin dilaurate), although there are also other possible options (such as organotitanates, which are the preferred catalyst compounds) (Tong *et al.*, 1988; Kim *et al.*, 1992; East *et al.*, 1996; Choi, 2005). The amounts of organometallic catalysts used vary generally from 0.01 wt-% to 0.3 wt-%, based on weight of the TPA; thus the tin content in the final polymer (without a purification step) may vary from 0.002 wt-% up to 0.1 wt-% (Tong *et al.*, 1988).

Organotin compounds are also utilized in the polymerization of urethane (Piver, 1973). Their use promotes the reaction between the raw materials (i.e. isocyanates and polyols), and they are useful even at very low usage levels. A combination of tin and tertiary amine catalysts is used in order to balance the urethane formation and the blowing reaction (urea formation) (Ulrich, 1997). Suitable catalyst compounds for the polymerization of flexible PU foam are stannous octoate, dibutyltin dilaurate, dibutyltin oxide and dibutyltin bis(isooctylmaleate). Concentrations for the tin compounds are determined by the grade of PU to be polymerized, but usually the tin content in the final polymer varies from 40 mg/kg up to 900 mg/kg (Gooch *et al.*, 2000; Aerts *et al.*, 1992; Grier *et al.*, 1996; Merten *et al.*, 1965; Richardson and Hustad, 1972; Bechara and Mascioli, 1984; Chen, 1994; Stone *et al.*, 1990; Valoppi and Bredeson, 1999). The catalysts used in the manufacture of rigid polyurethane foams include tin and tertiary amine compounds such as dibutyl tin dilaurate and stannous octoate, with concentrations usually similar to those used in the production of flexible foams (Stone *et al.*, 1990; Eaves, 2004; Naka *et al.*, 1988), but sometimes concentrations as low as 50–70 mg/kg are possible (Chen, 1994; Valoppi and Bredeson, 1999).Thus the tin content is not higher than 0.1 % by weight of the final polymer. Typical tin based catalysts and tin residue levels in PBT and PU resins are given in Table 7.

Table 7. Organotin catalysts, their applications and tin residue level in plastics.

Catalyst	Tributyltin acetate	Stannous octoate	Dibutyltin dilaurate	Dibutyltin oxide
Chemical formula	$(C_4H_9)_3SnOOCCH_3$	$C_{16}H_{30}O_4Sn$	$C_{32}H_{64}O_4Sn$	$C_8H_{18}OSn$
Target of use	PBT	PU	PU	PU
Sn residue in polymer (mg/kg)	20–700	150–900	40–600	200–1400

2.5.3 Tin compounds as flame retardants

Tin compounds can be utilized in several flame retardant systems. The most important compounds are zinc stannate $ZnSnO_3$ (ZS) and zinc hydroxystannate $ZnSn(OH)_6$ (ZHS), which are typically used as synergists in a combination with halogenated species by promoting the effectiveness of the halogenated flame retardant compounds, thus acting in similar way than antimony containing synergists (Horrocks, 2009; Horrocks *et al.*, 2010). Besides the synergist effect, ZS and ZHS also contribute to the smoke suppression and char formation activity, and since they are relatively non-toxic compounds compared particularly to antimony containing species, their wide-ranging use in plastics will be feasible in the future. ZHS decomposes already at temperatures around 180 °C releasing water, thus its use is recommended for plastics processed at temperatures below that. ZS is stable up to 400 °C and therefore it can generally be used in plastic applications.

ZS (Cusack and Hornsby, 1999) and ZHS (Cusack and Hornsby, 1999; Baggaley *et al.*, 1997) may be used as flame retardants in PVC, particularly in flexible PVC, where they may either act separately or in combination with ATH and MDH (Baggaley *et al.*, 1997). When ZHS is used alone, very low concentrations are required for sufficient flame retardant effect; usually concentrations as low as 1–3 wt-% give satisfying results. In that case the tin content in the final polymer can be in the range 0.4–1.2 wt-%. ZHS can also be used as a coating material for ATH (10 wt-% of ZHS and 90 wt-% of ATH), which leads to a significant reduction of the volume of ATH used; the tin content in the final polymer resin varies between 0.5–0.8 wt-%. The use of ZHS in rigid PVC formulations is also very profitable due to its combined additive flame retardant and smoke suppressant properties (Thomas, 2003). Here the concentration of ZHS is at the same level as in flexible PVC applications.

ZS and ZHS act as replacements of ATO also in PP, polyesters (PET and PBT) and sometimes PA, being effective even at low concentration levels (Vasile and Rusu, 2000; Horrocks, 2009; Weil and Levchik, 2004). ZS has been tested in PP both in combination with MDH and as a coating material of MDH (Cusack and Hornsby, 1999). The best results were obtained using ZS-coated MDH (coating level about 10 wt-% (Cusack *et al.*, 2000)), however the polymer resin has to be properly halogenated for a sufficient flame retardant effect. In the case of polyesters, concentration levels lower than 3 wt-% of ZHS give sufficient synergist effect, but not in systems where alicyclic chlorine or aromatic bromine compounds are the main flame retardant compounds (Cusack, 1997; Horrocks, 2009). Table 8 presents typical applications for flame retardant compounds containing tin, and also tin content in final polymers.

Table 8. Applications for FR tin compounds and tin content in polymer.

FR compound	Zinc stannate	Zinc hydroxystannate
Molecular formula	$ZnSnO_3$	$ZnSn(OH)_6$
Sn content in compound (%)	51	41–42
Application	PVC, PP, polyesters, PA	PVC, PP, polyesters, PA
Usage level of compound (%)	1–3	1–3
Sn content in polymer (mg/kg)	4000–12000	4000–10000

2.6 Zinc compounds in plastics and rubbers

Zinc is the most widely utilized transition metal in plastics. Zinc compounds can be used as heat stabilizers in PVC, inorganic pigments suitable for almost every type of plastics, acid scavengers for polyolefins, flame retardants in several types of plastics and also as antimicrobials especially in PVC and PU.

2.6.1 Zinc containing heat stabilizers in PVC

Organic zinc compounds, typically the zinc salts of fatty acids, can be used in several different heat stabilizing systems for PVC. They can be used in combination with organic barium compounds either in solid or liquid form in order to gain a synergist effect, or in corresponding systems with organic salts of calcium and inorganic hydrotalcite (Jennings and Starnes, 2005; Thacker *et al.*, 2007). Zinc compounds act as primary stabilizer compounds replacing reactive allylic chlorides in active PVC structure site by substitution reaction, whereas secondary stabilizer compounds such as organic calcium compounds, zeolites and hydrotalcites act as acid scavengers for HCl generated after the decomposition of some active PVC site.

The most widely used compound is zinc stearate (ZnSt), which can be used in both barium and calcium solid/liquid systems. Other possible zinc compounds are zinc-2-ethylhexanoate and zinc neodecanoate, which are mostly utilized in liquid stabilizer systems. The content of zinc in stabilizers is sometimes hard to evaluate due to the large amount of different liquid and solid stabilizer systems existing (where the proportions of metals vary significantly with respect to the property required), but rough estimates can still be made. Usually the zinc content in liquid Ba/Zn and Ca/Zn systems is in the range of 1–2 wt-%, whereas in solid systems the content is a somewhat higher, usually at the level of 2–3 wt-% (Jennings and Starnes, 2005; Starnes and Jennings, 2009; Thacker *et al.*, 2007). The usage level of these stabilizers varies according to the application, but is typically in the range of 1–2.5 wt-% (Starnes and Jennings, 2009; Andreas, 1993). Table 9 shows the typical usage levels for mixed metal stabilizers and the zinc content in the stabilized PVC resin.

Table 9. Typical mixed metal stabilizer usage levels and zinc residue in PVC.

Stabilizer type	Ba/Zn solid	Ba/Zn liquid	Ca/Zn solid	Ca/Zn liquid
Usage level of stabilizer (%)	1.0–2.0	1.0–2.0	0.5–2.0	1.0–2.0
Zn content in PVC (mg/kg)	250–500	200–400	100–500	200–400

2.6.2 Zinc compounds as catalysts

Zinc compounds have also been utilized in the polymerization of PET and PU. PET is typically produced by two routes: (1) transesterification of DMT with ethylene glycol to form an intermediate, followed by polycondensation to form PET, or (2) by direct esterification of TPA with ethylene glycol, followed by polycondensation to form PET (Lustig and Burch, 1999). Zinc salts, such as zinc acetate, zinc oxide, zinc sulfide and zinc bromide, are mainly used as catalysts during the transesterification step (Trojan, 1999; Lustig and Burch, 1999; Hovenkamp, 1971; Shin *et al.*, 1999) and occasionally in the direct esterification step (Nichols, 1991; Nichols and Mason, 1992). The elemental zinc content in the transesterification step is usually between 30–80 mg/kg (Trojan, 1999; Russin *et al.*, 1976). In the direct esterification, total metal concentrations up to 100 mg/kg are possible (the catalyst is usually a mixture of metals such as zinc, manganese and magnesium) (Nichols, 1991; Nichols and Mason, 1992).

The compounds used as catalysts in urethane polymerization are mainly zinc amino carboxylates (Zn-% ~ 10–12). The concentration of the catalyst compound is in the range of 0.12–0.35 wt-%, and the zinc residue in the polymer can be at level of 150–400 mg/kg. Since tin compounds are more efficient as catalysts in the polymerization of urethane, zinc compounds are not commonly used. Table 10 presents the typical zinc compounds, their usage levels and zinc residue levels in the final polymerization of PET and PU.

Table 10. Zinc catalyst compounds, their applications and zinc residue left in polymer.

Catalyst	zinc acetate	zinc oxide	zinc bromide	zinc amino carboxylate
Target of use	PET	PET	PET	PU
Zn residue in polymer (mg/kg)	30–100	30–100	30–100	150–1400

2.6.3 Zinc compounds as acid scavengers and antimicrobials

ZnSt and zinc oxide have been utilized as acid scavengers in polyolefins. Their function is to neutralize the acidic halogen components resulting from the halogenated catalysts used in the polymerization, or from the halogen containing additives such as brominated/chlorinated flame retardants (Holzner and Chmil, 2009). They are mainly used with polyethylenes (in PP calcium stearate is the dominant), and the volumes used depend on the catalyst system used in the polymerization (Holzner and Chmil, 2009). For example, if LLDPE is produced by the Z-N method (titanium based dominant polymerization system), the concentrations of zinc compounds required for the stabilization are in the range of 500–1500 mg/kg for ZnSt and 200–800 mg/kg for ZnO. ZnSt, due to its lubricating effect, can be used for both neutralization and lubrication in polymers; in this case higher ZnSt level at a concentration range of 1500–3000 mg/kg is required. Typical concentrations of zinc compounds used in LLDPE polymerized by the Z-N system and HDPE polymerized either by chromium or Z-N catalyst systems are shown in Table 11.

Zinc pyriothine is used as an antimicrobial (a compound used to prevent the growth of viruses, bacteria and fungi) (Ochs, 2009) mainly in PVC and PU, but it can also be used in other plastic applications. It is normally used as a 5 wt-% masterbatch (mixture which contains 5 wt-% Zn in some inert matrix), and the volumes for masterbatches are typically in the range of 2–3 wt-%; thus the zinc residue in the final polymer can be in the range of 200–300 mg/kg (Thacker *et al.*, 2007).

Table 11. Concentrations of zinc compounds as acid scavengers and antimicrobials in plastics.

Zinc compounds as acid scavengers/ antimicrobials	**LLDPE polymerized by Ti/Al catalysts**	**HDPE polymerized by Ti/Al catalysts**	**HDPE polymerized by Cr catalysts**	**PVC, PU and polyolefins**
ZnSt for acid scavenging (mg/kg)	500–1500	300–1000	200–500	–
ZnO for acid scavenging (mg/kg)	200–800	200–800	–	–
ZnSt for lubrication (mg/kg)	1500–3000	1500–3000	1500–3000	–
Zinc pyriothine as antimicrobial (mg/kg)	–	–	–	1000–1500
Total Zn content in polymer (mg/kg)	370–1100	350–1100	180–360	200–300

2.6.4 Zinc in flame retardants

Similar to tin compounds, zinc compounds are used mainly as synergists in combination with halogenated flame retardants. They are often used as partial or total replacements of more toxic antimony synergists. The most widely used compound is zinc borate (ZB) with chemical formula $2ZnO \cdot 3B_2O_3 \cdot 3{,}5H_2O$, used both in halogenated (mainly in combination with ATO) and halogen-free systems (in conjunction with mineral flame retardants such as ATH and MDH) (Beard, 2007; Formicola *et al.*, 2009). Unlike ATO and other zinc/tin containing additive flame retardants, ZB can sometimes be used as individual FR compound. ZB releases its crystal water at rather low temperatures thus absorbing heat and diluting the gaseous flammable components, and afterwards the dehydrated ZB melts at higher temperatures forming a layer which insulates the flammable surface (Yang *et al.*, 1999). In addition ZB acts as a smoke suppressant and a char promoter, which are beneficial features with respect to new fire standards (Formicola *et al.*, 2009, Ferm and Shen, 1997). ZB can be used in all types of plastics, particularly in PVC (Ferm and Shen, 1997; Pi *et al.*, 2003), but also in polyolefins (Beard, 2007), polyesters (Levchik and Weil, 2005) and PA (Markarian, 2005). As mentioned earlier in the tin section, ZS and ZHS may be utilized e.g. in PVC (Thomas, 2003), polyesters (Cusack, 1997) and polypropylene (Cusack and Hornsby, 1999). ZS and ZHS may be used either as separate ingredients in combination with halogenated/mineral based flame retardants, or as coating material for mineral based flame retardants (coating of ATH and MDH), particularly in flexible PVC (Baggaley *et al.*, 1997; Cusack *et al.*, 2000). Zinc sulfide is also utilized; it finds use in PVC as a partial replacement of antimony oxide (Schartel *et al.*, 2002; Levchik and Weil, 2005). Table 12 introduces zinc containing flame retardants, their applications and usage levels and the zinc content in the final polymer.

Table 12. FR compounds containing zinc and zinc content in final polymer.

FR compound	Zinc borate	Zinc stannate	Zinc hydroxystannate	Zinc sulfide
Molecular formula	$2ZnO \cdot 3B_2O_3 \cdot 3,5\ H_2O$	$ZnSnO_3$	$ZnSn(OH)_6$	ZnS
Application	Synergist/independent FR in PVC Synergist in unreinforced PA 6 In combination with halogenated FRs in polyolefins and polyesters	Synergist/ independent FR in PVC In combination with halogenated FRs in polyolefins and polyesters	Synergist/independent FR in PVC In combination with halogenated FRs in polyolefins and polyesters	A partial replacement of Sb_2O_3 in flexible PVC
Usage level of compound (%)	0.5–3.0	0.5–3.0	0.5–3.0	1.5–2.5
Zn residue in polymer (mg/kg)	1500–9000	1400–8500	1200–6900	10000–17000

2.6.5 Zinc compounds as pigments

Durable inorganic pigments containing zinc are generally suitable for plastics when white, brown and green shades of color are desired. White pigments such as zinc oxide ZnO and zinc sulfide ZnS, and green/brown complex mixed metal oxide pigments such as zinc ferrite $(Zn,Fe)Fe_2O_4$, iron zinc chromium oxide $(Zn,Fe)(Fe,Cr)_2O_4$ and chromium manganese zinc oxide $(Zn,Mn)Cr_2O_4$ can generally be used in plastics (Beebe, 1993; Rangos, 2005; Novotny *et al.*, 1996; Christensen, 2003; Rockwood Pigments, 2011). The use of zinc containing white pigments has decreased due to the more effective TiO_2 pigments, but ZnS is still preferred over TiO_2 in glass-fiber reinforced plastics (such as PA) because of the more abrasive nature of TiO_2 (Buxbaum and Pfaff, 2005; Scherrer and Sykes, 2009). Also lithopone, the mixture of ZnS and $BaSO_4$, finds still use in plastics, both as a white pigment and as a partial replacement of ATO in flame retarded plastic applications (Buxbaum and Pfaff, 2005). ZnS may also be used in combination with yellow cadmium sulfide pigments if greenish shades of color are desired (Tolinski, 2009). Complex inorganic pigments can be considered as solid solutions, where at least one individual metal oxide compound is distributed in the crystal structure of the host metal oxide compound (Buxbaum and Pfaff, 2005; Rangos, 2005). The most typical crystal structures are spinel and rutile, zinc is present only in spinel type of pigments. Since rutile type of pigments offer brighter and cleaner shades of yellow/brown color, they are by far the most commonly used mixed metal oxide pigments in plastics (Buxbaum and Pfaff, 2005; Rangos, 2005). Heat durable spinel types of pigments such as yellowish-brown zinc ferrite are mainly used in plastic applications processed at higher temperatures (Buxbaum and Pfaff, 2005). In green spinel type of pigments such as cobalt chromite $CoCr_2O_4$ and cobalt titanate $CoTi_2O_4$, cobalt ions may be partially replaced by zinc (and nickel) ions in order to gain different shades of color (Rangos, 2005; Sicopal Green K 9610, 2011; Charvat, 2000). In metal flake pigments zinc is used in brass (the alloy of Zn and Cu); the zinc content is in the range of 8–30 wt-% depending on the type of brass (Beebe, 1993). The most widely used zinc containing pigments, their applications/usage levels and the zinc content in the final plastic polymer are presented in Table 13.

2.6.6 Zinc compounds in rubbers

Zinc compounds, particularly zinc oxide ZnO, have gained a crucial importance in rubber industry; currently almost half of the annual production of ZnO is used in both natural and synthetic rubber applications (Buxbaum and Pfaff, 2005). The function of ZnO is to act as an activator compound for organic accelerators in the vulcanization procedure, in which the independent elastomer chains are chemically tied together by (sulfur) cross-links (Hertz Jr, 1984; Heideman *et al.*, 2005). Besides the activator compound, ZnO is also used as filler in some specific applications (Rodgers *et al.*, 2000). The concentration of ZnO in rubbers depends on application, but it is typically in the range of 0.5–3.0 wt-% (Kawasaki and Hattori, 2010; Suzuki, 2008; Miyazaki, 2012). Therefore the elemental zinc content in rubbers ranges between 4 000–25 000 mg/kg.

Table 13. Zinc pigment compounds, their applications and the zinc content in the polymer.

Compound	Molecular formula	Application	Usage level of compound (%)	Zn content in polymer (mg/kg)
Zinc oxide	ZnO	PVC, PE,PP, PS, PET, PA, PU	0.01–0.5	80–4000
Zinc oxide	ZnO	Natural and synthetic rubber	0.5–3.0	4000–25000
Zinc sulfide	ZnS	PVC, PE,PP, PS, PET, PA, PU	0.05–1	100–6700
Zinc ferrite	$(Zn, Fe)Fe_2O_4$	PVC, PE,PP, PS, PET, PA, PU	0.05–0.5	40–2000
Iron zinc chromium oxide	$(Zn, Fe)(Fe, Cr)_2O_4$	Not for rigid PVC	0.05–0.5	50–700
Zinc manganese chromate	$(Zn, Mn)Cr_2O_4$	Restricted use in rigid PVC	0.05–0.5	50–700
Cobalt nickel zinc titanate	$(Co, Ni, Zn)TiO_4$	PVC, PE,PP, PS, PET, PA, PU	0.05–0.5	50–600
Lithopone	$ZnS + BaSO_4$	PVC, PE,PP, PS, PET, PA, PU	0.05–0.5	100–1000
Modified cadmium sulfide	$CdS + ZnS$	PVC, PE,PP, PS, PET, PU	0.05–0.5	80–850
Brass flakes	Metallic $Cu + Zn$	PVC, PE,PP, PS, PET, PU	0.05–0.5	100–1500

2.7 Iron compounds in plastics and rubbers

Like many other metals, iron is mainly used in the coloration of plastics and rubbers, either as an individual metal compound or in combination with other transition metals, resulting in a wide variety of colors. In addition iron may be found as a residue in several inorganic fillers used in plastics.

2.7.1 Iron compounds as pigments

After white titanium oxide pigment, multi-colored iron oxide pigments are the most widely used and produced inorganic pigments; in 2002 the production of iron oxide pigments was about 0.9 million metric tons, in which the coloration of plastics and rubbers constituted around 6 % (i.e. 55 000 metric tons) (Buxbaum and Pfaff, 2005; Swiler, 2000). There are both natural and synthetic iron oxide pigments on the market, but in plastics (and rubbers) the synthetic compounds are preferred due to their higher color quality and more uniform particle size distribution (Swiler, 2000; Charvat, 2000).

The compounds with the simplest structure are different kinds of iron oxides for yellow, red and brown/black coloration with chemical formulas $Fe_2O_3 \cdot H_2O$, Fe_2O_3 and Fe_3O_4, respectively (Scherrer and Sykes, 2009; Novotny *et al.*, 1996). Red pigment Fe_2O_3 is widely suitable for plastics (excluding rigid PVC) and also for mineral filled rubber articles (Buxbaum and Pfaff, 2005; Ohm, 2000), but because of the limited thermal stability of other compounds, they are suitable only for plastics processed at lower temperatures. Thus yellow $Fe_2O_3 \cdot H_2O$ is only used for the coloration of flexible PVC and brown/black Fe_3O_4 is used for the coloration of PVC, PS and LDPE (Scherrer and Sykers, 2009).

Complex inorganic iron containing pigments are compounds with spinel structures, such as iron chromium oxide $(Fe,Cr)_2O_3$, iron zinc oxide $(Zn,Fe)Fe_2O_4$, iron zinc chromium oxide $(Zn,Fe)(Fe,Cr)_2O_4$ and iron titanium oxide Fe_2TiO_4 (Rangos, 2005; Rockwood Pigments, 2011; Sicopal Brown K 2595, 2011). These pigments are temperature and chemical resistant and thus widely suitable for plastics at concentrations typical for inorganic pigments.

2.7.2 Iron compounds as residues in fillers/reinforcements

As mentioned before in the case of aluminum, the concentrations of metal residues existing in the structures of fillers can amount to significant levels. Iron oxides are the most typical residue compounds existing at concentrations up to several percent by weight of the filler/impact modifier. Fillers containing iron residues are typically chalk, talc, calcium carbonate, dolomite, glass fibers, wollastonite, mica and kaolin clay (Robinson *et al.*, 2008; Hohenberger, 2009). Besides the use as fillers, talc, mica, clay and zeolites are widely used as anti-blocking additives for PVC, LDPE and LLDPE with concentrations from 2000 mg/kg up to 6000 mg/kg (Robinson *et al.*, 2008; Hohenberger, 2009).

Table 14 introduces the most typical iron based pigments, their applications and usage levels and iron residue content in the final polymer. It also presents the most typical fillers/impact modifiers, their targets of use and typical iron residue levels in plastics caused by the fillers.

Table 14. Iron containing pigments and fillers and their usage levels and contents in polymers.

Name	Chemical -ormula	Application	Target of use	Fe content (%)	Usage level of com-pound (%)	Fe content in plastics (mg/kg)
Hydrated iron oxide	$Fe_2O_3{\cdot}H_2O$	Pigment	Flexible PVC	63	0.05–0.5	60–3000
Iron oxide	Fe_2O_3	Pigment	Widely suitable for plastics and rubbers	70	0.05–0.5	300–3500
Iron oxide	Fe_3O_4	Pigment	PVC, PS, LDPE	72	0.05–0.5	300–3600
Iron chromium oxide	$(Fe,Cr)_2O_3$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	52	0.05–0.5	250–2600
Iron zinc oxide	$(Zn, Fe)Fe_2O_4$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	34	0.05–0.5	150–1700
Iron zinc chromium oxide	$(Zn, Fe)(Fe, Cr)_2O_4$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	36	0.05–0.5	150–1800
Iron titanium oxide	Fe_2TiO_4	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	50	0.05–0.5	250–2500
Chalk	$CaCO_3$	Filler	PVC, PE	0–0.1	10–30	0–560
Glass fibers	$SiO_2/CaO/Al_2O_3/B_2O_3$	Impact modifier	PVC, PE,PP, PS, PET, PA, ABS, PU	0–0.2	10–30	0–630
Dolomite	$CaCO_3/MgCO_3$	Filler	PVC	0–0.1	10–30	0–560
Wollastonite	CaO/SiO2	Filler	PVC, PP, PA, PU	0–0.3	10–20	0–560
Talc	$SiO_2/MgO/CaO$	Filler	PP	0.03–0.1	10–30	70–560
Mica	$SiO_2/Al_2O_3/K_2O$	Filler	PP, PBT, PA	0.7–7.0	10–30	700–14000
Kaolin	SiO_2/Al_2O_3	Filler	PVC, LDPE, PA	0–0.2	10–30	0–630

2.8 Nickel compounds in plastics

Nickel is a very versatile metal in plastics. It can be used as a catalyst in specific cases, but mainly nickel compounds are used as light/heat stabilizers in polyolefins, and as organic azo (structure containing at least one nitrogen group) and durable inorganic mixed metal pigments, where nickel is incorporated into the lattice of rutile.

Organic nickel compounds such as nickel octanoate may be used as catalysts in the polymerization of 1,4-butadiene to produce 1,4-cis-polybutadiene, which is an important impact modifier for both HIPS and ABS (Castner, 1992). The proportion of polybutadiene incorporated in the resin is usually in the range of 10–15 % of the polymer resin. The amount of nickel catalyst used during the polymerization is about 1 gram per 10 kg of polybutadiene product; considering the purification step and the small proportion of polybutadiene in plastic resin, it can be estimated that the nickel concentration in the final plastic matrix does not exceed 10 mg/kg.

Organic nickel compounds containing aromatic rings, amine groups and either sulfur or phosphorus have been used as heat stabilizers in polyolefins such as LDPE and PP for a long time. The metal content in the stabilizers varies between 6–10 wt-% and the usage level is typically in the range of 0.15–0.5 % of the polymer (Gugumus, 2009; Gugumus, 1993a). Nowadays their use is declining due to the more effective hindered amine based stabilizers (HALS), but they are still used in combination with UV absorbers in PP and LDPE polymers, mainly due to the economic reasons, and also in agricultural films for their antimicrobial effect (Gugumus, 2009; Kattas *et al.*, 2000).

If yellow, green and orange shades of color are desired, nickel containing organic and inorganic pigments are a good option. Pigment yellow 150 and Pigment Orange 68 are organic nickel complexes, which are usually utilized for the coloration of PP and PA fibers (yellow) and HDPE, PP, PA and PC (orange) (Scherrer and Sykes, 2009; Beebe, 1993; Herbst and Hunger, 1997). Complex inorganic rutile based pigments such as nickel antimony titanium oxide $(Ti,Ni,Sb)O_2$ and nickel niobium titanium oxide $(Ti,Ni,Nb)O_2$ are durable, chemical resistant and suitable for even extreme circumstances; they are widely used in plastics (Sicotan Yellow K 1010, 2011). Table 15 presents the most widely used nickel containing heat stabilizers and pigments, their targets of use and also the nickel content in final polymer resins.

Table 15. Nickel containing stabilizers and pigments and their targets of use.

Application	Stabilizer	Pigment Orange 68	Pigment yellow 150	Pigment Yellow 53	Pigment Yellow 161	Pigment Green 50
Chemical formula	Several possibilities	$C_{29}H_{18}N_4O_3Ni$	$C_8H_6N_6O_6Ni$	$(Ti,Ni,Sb)O_2$	$(Ti,Ni,Nb)O_2$	$(Co,Ni,Zn)_2TiO_4$
Main target of use	LDPE, PP	PVC, LDPE	HDPE, ABS, PA	PVC, PE, PP, PS, PET, PA, ABS, PU	PVC, PE, PP, PS, PET, PA, ABS, PU	PVC, PE, PP, PS, PET, PA, ABS, PU
Ni content in compound (%)	6–10	10–11	16.5–17.5	3.0–3.5	4–5	23
Usage level of compound (%)	0.15–0.5	0.05–0.5	0.05–0.5	0.05–0.5	0.05–0.5	0.05–0.5
Ni content in polymer (mg/kg)	100–500	50–600	80–900	20–200	20–200	100–1200

2.9 Copper compounds in plastics and rubbers

Like nickel, copper is mainly utilized in pigments. It also finds some use as a catalyst in the polymerization of styrene, as a heat stabilizer in polyamides (Gugumus, 1993a; Gugumus, 1993b) and as an antimicrobial agent mainly in PVC, polyolefins and polyurethane (Markarian, 2006; Jones, 2009).

Today the role of copper is crucial in the coloration of plastics. Copper phthalocyanine compounds impart strong color with good light and heat stability, and due to that they are currently the dominant pigments in the coloration of blue and green plastic articles (Christensen, 2003). Copper phthalocyanines without halogens (Babler, 1998) are used for blue color, and halogenated counterparts such as chlorinated/brominated copper phthalocyanines (Nonaka *et al.*, 1989) are the best choice for green color in plastics. Due to their beneficial properties, the usage level of both blue and green phthalocyanine pigments is significant in each individual type of plastic (Scherrer and Sykes, 2009). Some modifications of copper phthalocyanine pigments may also be used in rubbers, but due to the adverse effect of free copper for rubber matrix, the free copper content in pigments has to be strictly controlled (Herbst and Hunger, 1997). Metallic copper, either alone or in combination with zinc in brass/bronze mixtures, has achieved a significant level of use in plastics. Another inorganic copper containing pigment is copper chromite black with a chemical formula $CuCr_2O_4$ (Rangos, 2005).

Copper halide (mainly bromide and iodide) salts have been successfully used as heat/light stabilizers in polyamide plastics, either alone or in combination with other metal halide salts (Janssen *et al.*, 1995). Sufficient stabilizing effect can be attained at concentrations as low as 10–50 mg/kg (Gugumus, 1993a; Gugumus, 1993b). Copper compounds, mainly copper halides, are also used as catalysts in the polymerization of styrene by the atom transfer radical mechanism (Matyjaszewski *et al.*, 2000; Wang and Matyjaszewski, 1995a; Wang and Matyjaszewski, 1995b). Since the required concentrations of catalysts are high, the polymers need to be washed in order to reduce the metal catalyst content; after the purification the copper content is usually around 5 mg/kg or even less (Matyjaszewski *et al.*, 2000; Shen *et al.*, 2004; Hong *et al.*, 2001). Table 16 introduces different copper based pigments, stabilizers and copper residues in the final polymer resin.

Table 16. Copper compounds used as stabilizers and pigments.

Application	Stabilizer	Pigment-Copper phthalocyanine (blue)	Pigment-Copper phthalocyanine (green)	Pigment-Copper chromite black	Pigment (brass)
Chemical formula of compound	Copper halide	$C_{32}H_{16}N_8Cu$	$C_{32}Cl_{16}N_8Cu$	$CuCr_2O_4$	Mixture of metallic zinc and copper
Target of use	PA	PVC, PE,PP, PS, PET, PA, ABS, PU, rubber	PVC, PE,PP, PS, PET, PA, ABS, PU, rubber	PVC, PE,PP, PS, PET, PA, ABS, PU	PVC, PE,PP, PS, PET, PA, ABS, PU
Cu content in compound (%)	33–43	11	6	28	70–90
Usage level of compound (%)	–	0.05–0.5	0.05–0.5	0.05–0.5	0.05–0.5
Cu content in polymer (mg/kg)	10–100	50–600	30–300	100–1400	400–4500

2.10 Cadmium compounds in plastics

Like barium, cadmium is mainly utilized in heat stabilizer systems for PVC, and also in various inorganic heat resistant pigments. Due to its toxicity the use of cadmium is decreasing, and it has been replaced by less toxic pigments and stabilizers wherever possible (Thacker, 2008).

The most common organic cadmium compounds used in PVC heat stabilizers comprise cadmium stearate and cadmium laurate for solid systems and cadmium 2-ethylhexanoate and cadmium neodecanoate for liquid systems (Starnes and Jennings, 2009; Thacker *et al.*, 2007). The usage levels of stabilizers and the cadmium content existing in the PVC resin are shown in Table 17.

Cadmium selenide and cadmium sulfide are inorganic pigments with good heat and chemical stability. They can be used in the coloration of yellow/red plastic articles, and when used in combination with zinc sulfide or barium sulfate, different shades from greenish yellow through orange and red to a shade of brown can be obtained, as well as the decrease of the price of the pigment (Beebe, 1993; Rangos, 2005). Cadmium based pigments have been replaced by organic pigments and dyes in plastics processed at lower temperatures, but they may still be used when higher processing temperatures are needed (e.g. PA), although the replacement of cadmium pigments by complex inorganic pigments has proceeded also in this area (Beebe, 1993; Rangos, 2005). Typical cadmium pigments, their targets of use and the cadmium content in polymer resin are shown in Table 17.

Table 17. Cadmium containing applications in plastics.

Application	Ba/Cd solid stabilizer	Ba/Cd liquid stabilizer	Pigment	Pigment
Cadmium compound	Cadmium stearate/ cadmium laurate	Cadmium 2-ethylhexanoate	Cadmium selenide	Cadmium sulfide
Target of use	PVC	PVC	PVC, PE,PP, PS, PET, PA, PU	PVC, PE,PP, PS, PET, PA, PU
Usage level of compound (%)	0.5–2.5	0.8–2.5	0.05–0.5	0.05–0.5
Cd content in polymer (mg/kg)	300–1400	300–1100	300–3000	300–3900

2.11 Chromium compounds in plastics

Chromium compounds have been used in plastics for two purposes; as catalysts in the polymerization of polyethylenes such as LLDPE and HDPE, and as pigments (both organic and inorganic compounds) generally suitable for plastics. Contamination of plastic resin by chromium during the polymerization stage is not assumed to be a major issue, whereas coloration by chromium based compounds is a significant source of chromium in plastics.

Nowadays more than one-third of all polyethylenes sold worldwide are produced by chromium based catalysts covering polymers with a broad molecular weight distribution (Kissin, 1996a; Weckhuysen and Schoonheydt, 1999). Catalyst compounds are typically chromium oxides supported on porous materials such as silica SiO_2 and alumosilicates $[AlSiO_4]^-$, and the chromium content in finished catalyst mixtures ranges most commonly between 0.1–5 wt-% (Kissin, 1996a). Due to their high activity (small amounts of catalyst required for the polymerization) and purification (catalyst removed by filtration), the chromium residue content in finished polymer does not exceed the level of 5 mg chromium/kg total polymer (Bichinho *et al.*, 2005; Epacher *et al.*, 2000; Foster *et al.*, 1997).

Chromium compounds are utilized both in organic and inorganic pigments. Organic pigments are used mostly in polyamides, where premetallized dyes such as 1:2 azo/chromium complexes are used particularly in automotive upholstery because of their high wash and light fastness (Weber, 1996; Glover, 1993). For inorganic chromium pigments the scope is wider. Compound for green color is e.g. weather and chemically resistant but dull chromium oxide Cr_2O_3, which is used especially in large HDPE containers and crates planned for outdoor use, and also in rubber applications (Buxbaum and Pfaff, 2005; Essential Rubber Formulary, 2007). If more bright shade of green is required, cobalt chromite $CoCr_2O_4$ with a general applicability may be used (Scherrer and Sykes, 2009; Sicopal Blue K 6310, 2011). For brown color, either rutile based $(Ti,Sb,Cr)O_2$ compound or chromites containing manganese, zinc or iron are widely suitable options (Rangos, 2005). In addition cobalt chromium aluminate $Co(Al,Cr)_2O_4$ is generally applicable for blue coloring (Sicopal Blue K 6310, 2011), and combinations of chromium, lead, molybdenum and sulfate may be utilized in the coloration of PVC and polyethylenes. Table 18 introduces the most typical applications of chromium compounds in plastics, their usage levels and chromium residue concentrations in final polymers.

Table 18. Chromium containing catalyst compounds and pigments and their usage levels and concentrations in polymers.

Name	**Chemical formula**	**Application**	**Target of use**	**Usage level of compound (%)**	**Cr content in plastics (mg/kg)**
Chromium oxide	Cr_2O_3	Catalyst	LLDPE, HDPE	–	1–5
1:2 azo/chromium	$C_{34}H_{24}CrN_8O_6$	Pigment	PA, transparent applications	0.05–0.5	40–400
Chromium oxide	Cr_2O_3	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	0.05–0.5	300–3400
Cobalt chromite	$CoCr_2O_4$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	0.05–0.5	150–1800
Cobalt chromium aluminate	$Co(Al,Cr)_2O_4$	Pigment	PVC,PS,PO,ABS,PA	0.05–0.5	100–1000
Iron chromium oxide	$(Fe,Cr)_2O_3$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	0.05–0.5	150–1800
Chromium iron zinc oxide	$(Zn,Fe)(Fe,Cr)_2O_4$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	0.05–0.5	100–1100
Chromium titanium yellow	$(Ti,Sb,Cr)O_2$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	0.05–0.5	30–300
Mixed phase pigment	$Pb(Cr,Mo,S)O_4$	Pigment	PVC, LDPE,HDPE	0.05–0.5	50–600
Chrome yellow	$Pb(Cr,S)O_4$	Pigment	PVC, LDPE,HDPE	0.05–0.5	50–500
Copper chromite black	$CuCr_2O_4$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	0.05–0.5	200–2300

2.12 Cobalt and manganese compounds in plastics

Cobalt and manganese compounds have been utilized for similar purposes in plastics. They may be used as catalysts in the polymerization of polyesters and polyurethanes, and cobalt compounds are suitable to catalyze the polymerization of polybutadiene rubber, an important impact modifier for HIPS and ABS. As pigments, they offer several options. Both organic and inorganic manganese compounds have been used for violet and red coloration of especially PVC, and inorganic cobalt compounds are both heat and chemical resistant options with general applicability.

2.12.1 Cobalt and manganese catalyst compounds

Cobalt and manganese compounds are suitable as first stage catalysts for PET polymerization regardless of the process used (i.e. transesterification or direct esterification of raw materials). Suitable cobalt compounds for catalysis are e.g. cobalt chloride $CoCl_2$, cobalt acetate trihydrate $Co(CH_3COO)_2 \cdot 3H_2O$, and profitable manganese catalysts may be compounds such as manganese chloride $MnCl_2$ and manganese acetate tetrahydrate $Mn(CH_3COO)_2 \cdot 4H_2O$. The elemental concentrations for cobalt before the polymerization are in the range of 5–100 mg/kg, based on the weight of raw materials, and the corresponding range for elemental manganese is 25–110 mg/kg (Sublett, 1991; Russin *et al.*, 1976; Nichols, 1991; Nichols and Mason, 1992). Considering the purification steps of the polymer, the total amount of metal residue is likely to be well below the values mentioned above. For the polymerization of PBT via transesterification reaction, both cobalt and manganese acetate compounds have been used with elemental concentrations of 10–40 mg/kg for cobalt (based on the weight of raw materials) and similarly 15–25 mg/kg for manganese (Yuo *et al.*, 1996). However, when considering the possible metal sources in plastics, it has to be taken into account that zinc is the most widely used catalyst in the polymerization of PET, and in PBT polymerization titanium takes the leading role. Cobalt compounds, such as cobalt benzoate $Co(OOCC_6H_5)_2$ and cobalt acetate $Co(CH_3COO)_2$, are the most important catalysts for the polymerization of polybutadiene rubber (both cis/trans forms) (Castner, 1998a; Castner, 1998b). They are typically used at concentration levels of 15–75 mg/kg based on the weight of raw materials. Organic cobalt and manganese compounds, such as cobalt/manganese octoate and cobalt/manganese acetate, may also be utilized as co-catalysts in combination with tertiary amines in rigid urethane polymerization (Ulrich, 1997; Naka *et al.*, 1988).

2.12.2 Cobalt and manganese pigments and residues in fillers

Inorganic green and blue cobalt containing pigments with spinel type of structures are thermally and chemically stable compounds, and therefore find use particularly in plastics processed at higher temperatures, where organic pigments (with weaker thermal stability) cannot be used. Green pigments such as cobalt zinc chromite $(Co,Zn)Cr_2O_4$ and cobalt nickel zinc titanate $(Co,Ni,Zn)_2TiO_4$, blue pigments such as cobalt aluminate $CoAl_2O_4$ and cobalt chromium aluminate $Co(Al,Cr)_2O_4$ are good and durable options with general applicability in plastics (Scherrer and Sykes, 2009; Rangos, 2005; Christensen, 2003; Colorants for plastics colorations, 2011; Fischer and De Ahna, 1984). In addition Pigment Black 27 with chemical formula $Co(Cr,Fe,Mn)_2O_4$ (contains also manganese) is widely suitable. However, due to the higher price of cobalt pigments, blue and green copper phthalocyanine compounds are the dominant pigments for the most plastic applications.

Besides $Co(Cr,Fe,Mn)_2O_4$, other inorganic pigments containing manganese are generally applicable manganese titanium yellow $(Ti,Sb,Mn)O_2$ and brown zinc manganese chromite $(Zn,Mn)Cr_2O_4$; in addition violet manganese ammonium pyrophosphate $H_4MnNO_7P_2$ is suitable for the coloration of PVC (Beebe, 1993). An organic pigment such as the red Mn salt of a monoazo compound, with chemical formula $C_{18}H_{11}ClN_2O_6SMn$, is suitable for the coloration of PVC, PS and LDPE (Scherrer and Sykes, 2009, Beebe, 1993).

Manganese exists quite typically as a residue in dolomite mineral, which is widely used in plasticized PVC products. Up to 2 wt-% of manganese is possible in dolomite, therefore the elemental manganese in PVC products may lie between 100–500 mg/kg, depending on the amount of filler used. Table 19 introduces the most typical cobalt and manganese catalyst compounds, pigments and fillers, their applications and the final metal content in the polymer.

Table 19. Cobalt and manganese compounds as catalysts and pigments.

Compound name	**Chemical formula**	**Application**	**Target of use**	**Co/Mn content in compound (%)**	**Co/Mn residue in plastics (mg/kg)**
Cobalt acetate trihydrate	$C_4H_6CoO_4{\cdot}3H_2O$	Catalyst	PET, PBT	25–26	5–50
Co/Zn/Cr-oxide	$(Co,Zn)Cr_2O_4$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	19–21	100–1000
Co/Ti/Ni/Zn-oxide	$(Co,Ni,Zn)_2TiO_4$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	12–16	80–800
Cobalt aluminate	$CoAl_2O_4$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	28–29	150–1500
cobalt chromium aluminate	$Co(Al,Cr)_2O_4$	Pigment	PVC,PS,PO,ABS,PA	18–20	100–1000
Cobalt chromite	$Co(Cr,Fe,Mn)_2O_4$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	21–22	100–1100
Manganese acetate tetrahydrate	$Mn(CH_3COO)_2{\cdot}4H_2O$	Catalyst	PET,PBT	23–24	5–50
Manganese titanium yellow	$(Ti, Sb,Mn)O_2$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	3–4	20–180
Zinc manganese chromite	$(Zn, Mn)Cr_2O_4$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	18–19	100–950
Manganese pyrophosphate	$H_4MnNO_7P_2$	Pigment	PVC	22–23	100–1100
Lake manganese	$C_{18}H_{11}ClN_2O_6SMn$	Pigment	PVC, PS, LDPE	11–12	50–600

2.13 Silver and zirconium compounds in plastics

Silver and zirconium compounds have a quite narrow range of use in plastics. Silver is mainly utilized in antimicrobials, either in metallic form or as organic/inorganic compounds, and zirconium has found most use as a metallocene catalyst for polyolefins and as a coupling agent broadly suitable for plastics.

2.13.1 Silver containing antimicrobial compounds

Inorganic biocides are steadily increasing their share in the market of antimicrobial compounds for plastics, amounting now to about ten percent of the volume (Markarian, 2006; Markarian, 2009). They are primarily based on silver ions in an inert matrix of ceramic, glass or zeolite, and are mostly used on the surface of plastic parts in medical applications, suitable to be used in PE, PP, HIPS, ABS, PET, PC, PU, PA and PVC (Jones, 2009; Appendini and Hotchkiss, 2002; Kumar and Münstedt, 2005). Silver ion masterbatches containing 0.5 wt-% of silver were discovered to be efficient enough for gaining the antimicrobial effect (Simmons, 2001). For PA, PE and PP, silver zeolites containing less than 20 wt-% of silver in the zeolite matrix, were discovered to be efficient antimicrobials at a concentration range of 1–2 wt-% (Kumar *et al.*, 2005).

2.13.2 Zirconium catalyst compounds and coupling agents

Metallocene catalyst systems mainly utilize zirconium compounds as active catalysts. These compounds contain two components: a metallocene complex of zirconium usually with two cyclopentadienyl rings, and an organoaluminum compound such as methylaluminoxane (Kissin, 1996b). The support material comprises mainly silica, alumina or magnesium dichloride. Due to their high activity they can be left in the polymer without further purification; residue zirconium concentrations well below 1 mg/kg are typical (Kaminsky, 1998; Hoàng *et al.*, 2006; Hussain *et al.*, 2010; Bichinho *et al.*, 2005.

Zirconates, like titanates, are used as coupling agents in plastics in order to gain a binding effect between the filler and polymer resin (Hohenberger, 2009). Compounds such as pyrophosphate zirconates are widely suitable. The recommended concentration range is between 0.2–2.0 % by weight of the filler, and thus the zirconium residue in polymer may be as high as 250 mg/kg, depending on the type and amount of the filler used. Table 20 introduces silver antimicrobials and zirconium catalysts and coupling agents used in plastics, their applications and metal residue levels left in the polymer.

Table 20. Silver and zirconium compounds.

Name	Silver/zeolite	Zirconocene dichloride	Isopropyl tri(dioctylpyrophosphate) zirconate
Chemical formula	$Ag/AlSiO_3$	$C_{10}H_{10}Cl_2Zr$	–
Application	Biocide	Catalyst	Coupling agent
Target of use	PVC, PE,PP, PS, PET, PA, ABS, PU	LLDPE,PP, HDPE	PVC, PE,PP, PS, PET, PA, ABS, PU
Usage level of compound (%)	1–2	–	0.01–0.2
Ag/Zr residue content in plastics (mg/kg)	1–50	<1	10–250

3. Halogen compounds

3.1 Chlorine in plastics and rubbers

3.1.1 Chlorine containing polymers

3.1.1.1 Polyvinyl Chloride

The versatility of PVC is hard to overcome; its applications range from building and construction products (rigid pipe, siding and profile) to semi-rigid floorings and wall coverings to flexible wire and cable products (Summers, 2005). Due to its versatility, the annual consumption of PVC is vast; it is the second most produced plastic polymer after polyolefins with an approximate production of 33.5×10^6 tonnes worldwide in 2006, and the consumption is still increasing particularly in the Asian region (Global PVC Consumption and Capacity, 2012). The repeating structure of PVC is presented in Figure 3; there one hydrogen atom is replaced by a chlorine atom, and the degree of the polymerization usually ranges from 500 to 3500.

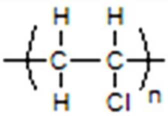


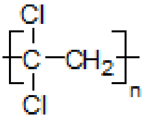
Figure 3. The repeating structure of PVC.

The polarity of PVC resulting from a chlorine atom attached to its structure is the key to PVC's versatility. This polarity causes the rejection of non-polar materials, and thus helps to protect PVC from oils and hydrocarbons. Also the degradation of PVC is different compared to other alternative plastics: exposure to UV and oxidation tends to cause some crosslinking after loss of HCl. This is opposite to polyolefins (PE and PP) whose polymer structure is decomposed under radiative/oxidative conditions via chain scission mechanism (Summers, 2005). The calculated chlorine content in pure PVC polymer is 56.7 wt-%, but due to its sensitiveness to radiation and heat, PVC is practically never used as a pure polymer. Ingredients added to the polymer improve its physical, chemical and microbial resistance and also lower the chlorine content of the polymer; therefore the chlorine content in the final polymer usually varies between 30–50 wt-%. In addition PVC is commonly copolymerized with other monomers, some examples being vinyl chloride-vinyl acetate copolymer used in floorings and coatings and vinyl chloride-vinylidene chloride (VDC) copolymer used in barrier films and coatings; this will also lead to various chlorine concentrations in final PVC products (Summers, 2000).

PVC can be used in a wide variety of applications requiring a wide range of properties. Most of the products have a long life cycle. In 2003, the use of PVC can be presented as follows: construction about 74 % (which includes pipe and tubing, siding, windows and floors and flooring), consumer goods 9 %, packaging 6 %, wire and cable coatings and electrical fittings 5 %, and transportation, home furnishing and others constituting the rest (Polyvinyl Chloride – Chemical Profile, 2003). A flexible type of PVC is used in applications such as flooring, wall covering, toys, wire and cable coatings and insulation, and films and fabrics (Markarian, 2004; Coaker, 2005). Rigid PVC which constitutes about two-thirds of the total PVC consumption (Braun, 2004) is used in applications such as pipe, siding, and window and door profiles. Due to health and environmental issues, PVC products in Western countries have been replaced by less toxic alternatives (polyolefin) wherever possible, and thus the consumption pattern of PVC is shifting towards Asia, especially China, which currently accounts for about one-third of the total annual consumption of PVC (Global PVC Consumption and Capacity, 2012; Global PVC Market, 2012).

3.1.1.2 Polyvinylidene Chloride

Polyvinylidene chloride (PVDC) copolymers are known as barrier polymers due to their low gas and vapor permeability (Wessling *et al.*, 2000). The homopolymer of PVDC with the repeating unit structure shown in Figure 4 is seldom used as a pure polymer due to its poor thermal stability. This difficulty has been solved by copolymerization with suitable co-monomers such as vinyl chloride, acrylates and acrylonitrile, with VDC content being in the range of 60–90 wt-% (Wessling, 2000). Therefore the chlorine content in the final formulation can be as high as 70 wt-%.



$$\left[-\overset{Cl}{\underset{Cl}{C}}-CH_2- \right]_n$$

Figure 4. The repeating structure of PVDC.

The global annual production of PVDC is nowadays around 200 000 tons (World Polyvinylidene Chloride Production, 2012). Molded parts of VDC copolymer plastics are used in applications requiring good chemical resistance and long service life, such as VDC-VC copolymers for valves, pipe fittings, gasoline filters, containers and chemical processing ware (Wessling *et al.*, 2000). Extruded VDC-VC copolymers are used in filaments, films and sheets (mono and multilayer films/sheets, which consist of a layer of PP/HIPS and a layer of co-polymer of PVDC connected with appropriate adhesive material) used for containers and food and medical packaging and tubing/pipe applications. With a suitable co-monomer and a blowing agent, foam formation is also possible, and the foam is mostly used in reinforced polyesters and composites for furniture and marine applications. Finally, VDC copolymers can be utilized as an ignition resistance/reinforcement (binding) material in PU foams, and also in latex form.

3.1.1.3 Halobutyl Rubber

Butyl rubber (IIR), as shown in Figure 5, is a copolymer of isobutylene and a small amount (1–3 %) of isoprene (Rodgers *et al.*, 2000). There are also some important modifications for IIR, particularly halobutyl derivatives of butyl rubber (HIIR) such as chlorobutyl rubber (CIIR), bromobutyl rubber (BIIR) or a combination of chloro- and bromobutyl rubber, whose halogenated structures are presented in Figure 5. The halogenation of IIR is carried out in a hydrocarbon solution by an ionic mechanism using an elemental chlorine or bromine with an equimolar ratio to attached isoprene co-monomer (Webb *et al.*, 2000; Kresge and Wang, 2000). Therefore the halogen content in the rubber polymer increases usually into the range of 0.5–1.5 wt-% for chlorine and 1.8–2.5 wt-% for bromine (Gardner *et al.*, 1985; Malatesta and Baldwin, 1974; Lanxess, 2010).

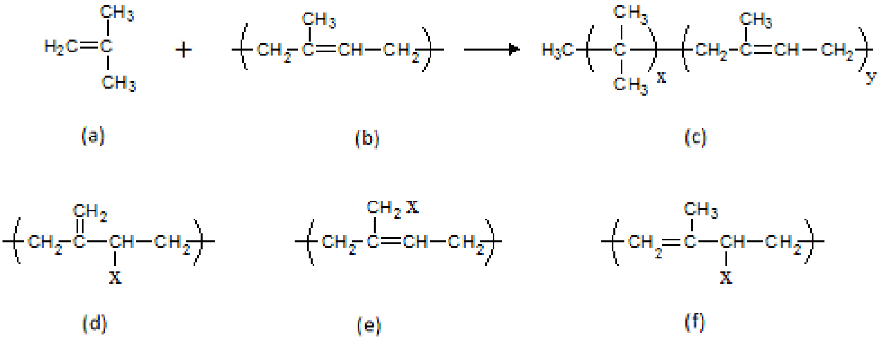


Figure 5. Monomers and isomers for IIR and HIIR: (a) isobutylene (b) isoprene (c) repeating structure of IIR (d)-(f) Halogenated structures of IIR, where structure (d) is the dominant (X = chlorine/bromine).

IIR and HIIR are typically used in tire applications such as inner tubes and tire inner liners due to their low degree of permeability to gases (Kresge and Wang, 2000). They can also be used in air cushions, high temperature service hoses and conveyor belts, pharmaceutical closures and construction sealants. Blends of HIIR and NR are used e.g. in tire sidewalls and tread compounds (Kresge and Wang, 2000). Due to their wide applicability, the total annual demand for IIR/HIIR is around 650 000 tons (Butyl rubber, 2012). When different HIIR rubbers are compared, the production of BIIR is larger due to its faster curing systems and better adhesion properties to high unsaturation rubbers (Butyl Rubber, 2012).

3.1.1.4 Specialty elastomers

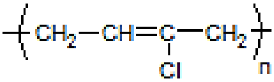
3.1.1.4.1 Chlorosulfonated polyethylene

Chlorosulfonated polyethylene (CSM) is a curable polymer with properties ranging from soft and elastomeric to hard. The chlorine content in the polymer depends on the type of the precursor resin (LDPE, HDPE and LLDPE), and it is usually in the range of 24–43 % by weight of the polymer (Ennis, 2000). End use applications for CSM are determined by the type of the polymer; solution grade polymers have been used in roof coatings and the manufacturing of tarpaulins and general-purpose grades are mostly used in applications such as hoses, tubing, electrical wiring, inflatable boats, industrial rolls and belts (Ennis, 2000). Polymers with high chlorine content are used in automotive and air conditioning hoses and also in some coating applications.

The biggest manufacturer of chlorosulfonated polyethylene (DuPont under the trade name Hypalon) has ceased the production of the polymer in April 2010, mainly due to environmental and economic reasons (DuPont elastomers, 2012). Before that the annual production of CSM was over 50 000 tons (Ennis, 2000).

3.1.1.4.2 Polychloroprene

Polychloroprene (CR), commonly known under the trade name Neoprene, was one of the first synthetic rubbers produced by DuPont, primarily due to its good solvent resistance (Morton, 2000; Glenn, 2000). The structure of the elastomer is largely composed of the trans-isomer shown in Figure 6. The calculated chlorine content in the pure polymer is about 40 wt-%, and due to the high chlorine content, the density of the polymer is also quite high. CR can also be co-polymerized with sulfur in order to obtain lower viscosity (partially gelled) polymer; in this case the sulfur content is usually in the range of 0.1–2.0 wt-% (Glenn, 2000; Emura *et al.*, 1986; Doyle and Schear, 1975; Musch *et al.*, 1981).



$$\left(CH_2-CH=\underset{\displaystyle Cl}{C}-CH_2 \right)_n$$

Figure 6. The repeating structure of polychloroprene.

In the class of the specialty elastomers, CR is one of the most important with a global annual consumption exceeding hundreds of thousands of tons (Glenn, 2000). However, the demand for CR products has declined (especially in automotive sector), mainly because of the relatively high price resulting from the high density value, thus substitution of CR by competing cheaper elastomers is taking place (Glenn, 2000).

Because of its good resistance to corrosive chemicals, CR and its derivatives can be used in multiple applications, both in the latex and the dry rubber form (Morton, 2000; Glenn, 2000). Sulfur modified grades possess excellent processing and dynamic properties, therefore they are used in applications such as automotive V-belts and hoses, and industrial and hydraulic hoses and belts. No-sulfur grades with better aging properties are used e.g. in rolls and wire and cable coverings and mechanical goods such as footwear, gasket and weather seal applications. CR latex modifications can be used as dipped goods and gloves as well as in adhesive applications.

3.1.1.4.3 Polyethers

Polyether elastomers possess excellent physical properties such as good resistance to ozone, gas and oil permeability even at low temperatures (Owens and Kyllingstad, 2000). The basic structure unit for these elastomers is polyepichlorohydrin (ECH), either as homopolymer (Vandenberg, 1964a) or in a combination with ethylene oxide (Vandenberg, 1964b) (EO), propylene oxide (PO) or allyl glycidyl ether (Vandenberg, 1964c) (AGE) to form copolymer/terpolymer. The examples of the different polymer types are shown in Figure 7.

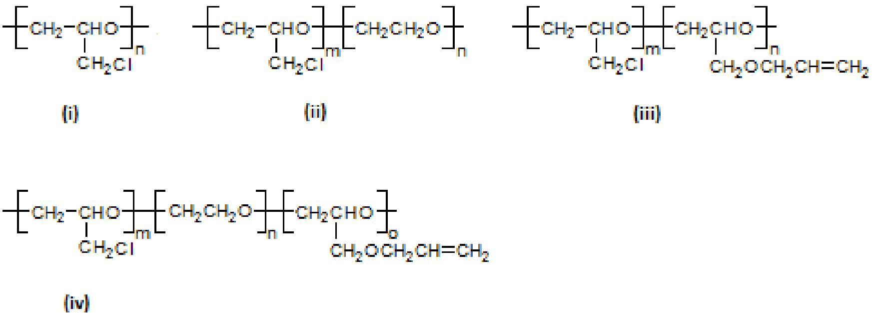


Figure 7. The basic structures of (i) ECH homopolymer, (ii) ECH-EO copolymer, (iii) ECH-AGE copolymer, and (iv) ECH-EO-AGE terpolymer.

The chlorine content in ECH polymers varies according to the polymer structure; it is about 38 wt-% for ECH homopolymer, 26 wt-% for ECH-EO copolymer, 35 wt-% for ECH-AGE copolymer, and in the range of 15–29 wt-% for ECH-EO/PO-AGE terpolymers (Owens and Kyllingstad, 2000).

Since vulcanized ECH homopolymer and ECH-EO copolymer have excellent gas, fuel and ozone permeability resistance, they are very useful in automotive applications such as hoses (fuel, air, vacuum) and vibration mounts (Owens and Kyllingstad, 2000). They are also used in drive and conveyor belts, as well as coatings for protective clothing and in seals and gaskets. Polymers containing

AGE can be used e.g. in mounting isolators and hose and wire covers. ECH-PO-AGE is used in high flex applications such as fuel hose covers and rubber boots, as well as coverings for cables. The global annual production of ECH elastomers is estimated to be several tens of thousands of tons (Epichlorohydrin, 2012).

3.1.1.4.4 Acrylic elastomers

Acrylic elastomers (ACM) possess two extraordinary properties not present in general-purpose rubbers (Spelta, 2000). As shown in Figure 8, the repeat structure of ACM consists of saturated chains of polyalkylene type hydrocarbons, which results in a high heat and oxidation resistance. In addition, the polarity of the elastomer chain originates from the ester side groups. The elastomer itself is chlorine free, but the structure usually contains labile chlorine containing monomers (Figure 8 (b)) functioning as cure-site monomers (Spelta, 2000; Cantalupo *et al.*, 1980). Examples of the monomers are p-vinyl benzyl chloride, vinyl chloroacetate and 2-chloroethyl vinyl ether (Spelta, 1993; Morris and Tucker, 1975). Usually the monomer is used at concentrations in the range of 1–3 wt-%; therefore the chlorine concentration in the final rubber formulation is typically below 2 wt-% (Cantalupo *et al.*, 1980; Ohira *et al.*, 1991; Kaizerman, 1965).

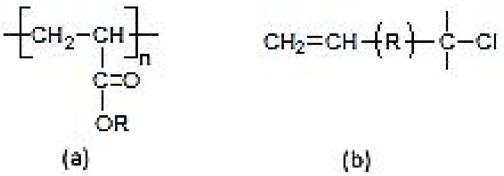


Figure 8. (a) The basic repeat structure of ACMs (b) The basic structure of labile chlorine containing curing-site monomer.

ACMs usually compete with the other specialty rubbers for the same application, and then not only the chemical, mechanical and elastic properties have to be taken into account, but also the price is a very significant factor (Spelta, 2000; Spelta, 1993). Traditionally ACMs are used as specialty rubbers mainly in automotive non-tire applications, such as seals, O-rings and gaskets. They also find use in electrical insulation, hose linings, noise control and vibration damping, wire and cable jacketing, as well as in plastic modifications such as processing agents for PVC (Morton, 2000; Spelta, 2000). The total annual consumption of ACM for the mid 1990s was estimated to be around 25 000 tons.

3.1.2 Chloride as a catalyst residue

Metal chloride compounds have gained extensive use in the polymerization of the plastics, particularly in the Z-N system for the polymerization of HDPE, LLDPE and PP. In Z-N system, titanium chlorides such as $TiCl_3$ and $TiCl_4$ in a combination with organoaluminum compounds catalyze the polymerization reaction on the surface of porous support material, which is typically magnesium chloride $MgCl_2$ (Kashiwa, 2004). The $TiCl_4/MgCl_2$ composition is the dominant catalyst system both for PE and PP due to its high activity; when this system is used, the purification of the polymer from the catalyst residues is not needed, unlike in the case of the lower activity $TiCl_3/MgCl_2$ system. The chloride residue in polyolefins (resulting from the polymerization) is below 100 mg/kg, typically in the range of 20–70 mg/kg (Goss *et al.*, 2003).

3.1.3 Chlorine containing pigments and dyes

3.1.3.1 Organic pigments

Many organic chlorine containing pigments used in plastics are structurally very similar to sulfur containing pigments (which have been presented in chapter 4) and quite often both sulfur and chlorine atoms are present in the pigments, such as metal salts of compounds containing azo groups. However, there are also only chlorine containing pigment types, such as phthalocyanines, isoindolinones, monoazo naphtols, quinophthalones, quinacridones, diazo condensation and pyrollopyrrole pigments, whose basic structures are shown in Figure 9.

Due to the high number of chlorine containing pigments, also the spectrum of colors is broad; at least yellow, brown, orange, red, green, blue and violet pigments are present with a wide variety of different shades for each specific color. Yellow pigments are usually derivatives of isoindolinone and disazo condensation compounds, and also calcium salts of monoazo compounds or arylide derivatives are widely used. In the red coloration the total number of pigments is about 20, and a majority of them are either derivatives of azo metal salts or disazo condensation compounds. In addition quinacridones, thioindigos and pyranthrones are used for red plastic articles. Green coloration is usually carried out by generally applicable chlorinated/brominated phthalocyanine compounds, or by nickel azo metal compound (used mainly for PE and PVC). Finally, there are also several orange pigments based on diarylide or benzimidazolone compounds, and brown azo based pigments.

The chlorine content of the pigments varies, but is typically in the range of 10–20 wt-%; for some compounds it can be as high as 45 %. Regarding the typical loading levels of organic pigments (<0.5 %), the average chlorine content in the final polymer (caused by coloration) can be estimated to lie between 50–1000 mg/kg. Table 21 introduces different kinds of chlorine containing organic pigments according to their structure type. Besides the structure, also the target of use and an estimate of the chlorine content in the final plastic article is presented.

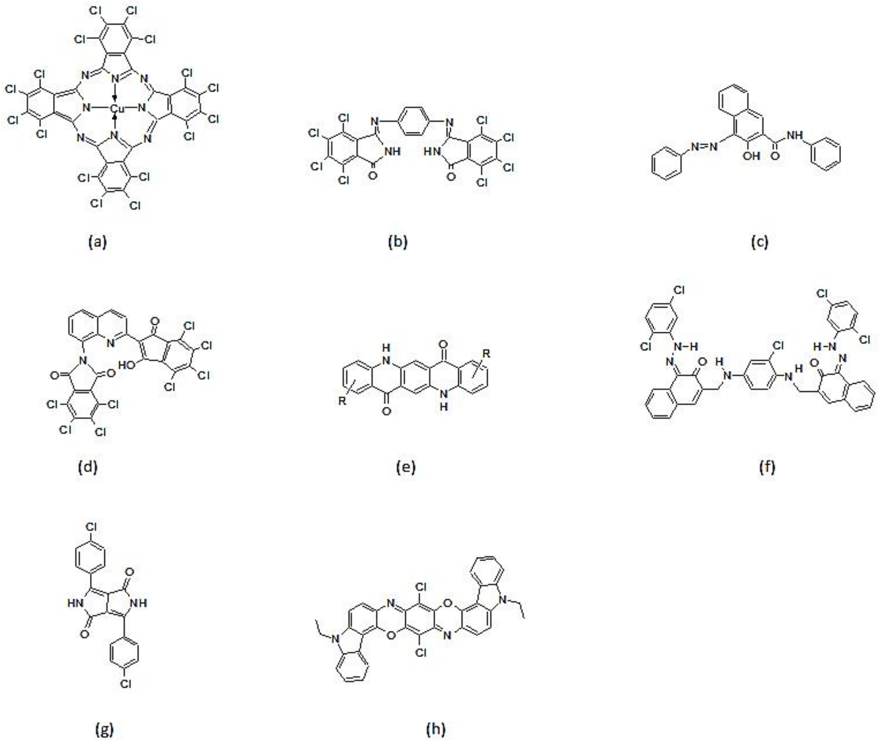


Figure 9. Chlorine containing organic pigments (a) Chlorinated phthalocyanine pigment (PG 7), (b) Chlorinated isoindolinone pigment (PY 110), (c) Basic structure of monoazo naphtol, (d) Quinophthalone pigment (PY 138), (e) Basic structure of quinacridone, (f) Diazo condensation pigment (PR 144), (g) Pyrollo-pyrrole pigment (PR 254), (h) Dioxazine pigment (PV 23).

3.1.3.2 Organic dyes

Organic dyes are used in clear plastics to offer bright colors and transparency where optical transmission is important (Weadon, 2005). The transparency of the dyes is based on the solubility of the dyestuff in the plastic polymer; thus the main difference between the dyes and organic pigments is that dyes are soluble in the polymer whereas pigments are not. The solubility brings also some challenges; the dye compounds may migrate to the surface of the polymer, or they may react with acidic/basic groups present in the polymer. In addition the structure of the dyes may decompose during the processing of plastics at high temperatures (organic pigments are more heat resistant). These features restrict the use of the dyes in plastics; they can be used in PS, SAN, ABS, acrylics, rigid PVC, PA, PC and polyesters, but not in flexible PVC, PE, PP and most of the rubbers (Weadon, 2005).

There is a wide variety of dye classes used in plastics, but only a few of them contain chlorine atoms in their structures. These classes are perinones and xanthenes, which are used in red coloration. Perinones can be used for the plastics presented above, but xanthenes are suitable only for PS and rigid PVC. These compounds are presented in more detail in Table 21.

3.1.4 Chlorine containing impact modifiers

Chlorinated polyethylene (CPE) finds use both as an individual polymer in construction and in electrical and automotive applications, and also as an additive compound used as impact modifier in other plastic formulations (Rodgers *et al.*, 2000). The chlorine content of the polymer varies between 25–42 wt-%, and in order to achieve good physical properties, both the use of carbon black and minerals is required. As an impact modifier, CPE finds use particularly in PVC and FR treated ABS resins due to its good compatibility and reinforcing effect. Typical concentrations are in the range of 3–5 wt-%, and considering the chlorine content of CPE, the chlorine residue in the plastic can be between 7500–20000 mg/kg (Cha, 2005).

Table 21. Chlorine containing pigments and dyes (Mathew and Grossman, 2007; Lewis, 2005; Scherrer and Sykes, 2009; Damm and Herrmann, 1993; Beebe, 1993).

Name	**Type of the structure**	**Chemical formula**	**Chlorine content (%)**	**Target of use**	**Chlorine content in plastic (mg/kg)**
PY 109, PY 110, PY 173	Isoindolinone	$C_{22-23}H_{6-12}Cl_{2-8}N_4O_2$	16–38	PVC, PS, polyolefins	40–1900
PY 93, PY 95, PY 128	Diazo condensation	$C_{44-45}H_{35-38}Cl_{4-5}N_8O_{6-8}$	14–19	PVC, polyolefins	10–900
PY 168, PY 183, PY 191	Ca salt of monoazo	$C_{16-32}H_{10-24}CaCl_{1-2}N_{4-8}O_{7-14}S_2$	7–13	PVC, PS, polyolefins, (ABS)	10–650
PY (13, 14,17), PY 81, PY 83	Diazo diarylide	$C_{34-36}H_{30-34}Cl_{2-4}N_6O_{4-8}$	9–18	PVC, polyolefins	10–900
PY 138	Quinophthalone	$C_{26}H_6Cl_8N_2O_4$	40–41	PVC, PS, LDPE	50–2000
PR 144, PR 166, PR 214, PR 242	Diazo condensation	$C_{40-42}H_{22-24}Cl_{4-6}(F_6)N_6O_4$	15–24	PVC, polyolefins	20–1200
PR 48, PR 52, PR 53, PR 243	Metal salt of monoazo	$C_{18-50}H_{11-38}Cl_{1-2}N_{2-6}O_{6-12}S_{1-2}M$ (M=Ba, Ca, Sr, Mn)	6–8	PVC, PS, PE, (PP)	10–400

PR 187	Monoazo Naphtol	$C_{34}H_{28}ClN_5O_7$	5–6	PVC, PE, PP fibers	10–250
PR 202, PR 207, PR 209	Quinacridone	$C_{20}H_{10\text{-}12}Cl_2N_2O_2$	18–19	PVC, PS, PE, (PP)	20–900
PR 88, PR 198	Thioindigo	$C_{16\text{-}18}H_{4\text{-}10}Cl_{2\text{-}4}O_2S_2$	18–32	PVC, PS, PE	20–1600
PG 7, PG 36	Phthalocyanine	$C_{32}H_{0\text{-}3}Br_{0\text{-}13}Cl_{3\text{-}15}CuN_8$	6–49	Generally applicable	10–2400
PV 23	Dioxazine	$C_{34}H_{22}Cl_2N_4O_2$	11–12	PVC, LDPE	10–600
PB 23, PB 25	Azo	$C_{24\text{-}40}H_{15\text{-}23}Cl_{2\text{-}3}N_{5\text{-}8}O_{3\text{-}8}$	12–14	PVC	20–700
PO 13, PO 34	Diazo diarylide	$C_{32\text{-}34}H_{24\text{-}28}Cl_2N_8O_2$	10–11	PVC, LDPE	10–550
PO 72	Azo	$C_{34}H_{26}Cl_2N_{10}O_6$	9–10	PVC, ABS, polyolefins, PS	10–500
Solvent Red 135	Perinone dye	$C_{18}H_6Cl_4N_2O$	34–35	PS, PC, PBT, PET, ABS	40–1700
Basic Red 1	Xanthene dye	$C_{28}H_{31}N_2O_3 \cdot Cl$	7–8	PVC-U, PS	10–400

3.1.5 Chlorine containing flame retardants

Due to their high carbon and often high hydrogen content, plastics are combustible materials. Some of the polymers are inherently flame retarded (such as PVC, the effect of chlorine), but usually additive compounds called flame retardants (FR), are required to decrease the flammability of the polymers used in challenging environments (electrical appliances, construction material etc.). FR compounds typically resist ignition either by diluting or cooling the combustible material, or participating in char formation to form a barrier against mass and heat transfer (Troitzsch, 1993). They may also remove thermal energy from the substrate by functioning as a heat sink. FR compounds may operate in both solid matter and gas phase. In the gas phase they interrupt the combustion chemistry through the interaction between halogen containing additive compounds and radicals formed during the combustion forming less energetic species, and thus interrupting the chain propagation necessary for fire initiation/continuation (Troitzsch, 1993).

Chlorine containing FR compounds are usually low cost materials with good light stability (Troitzsch, 1993), but due to the high concentrations needed for the required flame retardancy effect, bromine containing (both aliphatic and aromatic) organic FR compounds are currently the dominant halogenated FR compounds in the market. There are still some chlorine containing FR compounds used in specific polymers. Cycloaliphatic hydrocarbon compounds with trade names “Dechlorane plus” and “HET acid” are used in PVC, PA and polyolefins (Troitzsch, 1993; Ranken, 2009). The chlorine contents of these compounds are in the range of 40–

70 wt-%, and since the adding levels of FR compounds are quite high (between 5–15 % by weight of the polymer), chlorine content in the final plastic article can be as high as 100 000 mg/kg. Besides cycloaliphatic compounds, also chlorinated alkyl phosphates are used as FR compounds (Green, 1992; Halogenated Phosphate Esters, 2011; Weil and Levchik, 2004). Compounds such as tris(1-chloro-2-propyl) phosphate (TCPP) and tris-2-chloroethyl phosphate (TCEP) are used in rigid and flexible PU foam formulations, the latter also in polyester resins. Usually the compounds are added in concentrations between 5–15 wt-%, and therefore the chlorine content in PU foam may be in the range of 16 000–70 000 mg/kg. Chlorine containing FR compounds are introduced in detail in Table 22.

3.1.6 Chlorine containing light stabilizers, antimicrobials and antistatic additives

The market for chlorine containing light stabilizers is fairly narrow; there are only two (benzotriazole type) light stabilizer compounds, UVA-3 and UVA-4, which act as UV light absorbers (UVA) typically in combination with primary stabilizers such as HALS compounds. UVA-3 and UVA-4 can be used in polyolefins (PE, PP) and especially in rubbers, where combinations of different light stabilizers impart a great improvement to their stability properties (Ranken, 2009; Green, 1992). Chlorine contents of the compounds are between 9–11 %, and since the usage levels of UVAs are in the range of 0.1–0.3 wt-%, the chlorine content in the final polymer is typically between 100–300 mg/kg.

The majority of antimicrobial compounds contain halogen atoms in their structures. One of the most important chlorine containing compound is 2,4,4'-trichloro-2'-hydroxy-diphenyl-ether ($C_{12}H_7O_2Cl_3$), known also by the name Triclosan (Schweizer, 2001; Quintavalla and Vicini, 2002; Niall, 2001). It can be used in a wide variety of plastics, such as polyolefins, PVC, PU, PS and ABS, in concentrations ranging from 0.1 wt-% up to 1.0 wt-%. Since the chlorine content of the compound is high (about 36 %), the chlorine residue in the final plastic formulation is also high, typically between 300–3500 mg/kg. Other chlorine containing antimicrobial additives are the thio and sulfone compounds, and also pentachlorophenyl laurate ($C_{18}H_{23}Cl_5O_2$) and tetrachlorophthalonitrile ($C_8Cl_4N_2$), which are used in similar concentrations as Triclosan. These compounds are described more thoroughly in Table 22.

Although non-ionic antistatic additives such as fatty acid esters, ethoxylated alkylamines and diethanolamines are the most widely used antistatic compounds, chlorine containing cationic antistatic additives (with a general chemical formula $R\text{-}(CH_3)_3NCl$) find use in more polar polymers, particularly in rigid PVC and styrenics (Schweizer, 2001; Nakagawa *et al.*, 1985). The chlorine contents of the compounds vary between 6–13 wt-%, and since the adding levels are in the range of 0.5–1.5 wt-%, the chlorine residue may be between 200–2000 mg/kg in the plastic formulation.

3.1.7 Chlorine containing physical blowing agents

There are both chemical and physical blowing agent (BA) compounds, which can produce a foam structure for specific types of plastics (mostly polyurethane and polystyrene). Unlike chemical blowing agents, physical blowing agents are usually volatile liquids or compressed gases which vaporize during processing without the decomposition of their structures (Kattas *et al.*, 2000). There are several chlorine containing carbon compounds, which either were used or still find use in the manufacture of rigid and flexible polyurethane and extruded polystyrene closed cell foams used mainly in insulation applications. Since the mid-1990s, trichlorofluoromethane, known also by the name CFC-11, was the leading compound in closed cell rigid insulation PU foams, but due to its ozone depleting potential (ODP) it has been phased out in all developed countries (Phua and Wang, 2009; Elsner, 2009). Its first major replacements were different types of hydrochlorofluorocarbons (HCFC) with a similar nature to CFCs but with lower ODP values. Unfortunately they still contributed to the ozone destruction at some level, and therefore these transition blowing agent compounds have currently been replaced by either fluorinated hydrocarbons (HFC, contains only fluorine, hydrogen and carbon atoms), or halogen-free substances such as cycloalkanes, water and carbon dioxide CO_2. In spite of the detrimental effect of chlorinated fluorocarbons to both ozone depletion and global warming, HCFC and even CFC compounds still find some use in developing areas such as Africa (regions south from Sahara), Asia (South, South-East and North-East regions), and Latin America (Elsner, 2009). In Europe and North America the majority of blowing agents used are hydrocarbons (the biggest share), HFCs or other halogen free compounds such as CO_2 and chemical blowing agents. Even though the most harmful compounds such as CFCs and HCFCs are currently not used, they still can be found in older foams used for insulation of appliances and buildings. Typical concentrations are quite high; in rigid PU foams the CFC concentration can be as high as 15 wt-%, and typically it is in the range of 8–15 wt-% (Kjeldsen and Scheutz, 2003; Svanstrom, 1996; Scheutz *et al.*, 2007; Khalil and Rasmussen, 1986; Kjeldsen and Jensen, 2001). Concentrations of HCFC compounds are quite similar, usually more than 10 wt-% (Kjeldsen and Scheutz, 2003; Wishneski and Petroskey, 1993). Considering the high chlorine content of the blowing agent compounds, the chlorine concentration in PU foams treated with CFC and HCFC BAs can be very significant, usually between 60000–120000 mg/kg in the foamed PU polymer. Chlorine containing BAs are described in detail in Table 22.

Table 22. Chlorine containing flame retardants, light stabilizers, antimicrobials, antistatic additives and physical blowing agents (Ranken, 2009; Green, 1992; Weil and Levchik, 2004; Beard, 2007; Morf *et al.*, 2005; Hutzinger and Thoma, 1987; van Esch, 1997).

Name	**Common/ Trade name**	**Application**	**Chemical formula**	**Target of use**	**Chlorine content in plastic (mg/kg)**
Chlorinated paraffins	–	FR	$C_xH_{(2x-y+2)}Cl_y$	PVC, PU, rubbers	20000–100000
Hexachloro pentadiene dimer	Dechlorane Plus	FR	$C_{18}H_{12}Cl_{12}$	PA, PBT	100000–115000
Cycloaliphatic compounds	HET Acid	FR	$C_9H_4Cl_6O_4$	PVC	27000–82000
Chlorinated alkyl phosphates	–	FR	$C_{6-9}H_{12-18}Cl_{3-6}O_4P$	Rigid/ flexible PU	16000–74000
UVA-3, UVA-4	Tinuvin	Light stabilizer	$C_{17-20}H_{18-24}N_3OCl$	PE, PP, rubbers	100–300
Chlorinated hydroxydiphenyl ether	Triclosan	Biocide	$C_{12}H_7O_2Cl_3$	Polyolefins, PU, PS, ABS	300–3500
Chlorinated thio compounds	Fungitrol	Biocide	$C_9H_{4-8}Cl_3NO_2S$	PVC, PU, polyolefins, styrenics	100–1000
Tetrachloroisophthalonitrile	Fungitrol	Biocide	$C_8Cl_4N_2$	PVC, PU, polyolefins, styrenics	500–5000
Pentachlorophenyl laurate	Mystox	Biocide	$C_{18}H_{23}Cl_5O_2$	PVC, PU, polyolefins, styrenics	300–3900
Tetra-alkyl ammonium salt	–	Antistatic additive	$R\text{-}(CH_3)_3NCl$	PVC, styrenics	100–2000
Tetra-alkylbenzyl ammonium salt	–	Antistatic additive	$R\text{-}CH_3CH_3CH_2C_6H_5NCl$	PVC, styrenics	200–1800
Tri- and dichlorinated fluoromethane	CFC-11/CFC-12	Blowing Agent	CCl_3F/ CCl_2F_2	PU, PS	60000–120000
Chlorinated fluoroethane and methane	HCFC-22/141b/142b	Blowing Agent	$CHClF_2/C_2H_3Cl_2F/$ $C_2H_3ClF_2$	PU, PS	40000–70000

3.1.8 Concluding remarks

Chlorine containing organic pigments and dyes are the highest volume application of chlorine compounds used in plastics. The total number of pigments and dyes is more than 50, but since the majority of them are derivatives of some specific structure type, the pigments can be divided into the following sub-classes: isoindolinones, disazo condensation, metal salts of azo compounds, disazo diarylides, quinacridones, thioindigos, benzimidazolones, quinophthalones, phthalocyanines and pyrollo-pyrroles. The pigments belonging to these classes possess colors of yellow, brown, orange, red, green and blue in various shades. The chlorine content of these pigments is in the range of 5–30 wt-%, in general, and the resulting chlorine concentration in colored plastic articles usually varies between 10–800 mg/kg by weight of the plastic. When the usage levels of chlorine compounds are compared, chlorine containing FR compounds are the highest; species such as chlorinated paraffins, cycloaliphatic hydrocarbons and alkyl phosphates are used particularly in PVC, PU and rubbers with concentrations as high as 5–15 wt-%; therefore chlorine content in FR treated polymers may be huge, exceeding 100 000 mg/kg by weight of the polymer formulation. Chlorine compounds used in lower volumes are e.g. UV light absorbers designed to function in polyolefins and elastomers, antimicrobials finding approval in PVC, PU, PS and ABS, and cationic antistatic additives planned to be used in more polar polymers such as PVC. In these cases the chlorine content in plastics treated with additives is usually in the range of 100–300 mg/kg for UVAs, 100–3000 mg/kg for antimicrobials, and 100–2000 mg/kg for antistatic additives. The use of chlorine containing blowing agents in PU and PS foams was very significant in the 1990s, but nowadays they have largely been replaced by environmentally more friendly options. In the older foams the chlorine concentration was usually in the range of 40 000–120 000 mg/kg in the foamed polymer.

3.2 Bromine compounds in plastics

The market for bromine containing additive compounds used in plastics is narrow but very significant. Organic aromatic and aliphatic bromine containing FR compounds are used in almost every individual plastic polymer. Due to the great concentrations of FR compounds used, the bromine concentration in the plastics can be very high, exceeding 200 000 mg/kg in the plastic formulation. Besides FR compounds, there are some bromine containing pigments, and as mentioned in section (3.1.1.3), bromine is also used as an important ingredient in halobutyl rubber formulations.

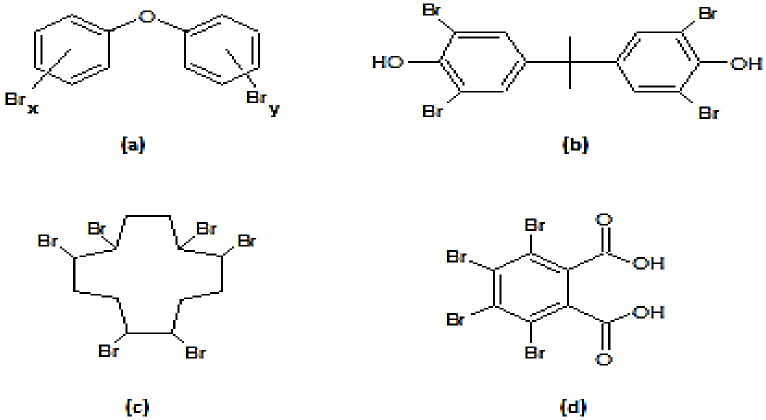
3.2.1 Bromine containing flame retardants

In the halogenated flame retardant market, versatile bromine containing aromatic and aliphatic hydrocarbon compounds are the dominant FR species, and overall they are the second most used FR class (by volume) after aluminum trihydroxide (ATH) (Beard, 2007), accounting for 25 % of the total FR consumption in 2001 (Morf *et al.*, 2005). The reason for their success is the suitable strength of the bromine-carbon bond; the weaker bonding to carbon (compared to the chlorine-carbon bond) enables it to interfere at a more favorable point in the combustion process. It is also assumed that an effective agent, hydrogen bromide (HBr), is liberated over a narrow temperature range, so that there is a high concentration of HBr in the flame zone (Troitzsch, 1993). That is contrary to hydrogen chloride (HCl), which is released over a wider temperature range, so that it is present at lower concentrations and thereby is less effective (Troitzsch, 1993). Brominated FR compounds are typically classified according to their mode of binding in the plastics: reactive flame retardants are chemically bonded into the polymer backbone, whereas additive FRs act as separate compounds simply blended with the plastic polymers (Hutzinger and Thoma, 1987).

Brominated aromatic FR compounds have the highest market share of halogenated FR species (van Esch, 1997). They are typically used in thermoplastics, either with or without the synergists (commonly antimony trioxide Sb_2O_3), depending on the processing temperature; the higher the processing temperature the higher the need for synergist compounds. There are both reactive and additive types of aromatic brominated FRs; compounds such as tetrabromobisphenol-A (TBBA) and its derivatives and the derivatives of tetrabromophthalic acid belong to reactive class, whereas polybrominated diphenyl ethers (PBDPE) such as decabromodiphenyl ether (DBDPE) represent the additive types of compounds. In addition oligomeric and polymeric FRs, such as TBBA carbonate oligomer ($(C_{18}H_{16}Br_4O_3)_n$) contain aromatic parts in their structures. The examples of FR compounds mentioned above are shown in Figure 10. TBBA and TBBA derivatives are dominant when the consumption of brominated FRs is considered (Alaee *et al.*, 2003; Birnbaum and Staskal, 2004). The typical adding levels vary from 10 to 20 wt-%; therefore the bromine concentration in flame retarded plastics may be up to 100 000 mg/kg by weight of the plastic or even more. Detailed information about aromatic FR compounds is presented in Table 23. In table it should be noted that two products of the PBDE family, pentadiphenyl ether and octadiphenyl ether, have been banned in Europe since 2004 (Beard, 2007; Bolgar *et al.*, 2008), and their replacement by alternative products has proceeded also in other continents, like in North America (Birnbaum and Staskal, 2004).

Brominated aliphatic FR compounds may be composed of either linear or cyclic structures, and usually these compounds are thermally less stable than aromatic FRs; they are easier to break down and thus they operate more efficiently at lower temperatures (Troitzsch, 1993). Some examples comprise additive type of FR hexabromocyclododecane (HBCD, the structure shown in Figure 10), which is utilized in PS foam formulations, and reactive type of compound dibromoneopentyl glycol ($C_5H_{10}O_2Br_2$) used in PU formulations (Troitzsch, 1993; Ranken, 2009; Birnbaum and Staskal, 2004). The concentrations of aliphatic FR compounds, particularly in the case of PS, are in the range of 2–4 wt-%, thus the bromine concentration in flame retarded PS foam is between 10 000–30 000 mg/kg. Aliphatic FR compounds are described in detail in Table 23.

Brominated phosphorus compounds have proved to be very effective flame retardants e.g. in PS and ABS formulation (Green, 1992), but due to the carcinogenic effects of some compounds (i.e. tris(2,3-dibromopropyl)phosphate) they have been withdrawn from the market (van Esch, 1997).



(a) (b)

(c) (d)

Figure 10. The chemical structures of (a) PBDE, (b) TBBA, (c) HBCD, and (d) Tetrabromophthalic acid.

Table 23. Bromine containing aliphatic and aromatic flame retardants (Cha, 2005; Troitzsch, 1993; Ranken, 2009; Beard, 2007).

Name	**Chemical composition**	**Br content (wt-%)**	**Target of use**	**Bromine content in plastic (mg/kg)**
Decabromodiphenyl ether	$C_{12}Br_{10}O$	82–83	PE, PP, HIPS, PBT, rubbers	83000–200000
Octabromodiphenyl ether	$C_{12}H_2Br_8O$	79–80	HDPE, PET, PBT, ABS, PA, PU	143000–175000
Pentabromodiphenyl ether	$C_{12}H_5Br_5O$	70–71	PU	40000–130000
Ethylenebis(tetra-bromophthalimide)	$C_{18}H_4N_2O_4Br_8$	66–67	PE, PP, HIPS, PBT, PA, PC	13000–80000
Tetrabromobis-phenol A	$C_{15}H_{12}Br_4O_2$	58–59	PP, HIPS, ABS	70000–130000
Tetrabromobis-phenol A derivatives	$C_{19-25}H_{20-24}Br_{4-6}O_{2-6}$	43–63	HDPE, PP	25000–95000
Brominated polystyrene	$C_8H_{5-6}Br_{2-3}$	61–70	PET, PBT, PA	73000–120000
TBBA carbonate oligomer	$(C_{18}H_{16}Br_4O_3)$	53-54	PC, PBT	40000–95000
Tetrabromophthalate diol	$C_{15}H_{16}Br_4O_7$	50–51	PU	75000–140000
Hexabromomcyclodo-decane	$C_{12}H_{18}Br_6$	74–75	EPS	15000–30000
Dibromoethyl dibromocyclohexane	$C_8H_{12}Br_4$	74–75	HIPS	37000–52000
Ethylenebis(dibromonorbornane-di-carboximide)	$C_{20}H_{20}Br_4O_4N_2$	47–48	PP	9000–19000

3.2.2 Bromine containing pigments

Unlike in the case of chlorine compounds, there are only a few bromine containing organic pigments used in plastics. The most important in terms of the consumption and the market share is brominated phthalocyanine compound, Pigment Green 36, with general applicability in the coloration of green plastic articles (Lewis, 2005; Scherrer and Sykes, 2009; Damm and Herrmann, 1993; Beebe, 1993). The typical chemical composition of the pigment is $C_{32}Br_{12\text{-}13}Cl_{3\text{-}4}CuN_8$, where the bromine content varies between 57–60 % by weight of the pigment. Considering the typical usage levels of the pigment, bromine residue in the plastics (caused by the coloration) ranges from 60 mg/kg up to 3000 mg/kg in the plastic formulation. Another bromine containing pigment is Pigment Red 216 with a pyranthrone backbone possessing excellent stability properties and general applicability in thermoplastics. However, due to its high price it is quite rarely used in plastics (Lewis, 2005).

3.2.3 Concluding remarks

The use of bromine differs significantly from the use of chlorine; there are only a couple of applications for bromine containing compounds used in plastics and rubbers, but these compounds are of crucial importance. The most important are bromine containing FR hydrocarbon species, both in aliphatic and aromatic forms. Examples of aromatics are tetrabromobisphenol-A and its derivatives and polybromodiphenyl ethers, which are generally applicable in engineering thermoplastics. Aliphatic FRs such as hexabromocyclododecane and dibromoethyl dibromocyclohexane are used e.g. in HIPS and PS foam. Due to the heavy loadings of FR compounds, the bromine content in FR treated plastics is huge, in the range of 10 000–175 000 mg/kg by weight of the plastic. Besides FR compounds, bromine compounds are used as pigments. Phthalocyanine and pyranthrone pigments for green and red coloration may cause high bromine concentration levels in polymers; concentrations even up to 3000 mg/kg are possible.

3.3 Fluorine in plastics and rubbers

Fluorine compounds are widely utilized in plastics and rubbers, either in the form of polymers with excellent mechanical, chemical and electrical properties (e.g. polytetrafluoroethylene (PTFE), commonly known as Teflon), or as pigments, stabilizers and processing aids with a general applicability. Fluorine may also exist (in an anionic form) as a residue in the structures of fillers and impact modifiers (e.g. mica and glass fiber).

3.3.1 Fluorine containing polymers

Polymers based on fluorine containing monomers have a unique position in the plastic industry due to their chemical inertness, heat resistance and electrical insulation properties. The only drawback of these polymers is their relatively high price (especially when compared to commodity plastics such as PE, PP, PS and PVC); therefore the growth of the consumption of fluoropolymers is mainly controlled by the price of the product.

3.3.1.1 Polytetrafluoroethylene

Polytetrafluoroethylene (PTFE), commonly known by name Teflon, has excellent heat resistance, electrical insulation and chemical inertness properties, resulting from the strong carbon-fluorine bond (Gangal, 2000c; Gangal, 2000b). Thus PTFE is a very useful polymer for high temperature applications, as well as for the components used in electrical and chemical articles. The basic structure of the polymer is composed of tetrafluoroethylene (TFE) ($CF_2{=}CF_2$) monomer units, which will further polymerize to form a polymer with the repeating structure shown in Figure 11. Pure PTFE contains about 76 wt-% of fluorine, and due to that it has extremely high density and viscosity values. PTFE can be manufactured by three different techniques to produce granular (Mueller and Salatiello, 1972), fine powder (Bankoff, 1952) and aqueous dispersion (Gangal, 1982) types of PTFE. Even though the properties of different types of PTFE polymers are different, the fluorine content does not change. PTFE is used also in the filled form; fillers such as glass fiber, graphite, carbon fiber and metal powder can be used (Ebnesajjad, 2011).

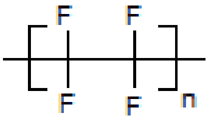


Figure 11. The repeating structure of PTFE.

Due to the new applications developed, the consumption of PTFE is increasing continuously; the approximate global annual consumption of PTFE is more than 50 000 tons (Gangal, 2000). Three major application areas for PTFE are electrical (about half of the total consumption), and mechanical and chemical applications with equal 25 % shares of the total consumption (Gangal, 2000). Among the electrical applications the biggest use of PTFE is for hookup wire used in electronic equipment. Also coaxial cables, computer wires, electrical tapes and electrical components may be manufactured of PTFE. When mechanical applications are considered, the biggest consumption of PTFE is for seals, piston rings, and for antistick uses such as coatings for e.g. cooking pots and frying pans. Some other significant targets for PTFE are in mechanical tapes, bearings and coated glass fabrics. Among the chemical area, the largest share of PTFE is consumed in the packaging applications. Besides that, the production of hose liners, fabricated gaskets, pipe-liners and thread-sealant tapes consume PTFE, as does the production of highly porous fabric structures such as Gore-Tex.

3.3.1.2 Polyvinylidene fluoride

Polyvinylidene fluoride (PVDF) is a semicrystalline polymer with the repeating formula $(CH_2–CF_2)_n$ containing 59.4 wt-% fluorine. Due to its regular structure with sequential $–CH_2$ and $–CF_2$ sections it has unique polarity end dielectric properties (Dohany, 2000). As other fluoropolymers, it shows good resistance to challenging chemical, thermal, weathering or high energy radiation environments.

PVDF has become the second largest volume fluoropolymer after PTFE due to its unique combination of properties, such as easy processing and lower price compared to other fluoropolymers (Dohany, 2000). The main application field for PVDF based products is in the electric and electronic industry, where particularly the flexible PVDF-hexafluoropropylene (HFP) co-polymer (Barber, 1992) with varying HFP content is utilized (the rubber-like VDF-HFP co-polymer with higher HFP content is presented in section 3.3.2.1). In the electric applications, plenum wire and cables, jackets for commercial aircraft and cathodic protection wires and cables are the dominant products. PVDF based products can also be used in the fluid handling systems in the chemical processing; products such as pipes, blow-molded bottles, pumps, and linings for tanks and trailers are typical (Dohany, 2000). PVDF homopolymer powder is used particularly as a base for durable coatings on aluminum and steel sidings, panel and roofing systems, and other building components (Dohany, 2000). PVDF microporous filters are used e.g. in water purification, biochemistry and medical devices, as well as in dairies and wineries. The good weather resistance of ABS-PVDF laminates caused by the protective PVDF cap layer makes these products very desirable in automotive dashboards, trailer/tractor roofs and motorcycle gas tank housings (Dohany, 2000).

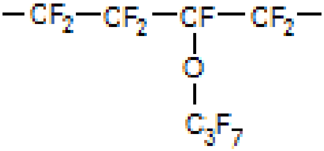
3.3.1.3 Perfluorinated ethylene-propylene copolymers

Perfluorinated ethylene-propylene (FEP) is a copolymer of TFE and HFP monomers, therefore the repeat structure of FEP consists of units of $–CF_2–CF_2–/ –CF_2–CF(CF_3)$, with the HFP content being in the range of 5–20 wt-% in the polymer (Nakagawa *et al.*, 1985; Khan and Morgan, 1983). Since both monomers have the same fluorine content, the variations in the compositions do not alter the total fluorine content of FEP, which is around 76 wt-%. Even though the fluorine content in the polymer is similar to PTFE, its properties (e.g. lower melting point) are different due to the presence of HFP monomers. Thus FEP can be processed with conventional melt processing methods while still possessing the desired durability properties of PTFE polymer.

Chemical inertness, corrosion resistance and good dielectric and insulation properties make FEP a good choice for chemical and electrical applications, and its mechanical toughness, low frictional properties, non-stickiness and thermal stability favor the use of FEP in mechanically and thermally challenging environments (Gangal, 2000). Among electrical applications, FEP is mostly utilized as coatings for different types of wires and cables, and as molded electrical parts (Gangal, 2000). When chemical applications are considered, coated pipes and fittings, heat exchangers, hoses and laboratory utensils are the most important articles. Mechanical applications comprise antistick applications (conveyor belts and roll covers), and the latest applications for FEP are light-weight and efficient films for solar collectors with good weatherability and solar transmission properties. The biggest drawback of FEP is its price; because of the high cost of HFP monomer, FEP is more expensive than PTFE. Thus the growth rate for FEP is expected to slow down since it can be replaced with lower price polymers.

3.3.1.4 Tetrafluoroethylene-perfluorovinyl ether copolymers

Perfluoroalkoxy (PFA) fluorocarbon resins, with repeat polymer structure presented in Figure 12, are melt-processible copolymers containing a fluorocarbon backbone with perfluorinated vinyl ether (PVE) side chains (Gangal, 2000). The polymer possess excellent chemical and mechanical properties (i.e. chemical inertness, heat resistance, toughness, flexibility, antistick features and low moisture absorption) even at elevated temperatures (Gangal, 2000). The fluorine content of PFA co-polymer varies according to the PVE content; usually the latter is in the range of 2.5–4 wt-% (Carlson, 1972; Carlson *et al.*, 1986; Dargaville *et al.*, 2001; Imbalzano and Kerbow, 1988), and thus the calculated total fluorine content of PFA is around 75 wt-%.



$$-CF_2-CF_2-\underset{\substack{|\\ O\\ |\\ C_3F_7}}{CF}-CF_2-$$

Figure 12. The repeating structure of PFA.

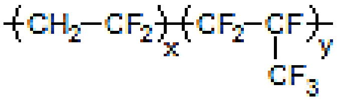
PFA co-polymers (depending on the ether content) may be used in high temperature electrical insulation applications, as well as in long life components used in mechanical parts (Gangal, 2000). They find use as a general-purpose resin for primary insulation, tubing, wire/cable jacketing, and as injection- and blow molded components. Other applications comprise semiconductors, fluid handling systems, and liners for chemical processing. As in the case of many other fluoropolymers, the relatively high price (especially the price of PVE co-monomer) limits the use of PFA copolymers.

3.3.2 Fluorine containing elastomers

Fluorine containing elastomers, such as copolymer of VDF and HFP and terpolymer of VDF, HFP and TFE, are synthetic polymers that show rubber-like properties after cross-linking (Fluorocarbon Elastomers, 2000). These polymers are the most resistant elastomers to heat, chemicals, and solvents, but due to their higher price their use is limited only to most challenging applications.

3.3.2.1 Vinylidene fluoride-hexafluoropropylene copolymer

The copolymer of VDF and HFP is the dominant fluoro rubber compound with the repeat polymer structure presented in Figure 13; typically the polymer contains about 60 wt-% VDF and 40 wt-% co-monomer (Fluorocarbon Elastomers, 2000; Hayashi *et al.*, 1989; Moran, 1960). In this case the calculated fluorine content of the rubber is about 70 wt-%. In the polymer structure the fluorine atom confers chemical inertness, but hydrogen must also be present to maintain rubbery properties.



$$\left(CH_2-CF_2 \right)_x \left(CF_2-\underset{CF_3}{\underset{|}{CF}} \right)_y$$

Figure 13. The repeat structure of VDF-HFP copolymer.

VDF-HFP rubbers are typically used in highly demanding applications primarily in the aircraft industry, but nowadays they are utilized in increasing volumes also as materials for engine oil seals, hoses and O-rings in automotive fuel systems. This is true particularly in the U.S, where about 60 % of the usage is consumed in ground transportation applications (Fluorocarbon Elastomers, 2000), and this sector will even grow due to the new and more challenging fuels and more demanding underhood temperatures. Other important targets of use are industrial hydraulic and pneumatic and petroleum/petrochemical applications, as well as applications designed for pollution control. The annual global consumption of fluoroelastomers is more than 7 000 metric tons (Fluorocarbon Elastomers, 2000), from which VDF-HFP rubbers constitute the majority.

3.3.2.2 Fluorovinyl methyl silicone

The polyfluorosilicones are polymers consisting of fluorinated alkyl substituents attached to silicon, which is part of siloxane sub-unit (Romenesko *et al.*, 2000). Due to the siloxane backbone structure and the presence of carbon-fluorine bonds, the polymers possess unique solvent resistance and stability properties; polyfluorosilicones are the only materials that combine high resistance to fuels, oils and solvents (resulting from C–F-bonds) with the high elasticity, good low temperature properties and good ozone and weathering resistance.

The annual production capacity of fluorosilicones was estimated to be between 2 000–3 000 metric tons in 2002 (Romenesko *et al.*, 2000). The majority of fluorosilicones are used in rubber applications, but there are also several non-elastomeric targets of use (Romenesko *et al.*, 2000; Bajzer, 2000). The main applications for non-rubber fluorosilicones are in surface protection (e.g. in nylon-cotton fabrics), medical devices (gastric feeding tubes), lubrication (fluorosilicone fluid polymers and oils used as lubricants for pumps and compressors), sealants, and in cosmetic applications. The fluorosilicone rubber formulations are particularly useful in applications such as automotive seals, gaskets and hoses, as well as in O-rings for gasoline and aviation fuels, and in wire/cable and electrical connectors. Fluorosilicone formulations are typically filled systems; additives such as fillers, pigments, stabilizers and acid acceptors are often used.

3.3.3 Fluorine containing fillers, pigments, processing aids and stabilizers

Besides fluorine containing polymers, there are also some fluorine containing additive compounds used in both plastic and rubber polymers. The most important are fluorine containing organic pigments, blowing agents for foamed polymers, inorganic fillers and glass fibers, and also processing aids with extended use particularly in polyolefins.

3.3.3.1 Pigments and fillers

The variety of fluorine containing pigments is not broad; there are less than ten commercial organic fluorine containing pigments, of which two yellow pigments and one red pigment have gained the broadest market share. Pigment Yellow 128 (used in PVC and LDPE) and Pigment Red 242 (finds use both in PVC and polyolefins) are disazo condensation pigments (Herbst, 1997). Pigment Yellow 154 with a benzimidazolone structure may be utilized in both PVC and polyolefins. The fluorine content in these pigments ranges from 9 wt-% to 14 wt-%; therefore the concentration of fluorine in the plastic articles does not exceed 1000 mg/kg.

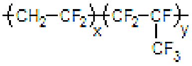
Some inorganic fillers and glass fibers may contain fluoride ions incorporated into the lattice structure of the filler. Minerals such as mica (Schlumpf, 1993) and glass fiber E might contain fluoride ions with maximum contents ranging from 0.7 wt-% (glass fiber E) (Wallenberger *et al.*, 2001; Kleinholz *et al.*, 1993) to 0.5 wt-% (mica, phlogopite) (Khalighi and Minkkinen, 1989; Tanner, 2000; Aoki, 1981). Glass fiber E is generally applicable for plastics, and mica is conventionally utilized in PVC, LDPE, PP and PU applications. The loadings of fillers/glass fibers may occasionally be high (up to 20 wt-%), thus the concentration of fluoride in plastics may be as high as 1500 mg/kg, but usually it is well below 1000 mg/kg. Due to environmental aspects (Kudryavtsev *et al.*, 2001), a new type of glass fiber E with low fluoride content has been developed; in this type fluoride exists only at trace levels (Wallenberger, 2004).

3.3.3.2 Processing aids and stabilizers

The market of fluorine containing stabilizer compounds is very narrow; there is only one compound, fluorophosphonite type secondary antioxidant known by names PS-7 or Ethanox 398, used typically in a combination with sterically hindered phenol compounds (Scwarzenbach *et al.*, 2009). Regarding the low fluorine content of the compound (3.9 wt-%) and the moderate loading levels of synergist stabilizer compounds (typically in the range of 0.1–0.3 %), the fluorine contamination caused by the stabilizer compound is less than 150 mg/kg in the polymer.

When fluorine based processing aids are considered, the market is a little bit broader: fluoroelastomers are widely utilized as processing aid additives for PE polymers (Amos *et al.*, 2009). Fluoroelastomers, typically copolymers of VDF and HFP, are used in concentrations between 0.01–0.1 wt-%, thus the fluorine content in PE may vary from 70 mg/kg up to 700 mg/kg, depending on the volume of the processing aid used. Fluorine containing pigments, fillers, processing aids and stabilizers are described in detail in Table 24.

Table 24. Fluorine containing pigments, fillers, stabilizers and processing aids (Troitzsch, 1993).

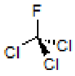
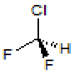
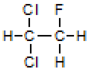
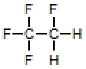
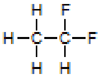
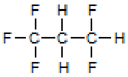
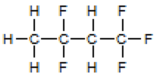
Name	**Application**	**Chemical composition**	**Fluorine content (%)**	**Target of use**	**Fluorine content in plastic (mg/kg)**
PY 128	Pigment	$C_{55}H_{37}Cl_5F_6N_8O_8$	8–9	PVC, LDPE	10–500
PY 154	Pigment	$C_{18}H_{14}F_3N_5O_3$	13–14	PVC, polyolefins	10–600
PR 242	Pigment	$C_{42}H_{22}Cl_4F_6N_6O_4$	11–12	PVC, polyolefins	10–700
Mica	Filler	$KMg_3(AlSi_3)O_{10}(OH,F)_2$	1–4.5	PVC, LDPE, PP, PU	0–1000
Glass fiber E	Impact modifier	–	0–0.7	Generally applicable	0–1400
PS-7	Stabilizer	$C_{30}H_{44}O_2PF$	3.5–4	polyolefins	40–150
Fluoro-elastomer	Processing aid	 $\left(CH_2-CF_2\right)_x\left(CF_2-\underset{\substack{\mid\\ CF_3}}{CF}\right)_y$	65–69	PE	70–700

3.3.4 Fluorine containing physical blowing agents

Fluorine containing physical blowing agents, such as fluorinated small hydrocarbons (HFCs based on ethane, propane and butane) are nowadays widely used in both PU and extruded PS foams. Due to the zero ODP of HFCs, their production is not prohibited by legislation, but HFCs still have a quite high global warming potential (GWP) compared with e.g. halogen-free hydrocarbons. Regarding also their quite high price, the future use of HFCs will concentrate on PU and XPS foam applications in which they cannot be replaced by e.g. cycloalkanes due to the higher flammability of halogen-free hydrocarbons. The structures of most commonly used HFCs are presented in Table 25. Besides HFCs, also CFCs and HCFCs contain fluorine, but they are either phased out (CFCs), or their use is continuously declining (HCFCs) due to environmental reasons. The structures of most commonly used HFCs are presented in Table 25.

HFCs are typically used in slightly smaller concentrations than former both chlorine and fluorine containing CFC and HCFC compounds. Their typical concentrations are between 1.5–8.0 wt-% (Bartlett and Creazzo, 1992; Valoppi and Bredeson, 2001), but for some applications concentrations up to 13 wt-% are needed (Kjeldsen and Scheutz, 2003). Therefore, due to the high fluorine content of the BAs, very high concentrations of fluorine can be found in the final PU and XPS foam formulations; concentrations in the range of 10 000–65 000 mg/kg and even up to 95 000 mg/kg are possible. In older foams where CFCs and HCFCs are used, fluorine concentrations are typically in the range of 5000–20 000 mg/kg in the PU/XPS foam. Typical fluorine containing BA compounds and fluorine concentrations in the final foam formulations are presented in Table 25.

Table 25. Fluorine containing physical blowing agents.

Name	**Structure**	**Application**	**Fluorine content in the foam (mg/kg)**
CFC-11		PU, PS	5000–22000
HCFC-22		PU, PS	40000–60000
HCFC-141b		PU, PS	15000–20000
HFC-134a		PU, PS	10000–65000
HFC-152a		PU, PS	30000–40000
HFC-245fa		PU, PS	10000–95000
HFC-365mfc		PU, PS	40000–60000

3.3.5 Concluding remarks

In spite of the fact that fluorine containing polymers and elastomers have achieved a strong foothold in the plastic market, the state of fluorine containing additive compounds is the opposite; there are only a few such compounds finding use in plastics and rubbers. Some organic pigments (PY 128, PY 154, and PR 242) with disazo condensation and benzimidazolone structures are used in PVC and polyolefins, and if the colorant is used in loadings varying between 0.05–0.5 wt-%, the fluorine residue in the final plastic products may be between 10–700 mg/kg, depending on the pigment. Besides pigments, fluorine containing blowing agents (along with cycloalkanes and carbon dioxide) are currently the dominant BA species in the market, and they are used most typically in PU and XPS foams. The fluorine concentration resulting from the use of BAs can be high, from 10 000 mg/kg up to 95 000 mg/kg in the foamed plastic article. Fluoride ions can also exist as a residue in some inorganic minerals (e.g. mica and glass fibers) used as fillers and impact modifiers in plastics. Here the fluoride content in a plastic article depends both on the concentration of filler used and the extent of the fluoride impurity in the filler; usually it is well below 1000 mg/kg. Finally, fluorine compounds are also utilized as stabilizers (fluorophosphonite type secondary antioxidant) and as processing aids for PE films (fluoroelastomers).

4. Sulfur and alkaline earth metal compounds

4.1 Sulfur in plastics and rubbers

4.1.1 Sulfur containing polymers

4.1.1.1 Polyphenylene sulfide

Poly(p-phenylene sulfide) (PPS) with the repeating structure presented in Figure 14, plays an important role among the group of engineering thermoplastics. The structure consists of alternating benzene rings and sulfur bridges, and its estimated sulfur content is around 30 wt-%.

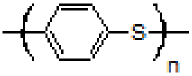


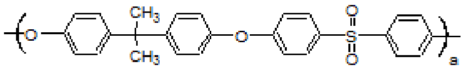
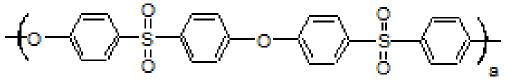
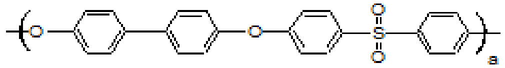
Figure 14. Repeating structure of PPS.

The total installed capacity of producing PPS was 35 000 tons in 1999, and nowadays it is possible to produce both linear and cross-linked types of polymers (Grabassi and Po, 2000). Due to the low toughness and T_g (softening temperature) values, PPS is commercialized only as a filled or reinforced formulation (Garbassi and Po, 2000). Due to its properties such as excellent electrical insulation, thermal stability, flame and chemical resistance, easy moldability and good mechanical properties, PPS is used mainly in mechanical parts, electrical components and components for challenging environments such as automotives (engine components and valves) and appliances (e.g. valves and high pressure nozzles) (Geibel and Leland, 2000). It finds acceptance also as coating, fiber and film material, and blends with other polymers.

4.1.1.2 Polysulfones

Polysulfones belong to a class of aromatic resins containing a sulfone group as a part of their repeating unit. There are three commercially important structures (El-Hibri, 2000): (1) polysulfones (PSF), (2) polyethersulfones (PES), and (3) polyphenylsulfones (PPSF), whose repeating unit structures and calculated sulfur contents are shown in Table 26.

Table 26. The structures and calculated sulfur content of polysulfones (Garbassi and Po, 2000).

Polymer	**Repeat unit structure**	**Sulfur content (wt-%)**
Polysulfone		7–8
Polyethersulfone		13–14
Polyphenylsulfone		7.5–8.5

Even though these polysulfones can be used interchangeably in many applications, generally PSF is selected due to its lower cost compared to PES and PPSF (El-Hibri, 2000). Due to that, the share of PSF constituted 70 % of the total consumption of polysulfones, which was 20 000 tons in 1998 (Garbassi and Po, 2000; El-Hibri, 2000). PES is selected when higher temperatures occur, whereas PPSF is a choice when better hydrolytic stability and impact and chemical resistance are needed. Polysulfones can be used in a wide variety of applications due to their chemically and electrically stabile nature, as well as good clarity and high heat deflection properties. They are used in consumer items (cookware and food service applications), electrical and electronic applications (circuit boards, circuit breaker components, connectors and sockets), and automotive and aerospace applications (El-Hibri, 2000). Besides that, the resistance to various sterilizing media and the asymmetric nature of PSF makes it suitable for many medical devices and membrane separations (e.g. ultrafiltration and artificial kidneys). PSF and PES are also available as glass-reinforced grades with the proportion of glass as high as 30 % by weight in the polymer, and due to their enhanced resistance and long service life they are mostly used in severe chemical environments.

4.1.1.3 Polysulfides

Polysulfide polymers (with the general structure $HS–(R–S_x)_n–SH$) are rubbers used in a wide variety of applications, such as insulating glass sealants, aircraft sealants and construction sealants. They also find use as below-ground sealants, epoxy flexibilizers, rubber articles (O-rings) and as protective coatings e.g. for fuel tanks (Vietti and Scherrer, 2000). Typical sulfur contents in their structures vary between 50–80 % by weight in the polymer.

The worldwide production capacity of polysulfides is about 33 000 tons, and approximately half of the production is used for insulating glass sealants, one third is for construction applications, and about 10 % for aircraft sealants (Vietti and Scherrer, 2000).

4.1.1.4 Chlorosulfonated polyethylene

Chlorosulfonated polyethylene (CSM) is a curable polymer with properties ranging from soft and elastomeric to hard. The sulfur content in the polymer depends on the type of the precursor resin (LDPE, HDPE and LLDPE), and it is usually in the range of 0.5–1.5 % by weight of the polymer (Ennis, 2000). End use applications are determined by the type of the polymer; solution grade polymers have been used in roof coatings and the manufacturing of tarpaulins, general-purpose grades are mostly used in applications such as hoses, tubing, electrical wiring, inflatable boats, industrial rolls and belts, and also in molded and extruded products (Ennis, 2000). Polymers with high chlorine content are used in automotive and air conditioning hoses and also in some coating applications.

The biggest manufacturer of chlorosulfonated polyethylene (DuPont under the trade name Hypalon) has ceased the production of the polymer in April 2010, mainly due to environmental and economic reasons (DuPont Elastomers, 2012). Before that the annual production of CSM was over 50 000 tons (Ennis, 2000).

4.1.2 Sulfur and sulfur compounds in rubber crosslinking

There is a wide variety of different kinds of polymers used for rubber compounding; the total number of elastomers is around 30. Despite of that, only six of them are produced in larger volumes and they represent the majority of all elastomers used (Klingensmith *et al.*, 1997). These so called general purpose rubbers (GPR) are styrene-butadiene rubber (SBR), polybutadiene (PBD), ethylene-propylene rubber (EPDM), butyl rubber (IIR), halobutyl rubber (HIIR) and nitrile rubber (NBR). Besides GPR, also special purpose rubbers such as acrylics, CSM, polysulfides, chlorinated polyethylene (CPE), epichlorohydrin (ECH), different kind of fluoroelastomers and thermoplastic elastomers are used in more specific applications (Klingensmith *et al.*, 1997; Rodgers *et al.*, 2000). Halogen containing rubbers (HIIR, ECH and fluoroelastomers) are introduced in detail in the following chapters.

In order to improve the performance (stiffness, elasticity) of the rubber polymers, a special treatment called vulcanization is carried out. In the vulcanization the three-dimensional structure of the polymer is formed in a reaction between reactive sites of polymer and so called curing agents, which usually contain sulfur. In order to optimize the reaction time and efficiency, some sulfur containing additive compounds such as accelerators, activators and retarders are also used. In the following sections the compounds most widely used in the vulcanization (i.e. vulcanizing agents, accelerators, activators and retarders) and their typical concentration ranges are introduced in detail.

4.1.2.1 Vulcanizing agents

Elemental sulfur is the most common vulcanizing agent for diene-containing elastomers, such as natural rubber (NR), SBR and PBD (Klingensmith *et al.*, 1997; Rodgers *et al.*, 2000). Sulfur (rhombic form) is conventionally used as a cyclic or eight-member ring structure. Some sulfur containing compounds usually functioning as accelerators (i.e. morpholinyl disulfide and thiuram disulfides) can also be used as vulcanizing agents (these compounds are introduced in detail in section 2.2.2). The concentration level of the elemental sulfur and sulfur donor compounds in the vulcanization is typically in the range of 0.3–1.0 wt-% and 1–3 wt-%, respectively, depending on the compounds and the curing systems used (Klingensmith *et al.*, 1997; Rodgers *et al.*, 2000).

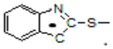
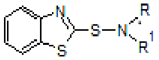
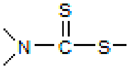
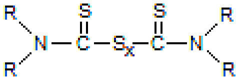
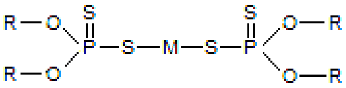
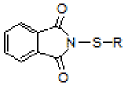
Many specialty elastomers do not contain diene parts in their structure, and thus sulfur curing is not possible (Rodgers *et al.*, 2000). Non-sulfur curatives may be e.g. peroxides or metal oxides. Elastomers containing halogens are usually cured with metal oxides, such as zinc oxide, and also fluoroelastomers and polyacrylates utilize non-sulfur curative systems. Even though these elastomers are cured without sulfur, accelerators, activators and retarders used in the vulcanization typically contain sulfur.

4.1.2.2 Accelerators

During the vulcanization, organic (usually sulfur containing) compounds called accelerators are used to control the rate and the reaction time of vulcanization (Klingensmith *et al.*, 1997). Besides that, accelerators control the number and type of the crosslinks formed in the vulcanization. In order to obtain the optimum rate for the reaction, activators such as combinations of zinc oxide and fatty acids are added; they react with accelerators forming rubber-soluble complexes, which further can react with the sulfur to attain the desired structure of the polymer (Klingensmith *et al.*, 1997; Rodgers *et al.*, 2000).

There are eight principal classes of accelerators used for vulcanization: sulfur containing accelerators benzothiazoles, sulfenamides, dithiocarbamates, thiuram sulfides, xanthates, dithiophosphates, thioureas, and nitrogen based guanidines (Rodgers *et al.*, 2000; Ohm, 2000). Table 27 introduces the basic structures of the sulfur containing accelerator classes and also the range of sulfur concentration for every class. The usage levels of the accelerators vary according to the curing system and the polymer resin used, but usual concentrations are in the range of 0.2–2.0 % by weight of the total rubber formulation.

Table 27. Sulfur containing accelerator and retarder compounds (Schwarzenbach *et al.*, 2009; Gugumus, 2009, Gugumus, 1993a).

Accelerator class	**Basic structure**	**Sulfur content (wt-%)**
Benzothiazoles		34–42
Sulfenamides		17–34
Dithiocarbamates		24–42
Thiuram sulfides		24–57
Xanthates	 $R-O-C(=S)-S-M-S-C(=S)-O-R$	38–43
Dithiophosphates		23–26
Thioureas	 $R-NH-C(=S)-NH-R$	14–31
Thiophthalimides		11–12

4.1.2.3 Retarders

In the vulcanization, retarders are used to delay the onset of cross-linking and also to slow down the vulcanization reaction itself (Rodgers *et al.*, 2000; Ohm, 2000). There are two sulfur containing classes of retarders, thiuram sulfides and particularly thiophthalimides such as cyclohexylthiophthalimide (known as PVI), whose basic structures are presented in Table 27. The sulfur content of the compounds is in the range of 12–27 wt-%, and the usage levels of the retarders are usually quite low, often below 0.5 % by the total weight of the polymer (Datta, 2002).

4.1.2.4 Rubber compounding

As discussed in the previous sections, sulfur containing compounds can be used for many tasks during the vulcanization. When evaluating the total concentration of the elemental sulfur in the final rubber formulation, one has to consider both the curing system (sulfur/non-sulfur) and the accelerators/retarders used for the vulcanization. The specific curing compounds are primarily used for the specific type of rubber polymer (i.e. whether it contains diene parts or not), but the same accelerators can be used interchangeably in different kind of polymers. Table 28 introduces the most widely used sulfur containing curing chemicals, accelerators and retarders used for specific rubber formulations. Besides that, the elemental sulfur concentrations in the final polymer are estimated.

Table 28. Curing systems used for different types of elastomers (Ennis, 2000; Kilngensmith *et al.*, 1997; Datta, 2002; Morton, 2000; Spelta, 2000; Laakso *et al.*, 2008, Kresge and Wang, 2000) In the table the following abbreviations are used: NR = Natural Rubber, SBR = Styrene-Butadiene Rubber, EPDM = Ethylene-propylene Rubber, BR = Polybutadiene rubber, IIR = Butyl Rubber, HIIR = Halobutyl Rubber, NBR = Nitrile Rubber, CSM = Chlorosulfonated polyethylene, CPE = Chlorinated Polyethylene, ECH = Polyepichlorohydrin, ACM = Acrylic Elastomer, CR = Polychloroprene Rubber.

Elastomer	**Typical curing compound**	**Typical accelerators and retarders**	**Sulfur content in the polymer (mg/kg)**
NR	Sulfur	sulfenamides, thiurams, thiazoles, thiophthalimides	10000–30000
SBR	Sulfur	sulfenamides, thiurams, thiazoles, thiophthalimides	9000–17000
NR/BR	Sulfur	sulfenamides, thiurams, thiazoles, thiophthalimides	6000–25000
EPDM	Sulfur	sulfenamides, thiurams, thiazoles, carbamates	6000–12000
SBR/BR	Sulfur	sulfenamides, thiurams, thiazoles, thiophthalimides	13000–18000
NR/BR/SBR	Sulfur	sulfenamides, thiurams, thiazoles, thiophthalimides	9000–11000
IIR	Sulfur	sulfenamides, thiazoles, thiophthalimides	9000–13000
HIIR	Non-sulfur	sulfenamides, thiazoles, thiophthalimides	5000–7000
NBR	Sulfur/ non-sulfur	sulfenamides, thiurams, thiazoles, thiophthalimides	4000–11000
CR	ZnO	thioureas, thiazoles thiones	700–3000
CSM	Sulfur/ non-sulfur	thiazoles, carbamates, thiurams	7000–9000
CM	Non-sulfur	thiomorpholines	8000–11000
ECH	Sulfur	mercapto-triazines, thiophthalimides	1000–5000
ACM	Non-sulfur	carbamates, thiophthalimides	500–2500

4.1.3 Sulfur containing inorganic pigments and fillers and organic pigments and dyes

There is a wide variety of both inorganic and organic sulfur containing pigments and dyes available for plastics and rubbers. Typical inorganic fillers are calcium and barium sulfates, as well as different modifications of carbon black with varying sulfur content. Common inorganic sulfur containing pigments are e.g. various sulfides and sulfates of lead, zinc, cadmium and chromium. When organic sulfur based pigments are considered, the supply is much wider; there are over 20 different kind of yellow, orange or red sulfur containing pigments applicable for plastics.

4.1.3.1 Inorganic pigments and fillers

The use of carbon black as a reinforcing filler in rubber tire formulations and other rubber applications is very significant; e.g. in the U.S it comprises about 90 % of the total carbon black consumption (Wang *et al.*, 2000). More than 30 different grades of carbon black fillers are used, and the majority of them contain sulfur resulting from the aromatic feedstock of the filler (which may contain thiophenes, mercaptans and sulfides). As much as 1.2 wt-% of sulfur can be found in carbon black (Wang *et al.*, 2000), and due to the high loading levels the sulfur “contamination” may amount to 2000–4000 mg/kg in the rubber polymer. The use of carbon black in plastic applications is the second largest market constituting about 5 % of the total consumption. Here the grades of carbon blacks are mainly used as pigments (Pigment Black 7), and also as conductive fillers particularly in plastics used in electrical applications (IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, 2006). Again, depending on the grade of carbon black used, the filler may contain some sulfur, but due to the lower loading levels (particularly in pigmentation) the maximum sulfur residue is a couple of hundreds of mg/kg.

Barium sulfate $BaSO_4$ (known also as baryte or barite) is used in plastics (mainly PVC, PU and PP) and rubbers in many functions. Its main feature is its high unit weight; it is therefore used in applications where added weight is desired (Robinson *et al.*, 2007; Zazyczny and Matuana, 2005; Evans and Huber, 2001). Main applications for $BaSO_4$ are in sound deadening for foams and plastisols, floorings, sport equipment (tennis and golf balls), carpet backing, and in blankets/shields for X-ray protection (Robinson *et al.*, 2007; Hohenberger, 2009; Dibello, 1992). It also finds use as an additive to improve the gloss and surface properties of PP formulations planned for outdoor use, and as a white pigment (Hohenberger, 2009). Unlike $BaSO_4$, the use of calcium sulfate $CaSO_4$ is restricted mainly due to its sensitivity against moisture; in the presence of water, the formation of hydrated crystalline calcium sulfate $CaSO_4 \cdot 2H_2O$ occurs, which will diminish the dispersability of the filler (Robinson *et al.*, 2007; Hohenberger, 2009). $CaSO_4$ finds use in specific applications for polyesters, foams and PVC (Zazycny and Matuana, 2005; Hohenberger, 2009).

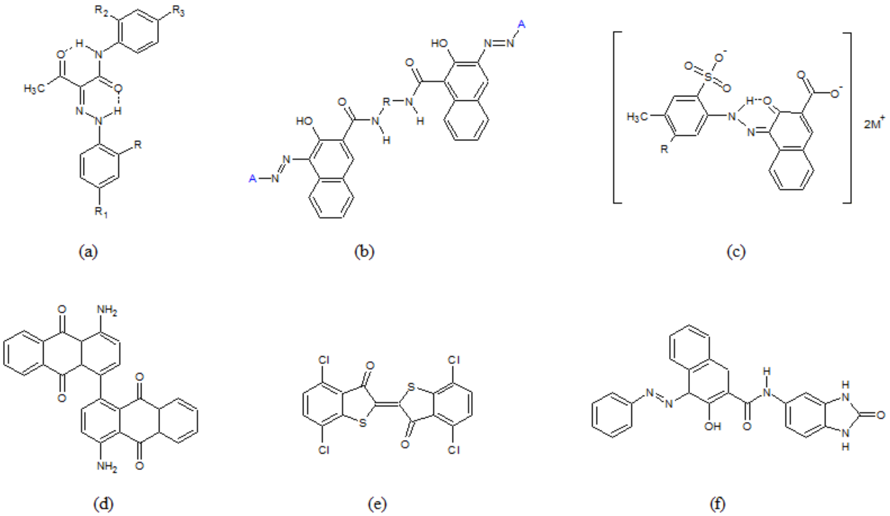
Inorganic sulfur containing yellow, orange and red pigments such as cadmium yellow (Cd,Zn)S, cadmium sulfoselenide Cd(Se,S), the combination of lead chromate and sulfate $Pb(Cr,S)O_4$ and the combination of lead chromate, molybdate and sulfate $Pb(Cr,Mo,S)O_4$ may be used particularly in PVC, HDPE and LDPE (Scherrer and Sykes, 2009). Due to their heavy metal content, cadmium and lead containing pigments are being replaced by less toxic options such as complex mixed metal pigments. Also ultramarine blue pigment with the chemical formula $Na_{6-8}Al_6Si_6O_{24}S_{2-4}$ is used in blue PS, LDPE, HDPE and PVC plastic articles. Table 29 presents different kinds of sulfur containing fillers and inorganic pigments, their typical concentrations and the targets of their use in plastics. The sulfur content in the final polymers is also estimated.

Table 29. Sulfur containing inorganic fillers and pigments (Dibello, 1992; Scherrer and Sykes, 2009; Damm and Herrmann, 1993; Beebe, 1993.

Name	Chemical formula	Application	Target of use	Usage level of compound (%)	Sulfur content in plastics (mg/kg)
Barium sulfate	$BaSO_4$	Filler/Pigment	PVC, PP, PU, foams, rubbers	1–30	1000–41000
Calcium sulfate	$CaSO_4$	Filler/FR	PVC, PET, PBT, foams	1–20	1500–35000
Pigment yellow 34	$Pb(Cr,S)O_4$	Pigment	PVC, LDPE, HDPE	0.05–0.5	30–300
Pigment yellow 37	$(Cd,Zn)S$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	0.05–0.5	140–1400
Pigment Red 108/ Pigment Orange 20	$Cd(Se,S)$	Pigment	PVC, PE,PP, PS, PET, PA, ABS, PU	0.05–0.5	50–500
Pigment Red 104	$Pb(Cr,Mo,S)O_4$	Pigment	PVC, LDPE, PS	0.05–0.5	20–200
Pigment Blue 29	$Na_{6\text{-}8}Al_6Si_6O_{24}S_{2\text{-}4}$	Pigment	PVC, PS, LDPE, HDPE	0.05–0.5	70–700

4.1.3.2 Organic sulfur containing pigments and dyes

When the number and the types of sulfur containing inorganic and organic pigments are considered, the supply of the organic sulfur containing pigments is much broader. There are over 20 such pigments in the market, and the majority of them are used in the coloration of yellow, red and orange plastic articles. Most of the pigments contain azo groups in their structures; they can be di- or monoazo compounds, or they can be metal salts of some azo derivatives. In addition, monoarylide, anthraquinone, thioindigo and benzimidazolone pigments may contain sulfur in their structures. Figure 15 shows some examples of the basic structures of the sulfur containing pigments.


(a) (b) (c)

(d) (e) (f)

Figure 15. Examples of the structures of (a) monoazo pigment (b) diazo pigment (c) metal salt of azo pigment (d) anthraquinone pigment (e) thioindigo pigment (f) benzimidazolone pigment (Beebe, 1993; Lewis, 2005).

When plastics are colored with organic pigments, the volume of the pigment or the pigment masterbatch added to the polymer is slightly smaller than in the case of inorganic pigments. Besides that, organic pigments (as well as inorganic colored pigments) may be diluted with white pigments such as titanium dioxide in order to obtain the different shades of the specific color. That is why the amount of the colorant loaded into the plastics typically does not exceed 0.5 % by weight of the polymer.

Table 30 introduces different kinds of sulfur containing organic pigments; the types of the structures, sulfur contents, and the targets of the use are clarified, as well as the sulfur concentration in the final plastic articles.

Table 30. Sulfur containing organic pigments (Dibello, 1992; Scherrer and Sykes, 2009; Damm and Herrmann, 1993; Beebe, 1993).

Name	**Type of the structure**	**Chemical formula**	**Target of use**	**Sulfur content in plastics (mg/kg)**
Pigment Yellow 62	Ca salt, monoazo	$2(C_{17}H_{15}N_4O_7S)\cdot Ca$	LDPE, PVC, PP fibers	7–370
Pigment Yellow 168	Ca salt, monoazo	$2(C_{16}H_{12}ClN_4O_7S)\cdot Ca$	PVC, LDPE, HDPE, PP, PS	7–350
Pigment Yellow 183	Ca salt, monoazo	$C_{16}H_{10}CaCl_2N_4O_7S_2$	PVC, PS, ABS	10–600
Pigment Yellow 191	Ca salt, monoazo	$C_{17}H_{13}CaClN_4O_7S_2$	PVC, PS, LDPE, HDPE, PP	10–600
Pigment Yellow 97	Diazo, monoarylide	$C_{26}H_{27}ClN_4O_8S$	PVC, PS, PE, PP, ABS	5–300
Solvent Yellow 163	Anthraquinone dye	$C_{26}H_{16}O_2S_2$	PS, PC, PBT, PET, ABS	10–800
Derivatives of Pigment Red 48	Metal salts of monoazo acid dye	$C_{18}H_{11}ClN_2O_6SM$ (M=Ba,Ca,Sr,Mn)	PVC, PS, LDPE, (PP)	5–350
Derivatives of Pigment Red 53	Metal salts of monoazo acid dye	$2(C_{17}H_{12}ClN_2O_4S)\cdot Ba$	PVC, PS, LDPE	5–370
Pigment Red 57	Ca salt, monoazo	$C_{18}H_{12}N_2O_6S\cdot Ca$	PVC, PS, LDPE, PP	10–380
Pigment Red 247	Ca salts of monoazo acid dye	$C_{64}H_{50}CaN_8O_{14}S_2$	PVC, LDPE, HDPE, PS	5–260
Pigment Red 88	Thioindigo	$C_{16}H_4Cl_4O_2S_2$	PVC, LDPE, HDPE, PS	10–740
Pigment Red 198	Thioindigo	$C_{18}H_{10}O_2Cl_2S_2$	PVC, LDPE, HDPE, PS	10–820
Pigment Red 185	Benzimidazolone	$C_{27}H_{24}N_6O_6S$	PVC, LDPE, HDPE, PS	5–300

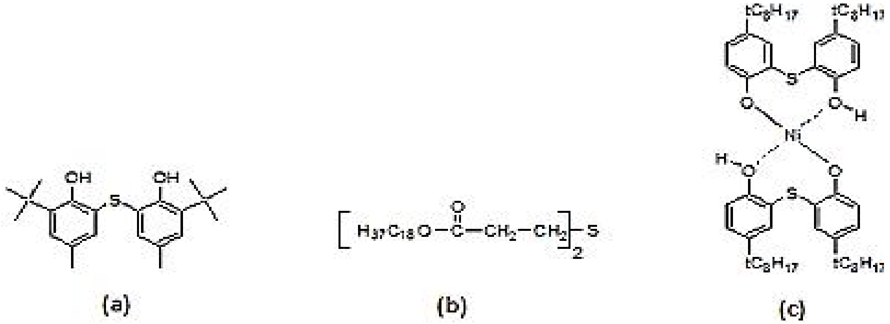
4.1.4 Sulfur compounds as stabilizers and antimicrobials

Organic materials such as polymers may readily react with oxygen (Scwarzenbach *et al.*, 2009; Gugumus, 2009), and also UV/Vis radiation may be detrimental to them by causing the formation of hydrocarbon radicals, which will further cause the decomposition of the polymer (Gugumus, 2009, Gugumus, 1993a). These phenomena are crucial especially in plastics, since even very low concentrations of oxidized/damaged polymer may have a significant impact on its properties. In order to prevent the oxidation and inhibit the radical reactions, additives called antioxidants and light/heat stabilizers are added into the polymer.

Sulfur compounds (mainly organic) have been extensively used for the stabilization of plastic and rubber polymers. As stabilizers, they are used as synergists in combination with hindered phenol antioxidants, or as primary heat stabilizers for PVC. Besides that, there is a wide variety of sulfur containing antimicrobial compounds generally applicable for plastics to prevent the growth of bacteria and fungi.

4.1.4.1 Antioxidants and light stabilizers

There are two main types of sulfur containing antioxidants in the market; primary antioxidants acting as individual compounds, and secondary antioxidants acting as synergists in a combination with the primary antioxidants and thus improving the efficiency of the primary compound. The primary sulfur containing antioxidants are phenolic compounds with one or two sulfur atoms incorporated into their structures, and their key reaction is to form hydroperoxides by H-removal from the phenolic group (Scwarzenbach *et al.*, 2009; Kattas *et al.*, 2000). The secondary type of antioxidants, so called thiosynergists, are different kind of esters of 3,3-thiodipropionic acid, and their role is to act as hydroperoxide decomposers (Schwarzenbach *et al.*, 2009; Kattas *et al.*, 2000). The basic structures of these antioxidants are presented in Figure 16.



(a) (b) (c)

Figure 16. Examples of the structures of (a) phenol type primary antioxidant with thiosubstituent (b) thioproponionic acid derivative type thiosynergist (c) nickel containing stabilizer.

Phenols with thiosubstituents (such as AO-22, AO-23, AO-24, AO-25, AO-26 and AO-42) are widely used in rubbers such as BR, IIR, SBR, EPDM and NBR, and in thermoplastic rubbers (Rodgers *et al.*, 2000; Schwarzenbach *et al.*, 2009). They can also be used in PA-66, and generally in applications requiring higher processing temperatures (Kattas *et al.*, 2000). Secondary thiosynergists are mainly used in a combination with hindered phenol antioxidants to gain an improved stabilizing effect, particularly in filler modified applications for PE, PP, and ABS. Generally speaking, the type and volume of antioxidants used depend on the type of the resin and the application, but usually the concentrations range from 0.05 % to 1.0 % by weight of the polymer. Table 31 presents the final sulfur concentrations in plastics treated with sulfur containing antioxidants.

There are only two sulfur containing light stabilizers: nickel complexes Ni-1 and Ni-3 that contain aromatic rings, long alkyl chains and sulfur bridges in their structures as shown in Figure 16. Their key reaction is to take over the energy absorbed by the chromophores present in the plastic material and dispose of it efficiently in order to prevent degradation (Gugumus, 2009). Because of their heavy metal content, these compounds have largely been replaced by more environmentally friendly and effective hindered amine stabilizers, but they still find some use in a combination with UV light absorbers in LDPE agricultural films because of their antimicrobial nature, and in some PP formulations due to economic reasons (Gugumus, 2009; Kattas *et al.*, 2000; Markarian, 2007). Nickel quenchers are used at concentrations similar to those of antioxidants, about 0.15–0.5 % by weight of the polymer. Final sulfur concentrations in plastics treated with sulfur containing nickel complexes are presented in Table 31.

4.1.4.2 PVC heat stabilizers

Organotin heat stabilizers, a majority of them containing sulfur, are by far the most effective primary heat stabilizers used in PVC. Therefore it is possible to attain sufficient stabilization with lower amounts of stabilizer used compared to e.g. lead stabilizers.Due to this (and also due to the toxicity of lead) tin based heat stabilizers have gained a high level of use particularly in the U.S, where lead based heat stabilizers are used only for wire and cable insulation (Jennings and Starnes, 2005; Dworking, 1989). Organotin stabilizers can be used in both rigid PVC and flexible PVC applications, and due to their transparency, they may also be used in the manufacturing of crystal clear PVC articles (Jennings and Starnes, 2005; Dworkin, 1989; Starnes and Jennings, 2009; Andreas, 1993; Tin Compounds, 1997; Summers, 1997). Typical applications for organotins are in potable pipe and profile extrusion, and some of them (octyl tins) have been approved also for food contact applications. The most typical sulfur containing organotins are mono- and/or dialkyltins with the general formula $RSnX_3$ and R_2SnX_2, where the R-group is methyl, n-butyl or n-octyl and the ligand X is mercaptoester, carboxylate or sulfide (Piver, 1973). Some examples of these comprise dialkyltin sulfides, methyltin mercaptides, dialkyltin bis-isooctylthioglycolates, and complex reverse esters containing sulfur bridges in their structures (Dworking, 1989). Their sulfur content varies according to the type of the stabilizer, but it is usually 5–15 percent by weight of the stabilizer compound. For final sulfur concentration in the plastics see Table 31.

Tribasic lead sulfate, $3PbO \cdot PbSO_4 \cdot H_2O$, used as a heat stabilizer in both rigid and the flexible PVC applications, is one of the most effective and most widely used primary heat stabilizer compounds (Dworkin, 1989). Its biggest drawback is the toxicity of lead; thus lead containing stabilizers will be (or have already been) replaced by less toxic options such as mixed metal stabilizers when the use of lead compounds is not necessary. They still find use in the areas where other stabilizer compounds do not result in an adequate stabilizing effect; applications such as wire and cable insulation, rigid and flexible PVC foam and rigid pipe still use these compounds. The sulfur content of the compound is quite low (around 3 wt-%), thus the sulfur residue does not exceed the value of 1000 mg/kg in the final polymer.

4.1.4.3 Antimicrobials

The use of antimicrobials in plastics is continuously expanding. The primary targets for biocides are polymers such as flexible PVC, PU and polyesters, but also new types of plastic materials are going to be protected by antimicrobial compounds. Approximately two-thirds of the global consumption is used in the construction applications (such as floorings and hygienic surfaces), and other big end-use applications are films, sheets, liners and textiles (Niall, 2001). The majority of antimicrobials contain either sulfur or halogen atoms. Among sulfur containing biocides, the compound most widely used particularly in PVC and PU is zinc pyrithine (ZPT) with the chemical formula $C_{10}H_8N_2O_2S_2Zn$. It is normally added to the plastics as masterbatch with volumes ranging from 0.1 % to 0.5 % by weight of the polymer (Thacker *et al.*, 2007; Ochs, 2009; BIOCIDE Selection Guide - Building Products, 2012). Other suitable antimicrobials with wide applicability in plastics are the derivatives of isothiazolin compounds (BIOCIDE Selection Guide – Plastics & Flooring, 2012) such as benzisothiazolin (BIT), and also the derivatives of thiophthalimides (Fungitrol and PlastiGuard Biocides for Plastics, 2012) such as N-(trichloromethylthio)phthalimide; both are used at concentrations similar to those of ZPT. Since biocides containing arsenic and heavy metals are not used anymore, the market for ZPT and the derivatives of isothiazolins and thiophthalimides will increase in the future (Thacker *et al.*, 2007).

Table 31. Sulfur containing antioxidants, light stabilizers, PVC heat stabilizers and antimicrobials used in plastics (Schwarzenbach *et al.*, 2009; Gugumus, 2009; Gugumus 1993; Jennings and Starnes, 2005; Dworkin, 1989; Starnes and Jennings, 2009; Ochs, 2009; Quintavalla and Vicini, 2002; Cutter *et al.*, 2001; Siragusa *et al.*, 1999).

Name	**Type of the structure**	**Chemical formula**	**Target of use**	**Usage level of compound (%)**	**Sulfur content in plastics (mg/kg)**
AO 22–AO 26, AO 42	Phenolic	$C_{22\text{-}38}H_{30\text{-}58}O_{1\text{-}6}S_{1\text{-}2}$	Rubbers, PA	0.05–0.2	20–300
TS-1–TS-4	Esters of thiopropioninc acid	$C_{30\text{-}42}H_{58\text{-}82}O_4S$	Filler filled polymers, rubbers	0.1–0.6	50–400
Ni-1, Ni-3	Nickel containing benzo compounds	$C_{32\text{-}56}H_{51\text{-}82}O_{2\text{-}4}S_{1\text{-}2}Ni$	LDPE, PP	0.1–0.5	50–350
Organotin stabilizers	Sulfides, mercapto esters, thioglycolates	$RSnX_3$, R_2SnX_2	PVC	0.2–1.5	100–2500
Lead stabilizers	Tribasic lead sulfate	$3PbO{\cdot}PbSO_4{\cdot}H_2O$	PVC	0.5–2.5	70–850
zinc pyriothine	Pyridinethiol-1-oxide zinc salt	$C_{10}H_8N_2O_2S_2Zn$	PU, PVC	0.1–0.5	200–1200
Fungitrol 11, FOLPET	Derivatives of thiophthalimide	$C_9H_4Cl_3NO_2S$	PVC, PU, PE, PP, PS, ABS	0.1–1	100–1000
BIT, OIT, BBIT	Isothiazolin	$C_{7\text{-}11}H_{5\text{-}19}NOS$	PVC, PU, acrylics	0.1–0.5	50–1100
Nisin	Polycyclic peptide	$C_{143}H_{230}N_{42}O_{37}S_7$	PVC, PE, PA	0.05–0.1	30–70

4.1.5 Sulfur compounds as fluorescent whitening agents, blowing agents and anti-static additives

Sulfur containing compounds are also utilized in niche applications, such as brightening the color of plastics, producing a foam structure, and increasing the conductivity of plastics to prevent charge accumulation. Usually the volumes of the additives used are quite low; therefore the sulfur content in the final plastic article does not increase to significant levels.

4.1.5.1 Fluorescent whitening agents

Fluorescent whitening agents (FWAs) have traditionally been used to improve the appearance of finished articles in the paper and textile industries, and as the markets for thermoplastic have grown, the use of FWAs has also expanded into this field (Oertli, 2009). Adding FWAs will improve or mask the initial (often slightly yellowish) color of the plastics (Oertli, 2009), and with them it is possible to produce bright white end use articles. They will also emphasize and brighten the shades of colored and black plastic articles.

Only a few chemical classes of FWAs possess the properties required for plastics and fibers. Two of these, benzoxazole FWAs and biphenyl FWAs may contain sulfur (Oertli, 2009; Christie, 1994). The compound with the trade names Uvitex and Benetex is a benzoxazole FWA with the chemical formula $C_{26}H_{26}N_2O_2S$ (CIBA Uvitex OB Fluorescent Whitening Agent, 2012; Benetex OB Plus – Optical Brightener, 2010). Distyryl biphenyl (DSBP) with the chemical formula $C_{28}H_{20}Na_2O_6S_2$ and diaminostilbenes (DAS-1/2) with the general chemical formula $C_{40\text{-}44}H_{38\text{-}48}N_{12}Na_{2\text{-}4}O_{8\text{-}16}S_{2\text{-}4}$ are examples of biphenyl FWAs (Kramer *et al.*, 1996; Fluorescent Brightener FWA-1, 2005; Fluorescent Brightener FWA-5, 2003). The concentrations of FWAs used in the plastics are quite low ranging between 50–500 mg/kg (Oertli, 2009; Benetex OB Plus – Optical Brightener, 2010). Higher volumes (up to 1000 mg/kg) are required for recycled thermoplastics. Due to the low sulfur content of FWA compounds and their low usage levels, the concentration of sulfur in the final polymer is well below 100 mg/kg.

4.1.5.2 Blowing agents

The blowing agents (BA) used in foam polymers are divided into chemical and physical blowing agents according to their mode of liberating the blowing gas (Hurnik, 2009). Physical blowing agents, which comprise over 90 % of the BA market in plastics (Kattas *et al.*, 2000), are usually volatile liquids or compressed gases that change state during processing, and they do not contain sulfur in their structures. Chemical blowing agents are products that undergo chemical reactions (such as decomposition) during the processing at elevated temperatures releasing at least one gaseous component (Hurnik, 2009). Chemical BAs may be divided into sub-categories according to their mode of action, and sulfur containing BAs are found in a sub-class of compounds that liberate gaseous components in consequence of an irreversible thermal decomposition of the structure of BA compound. Examples of compounds belonging to this class are e.g. hydrazine derivatives such as p-toluenesulfonylhydrazide (TSH), which is mainly used in rubbers, and oxibis(benzenesulfonylhydrazide) (OBSH) (Genitron OB, 2005; Actafoam OT Chemical Foaming Agent, 2007), which is used in LDPE and PVC foamed insulations and rubbers due to its crosslinking ability (Kattas *et al.*, 2000; Hurnik, 2009). Besides hydrazide derivatives, also semicarbazides such as p-toluenesulfonyl semicarbazide (TSSC) which is mainly used in the applications requiring higher temperatures (PP, ABS, HDPE, PVC-U, HIPS, PA) contain sulfur (Hurnik, 2009). The amounts of blowing agents needed to achieve the required foaming level start from 0.1 wt-% and can be more than 5 wt-% in the foamed elastomers (Hurnik, 2009; Genitron OB, 2005; Genitron EP-range, 2005).

4.1.5.3 Antistatic additives

Due to the inherently insulative nature of plastics they cannot readily dissipate a static charge (Kattas *et al.*, 2000). Antistatic additives help with this by preventing the buildup of static electrical charge resulting from the transfer of electrons to the surface (Kattas *et al.*, 2000; Wylin, 2009). Antistatic additives may be external (plastics are coated with the additive by spraying), or internal (additives are incorporated into the polymer matrix), which is the dominant technique. Internal additives act via two mechanisms: (1) They can act as lubricants, which will decrease friction and further static charge generation in plastics, or (2) The static charge in plastics is dissipated by forming a conductive pathway from the inner part of the polymer to the surface (Wylin, 2009).

Non-ionic antistatic additives such as fatty acid esters, ethoxylated alkylamines and diethanolamines are the most widely used antistatic class. These compounds are sulfur-free, but sulfur containing antistatic compounds, alkylsulfonates, may be utilized in more polar polymers such as PVC and styrenics. The usage levels depend on the type of the polymer, and they are usually in the range of 0.5–1.5 wt-% for PVC, 1–2 wt-% for PS/HIPS and 1.5–3 wt-% for ABS/SAN (Wylin, 2009).

The most common sulfur containing FWAs, blowing agents and anti-static additives are introduced in Table 32. Besides the structures of compounds, also the usage levels and the sulfur content in the final polymer are presented.

Table 32. Sulfur containing FWAs, blowing agents and anti-static additives (CIBA Uvitex OB Fluorescent Whitening Agent, 2012; Mujkanovic *et al.*, 2009; Kleinholz *et al.*, 1993; Novotny *et al.*, 1996; Buxbaum and Pfaff, 2005; Christensen, 2003; Eaves, 2004; Pokasermsong and Praserthdam, 2009; Goodall *et al.*, 1983; Kashiwa, 2004; Woo *et al.*, 1993; Kablitz and Strametz, 1984; Atakul *et al.*, 2005).

Name	**Application**	**Chemical formula**	**Target of use**	**Usage level of compound (wt-%)**	**Sulfur content in polymer (mg/kg)**
Benzoxazole derivatives	FWA	$C_{26}H_{26}N_2O_2S$	Generally applicable	0.005–0.05	5–40
Biphenyl derivatives	FWA	$C_{28}H_{20}Na_2O_6S_2$	Generally applicable	0.005–0.05	6–60
Hydrazide derivatives	Blowing agent	$C_{7\text{-}12}H_{10\text{-}14}N_2O_2S_{1\text{-}2}$	Rubbers, PVC, LDPE	0.1–5	90–6500
Semicarbazide derivatives	Blowing agent	$C_8H_{11}N_3O_3S$	HDPE, PP, ABS, HIPS	0.1–5	70–5000
Alkyl-sulfonates	Antistatic additives	$CH_3(CH_2)_nSO_3Na\cdot mH_2O$	PVC, HIPS, ABS, SAN	0.5–3	300-4500

4.2 Calcium compounds in plastics and rubbers

Calcium compounds are mostly utilized as fillers and reinforcements in plastics and rubbers at very high loadings. Due to that the elemental calcium content in polymers may be several percent by weight of the application. Besides fillers, organic calcium compounds may be used as heat stabilizers in PVC and generally applicable pigments.

4.2.1 Calcium containing heat stabilizers in PVC

Organic calcium compounds are used in several different heat stabilizing systems for PVC. They are mostly used in combination with organic zinc compounds and inorganic hydrotalcites/zeolites in order to gain a synergist effect (Jennings and Starnes, 2005; Thacker *et al.*, 2007). In the stabilization mechanism, zinc compounds act as primary stabilizers replacing reactive allylic chlorides in PVC structure. The formed zinc chloride can be re-converted to initial organic salt form by organic calcium compounds (Starnes and Jennings, 2009). Besides regenerating primary zinc stabilizers, organic calcium compounds as well as inorganic hydrotalcites and zeolites act as secondary stabilizer compounds neutralizing HCl generated after the decomposition of some active PVC site (Folarin and Sadiku, 2011; Bacalogulu *et al., 2001*). The most widely used calcium containing compound is calcium stearate (CaSt), which is mostly used in combination with zinc compounds such as zinc stearate and zinc neodecanoate. Usually the calcium content in Ca/Zn stabilizer mixtures is in the range of 0.5–1.5 wt-% (Jennings and

Starnes, 2005; Starnes and Jennings, 2009; Thacker *et al.*, 2007). The usage level of these stabilizers varies according to the application, but is typically in the range of 1–2.5 wt-% in PVC (Starnes and Jennings, 2009; Andreas, 1993; Watanabe *et al.*, 2002; Tsuji and Sato, 2000), thus the elemental calcium content in PVC (resulting from stabilizer compounds) is not higher than 500 mg/kg.

4.2.2 Calcium containing fillers, reinforcements and pigments

When inorganic fillers or reinforcements are incorporated in the plastic and rubber resins in order to gain both economical and strengthening effect, the loadings of these additives are typically very high, up to several tens of percent of the plastic polymer. Since these materials typically consist of several different metal compounds, the elemental metal concentrations may also be very high.

When calcium containing fillers and reinforcements are considered, calcium carbonate $CaCO_3$ is in its own class regarding both its usage levels and applicability in both plastic and rubber polymers (Evans and Huber, 2001; Hohenberger, 2009; Schlumpf, 1993; Skelhorn, 1997; Mujkanovic *et al.*, 2009). Due to its good dispersibility in different type of polymer structures (especially PVC, but also PE, PP, PU, and rubbers), it is the most widely used inorganic compound in plastics. For more expensive engineering plastics (such as PA, PET/PBT, PC and ABS) fibrous or other more advanced fillers are preferred over $CaCO_3$. When $CaCO_3$ is used as filler, its use both improves elastic modulus/impact strength in the product and lowers the overall cost of the product due to the economical price of $CaCO_3$. Calcium carbonate is commonly used at high loadings, and thus it can be considered also as flame retardant compound due to the dilution of organic polymer matrix. Typical loading levels start from 1 wt-%, and can be as high as several tens of percent by weight of the final product. Thus the elemental calcium content in the product may amount up to 15 wt-%. Other widely used calcium containing fillers are dolomite, the combination of magnesium and calcium carbonate, which is used similarly to calcium carbonate (Hohenberger, 2009), and wollastonite $CaSiO_3$, which is used particularly in PP, PA and PU automotive applications such as bumpers and front panels (Hohenberger, 2009; Schlumpf, 1993). Calcium sulfate $CaSO_4$ is occasionally used as filler in PVC, polyesters and plastic foam applications, but its use is restricted mainly due to its sensitivity against moisture; the presence of water will lead to a difficult-to-disperse filler product (Robinson *et al.*, 2007; Hohenberger, 2009).

Glass fibers, which are used to reinforce and gain impact strength in polymers, can be used in every individual type of plastics. However, they are mostly used in polymers where their use improves the properties of polymers most; therefore glass fibers find use particularly in PP, PA, PC, PET/PBT, ABS and SAN (Kleinholz *et al.*, 1993). There are several different classes of glass fibers on the market, but types E and S, which both contain calcium, are mostly utilized in plastics. The loadings for glass fibers in polymers may be as high as 30 wt-%, and thus the elemental calcium content may also be very high, up to several percent by weight of the product.

Calcium can occasionally be found in pigments used for yellow and red coloration of plastics. Calcium salts of monoazo dyes, such as Pigment Yellow 62, 97, 168 and 183, and Pigment Red 48, 52, 57 and 247 are the most abundant in plastics, particularly in PE, PP, PS and PVC (Scherrer and Sykes, 2009; Beebe, 1993; Lewis, 2005). The use of calcium containing pigments do not result with high calcium content in final plastic articles; typically the elemental calcium content does not exceed 500 mg/kg by weight of the product.

Table 33. Calcium compounds in plastics and rubbers.

Compound/ material	**Chemical formula**	**Application**	**Target of use**	**Usage level of compound (%)**	**Calcium content in product (mg/kg)**
Calcium stearate	$Ca(C_{17}H_{36}COO)_2$	Heat stabilizer	PVC	1.0–2.5	50–500
Calcium carbonate	$CaCO_3$	Filler	PE, PP, PVC, PU, rubbers	2.5–30	10000–120 000
Calcium sulfate	CaSO4	Filler	PVC, PET/PBT, PU	5–30	10000–90 000
Glass fiber E	$SiO_2/CaO/MgO/Al_2O_3/B_2O_3$	Impact modifier	PP, PA, PET, PBT, PC, PS, ABS	5-30	10000–50 000
Wollastonite	$CaSiO_3$	Filler	PP, PA, PU	10–30	30000–100 000
Pigment Yellow 62, 168, 183 and 191	$C_{17\text{-}34}H_{13\text{-}30}CaCl_{0\text{-}1}N_{4\text{-}8}O_{7\text{-}14}S_2$	Pigment	PE, PP, PVC, PS	0.01–0.5	10–400
Pigment Red 48, 52 and 57	$C_{18}H_{11\text{-}12}CaCl_{0\text{-}1}N_2O_6S$	Pigment	PE, PP, PVC, PS	0.01–0.5	10–500
Pigment Re 247	$C_{64}H_{50}CaN_8O_{14}S_2$	Pigment	PE, PP, PVC, PS	0.01–0.5	5–200

4.3 Barium compounds in plastics and rubbers

The use of barium compounds in plastics has a long history. Fatty acid salts of barium can be used as heat stabilizers in PVC, and other organic barium compounds as generally suitable pigments. Inorganic barium compounds such as barium sulfate can be utilized as both filler and pigment.

4.3.1 Barium heat stabilizers in PVC

Barium has been used in mixed metal stabilizers in various forms and compounds. Nowadays the most widely used barium containing stabilizers are Ba/Zn stabilizers, which can exist in both solid and liquid forms. Solid barium compounds such as barium stearate, and liquid compounds such as barium nonylphenate and barium octoate, are convenient to use (Jennings and Starnes, 2005; Starnes and Jennings, 2009; Thacker *et al.*, 2007). Organic barium compounds have also been utilized in liquid/solid Ba/Cd mixed metal systems, where barium compounds such as barium stearate and barium laurate (powder stabilizer) and barium nonylphenate (liquid) are commonly used (Jennings and Starnes, 2005). The proportion of barium compounds in stabilizer systems is usually about 35 wt-% and 25 wt-% in solid and liquid Ba/Zn stabilizer compositions, respectively, and about 60 wt-% and 25 wt-% in Ba/Cd solid and liquid stabilizer systems, respectively (Jennings and Starnes, 2005). The use of Ba/Cd heat stabilizers has declined due to the toxicity of cadmium, and the replacement of these stabilizers with less toxic Ba/Zn stabilizers will also continue in the future wherever possible. The usage level of the stabilizer depends on the application and other additives used in the PVC, but it is usually in the range of 0.5–2.5 % by weight of the PVC resin. The typical barium based heat stabilizer systems, their usage levels and barium content in PVC are shown in Table 34.

Table 34. Barium heat stabilizers; the usage levels and barium content in PVC.

Stabilizer type	Ba/Zn solid	Ba/Zn liquid	Ba/Cd solid	Ba/Cd liquid
Typical barium compound	Barium stearate	Barium nonylphenate	Barium stearate/ barium laurate	Barium nonylphenate
Typical usage level of compound (%)	0.7–2.0	0.7–2.0	0.5–2.5	0.8–2.5
Ba content in PVC (mg/kg)	500–1500	500–1300	600–3200	500–1600

4.3.2 Barium compounds as pigments and fillers

Barium containing inorganic and organic pigments are used for white and red shades of color. The most widely used inorganic pigments are white lithopone (the mixture of ZnS and $BaSO_4$), which can be utilized as a pigment and reinforcing agent in plastics (Novotny *et al.*, 1996; Buxbaum and Pfaff, 2005) (mostly in PP and PU), and $BaSO_4$, which can be used both as a filler and a pigment in plastics (see section 2.3.1) and also in rubbers, when higher density of rubber article (such as stoppers and seals) is wanted (Evans and Huber, 2001). The most important organic pigments are barium salts of monoazo (i.e. structure containing one nitrogen group) dyes such as Pigment Red 53:1 and Pigment Red 48:1, which are widely utilized in PVC, LDPE and PS (Scherrer and Sykes, 2009; Beebe, 1993; Christensen, 2003). The role of inorganic white pigments such as lithopone and $BaSO_4$ has decreased due to the dominance of TiO_2 in the white pigment market, but they still find some use, particularly in PP planned for outdoor applications, PVC (Robinson *et al.*, 2007) and PU (Eaves, 2004) as a filler, and generally as diffusing pigments for light fixtures (Beebe, 1993; Novotny *et al.*, 1996). Table 35 presents the most typical barium based pigments, their applications and usage levels and also barium content in plastic resin.

Table 35. Typical inorganic and organic barium pigments, their applications and barium content in polymer resin.

Pigment type	Lithopone	Barium sulfate	Pigment Red 53:1	Pigment Red 48:1	Pigment yellow 61:1
Molecular formula of pigment	ZnS + $BaSO_4$	$BaSO_4$	$2(C_{17}H_{12}ClN_2O_4S)\cdot Ba$	$C_{18}H_{11}BaClN_2O_6S$	$C_{32}H_{26}BaN_8O_{14}S_2$
Ba content in compound (%)	41–42	58–59	15–16	24–25	14–15
Application	PVC, PE,PP, PS, PET, PA, PU	PVC, PE,PP, PS, PET, PA, PU, rubbers	PVC, LDPE, PS	PVC, LDPE, PS	PVC, LDPE, PS
Typical usage level (%)	0.1–1.0	0.5–30.0	0.05–0.5	0.05–0.5	0.05–0.5
Ba content in polymer (mg/kg)	400–4000	3000–175000	80–800	100–1300	70–700

4.4 Magnesium compounds in plastics and rubbers

4.4.1 Magnesium compounds as catalysts

Magnesium compounds, particularly magnesium chloride $MgCl_2$, are nowadays very important support materials in the polymerization of polyolefins such as PE and PP (Pokasermsong and Praserthdam, 2009; Goodall *et al.*, 1983); more than 90 % of PP and about half of PE is produced by these catalysts (Kashiwa,2004). In the catalyst mixture, the primary catalyst such as $TiCl_4$ is bound to high surface area $MgCl_2$ compound in order to stabilize the active centre of catalyst. Due to the higher activation of $MgCl_2$ supported $TiCl_4$ catalysts, the catalyst system is nowadays so effective that the purification of polymer from catalyst compounds is not needed any more (Kashiwa, 2004). However, magnesium may still be found in polymers as a catalyst residue, but typically its concentration is well below 100 mg/kg in the polymer (Woo *et al.*, 1993; Kablitz and Strametz; 1984).

4.4.2 Magnesium compounds as co-stabilizers and flame retardants

Hydrotalcite, which is a combination of magnesium oxide, aluminum oxide, water and carbonate, is nowadays used as co-stabilizer compound with primary lead/tin/mixed metal stabilizer compounds in PVC (Starnes and Jennings, 2009; Thacker *et al.*, 2007; Atakul *et al.*, 2005; Misra and Perrotta, 1992). The function of hydrotalcite is to act as acid scavenger/neutralizer, thus this material does not contribute directly to the stabilization. When they are used in combination with e.g. tin, Ca/Zn and Ba/Zn systems, a synergist effect is generated, and therefore they can reduce the amount of primary metal stabilizer used even to one half (Misra and Perrotta, 1992). Usually the proportion of hydrotalcite in the stabilizer mixture varies between 30–65 wt-%, and the total amount of stabilizer used is in the range of 0.5–2 % by weight of the PVC (Starnes and Jennings, 2009; Thacker *et al.*, 2007).

Magnesium hydroxide (MDH) with chemical formula $Mg(OH)_2$, is a flame retardant compound used particularly in cables and PP and PA applications (Hohenberger, 2009; Ranken, 2009; Hornsby, 2007; Beard, 2007; Coaker 2003). The flame retardant mechanism is based on the release of water by decomposition of $Mg(OH)_2$ which consequently will lead to the dilution and cooling of the flame zone. MDH has a higher decomposition temperature than aluminum trihydroxide (ATH), thus its use is preferred in plastic applications used at more challenging environments, such as cables and some electronic devices. Due to the flame retardant mechanism, very high concentrations (20–60 %) of MDH are required to impart an efficient flame retardant effect (Hohenberger, 2009). Therefore the elemental magnesium content in polymer may amount to 10 wt-% or even more.

4.4.3 Magnesium based fillers and reinforcements in plastics and rubbers

There are several inorganic magnesium containing fillers on the market, but the materials finding most use in plastics and rubbers are talc, dolomite, and glass fiber type E. The loadings of these additives can again be very high, up to several tens of percent by weight of the plastic polymer, which will lead to high elemental magnesium content in final products, even more than 10 wt-% in the final product.

The use of talc in polymers possesses several beneficial effects; particularly a good reinforcing and a low wear effect (Hohenberger, 2009; Schlumpf; 1993). Its basic structure is hydrated magnesium silicate in a platelet form, which also contains small proportions of oxides of aluminum, calcium and iron. The major use for talc is among PP applications in automotive industry, and its use in other commodity plastics such as PE, PVC and PS is relatively low. In rubbers talc is mostly used in tire innerliners, automotive houses and barrier films, typically in combination with other mineral fillers (Rodgers *et al.*, 2000; Evans and Huber, 2001). Dolomite, the combination of calcium and magnesium carbonate as mentioned already in section 4.2.2, is used particularly in PVC with similar loadings than calcium carbonate. Glass fibers are mostly used in polymers where their use improves the properties of polymers most, particularly in PP, PA, PC, PET/PBT, ABS and SAN.

Table 36. Typical magnesium containing compounds used in plastics and rubbers.

Name	Hydrotalcite	Magnesium hydroxide	Dolomite	Talc	Glass fiber E/S
Molecular formula	$Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$	$Mg(OH)_2$	$MgCO_3/CaCO_3$	$Mg_3Si_4O_{10}(OH)_2$	$SiO_2/CaO/MgO/Al_2O_3/B_2O_3$
Application	Stabilizer/acid scavenger	Flame retardant	Filler	Filler	Impact modifier
Target of use	PVC	PP, PA, cables	PE, PP, PVC, PS, PET/PBT, PA, PC, rubbers	PP, (PVC, PA, PBT, PE), rubbers	PP, PA, PET, PBT, PC, PS, ABS
Typical usage level (wt-%)	0.5–1.5	20–60	2.5–30	2.5–30	2.5–30
Mg content in polymer (mg/kg)	200–1600	80000–250000	3000–40000	3000–60000	100–18000

5. Conclusions

In this paper, metals and their compounds most widely used in plastics and rubbers have been reviewed. Each metal has been separately presented, beginning with the evaluation of the chemical formula of the metal containing additive compounds, going through their typical targets of use, and estimating the concentration range of the element in the final polymer. The plastics include PVC, LDPE/LLDPE, HDPE, PP, PET/PBT, PS and its derivatives, ABS, PA, PC, PU, and the most important rubber polymers. The most important metals in plastics include Pb, Al, Sb, Ti, Sn, Zn, Fe, Ni, Cu, Cd, Cr and also Co, Mn, Ag and Zr in some particular cases. The purpose of this paper was to enlighten the role of plastics as a source of metals in waste-to-energy systems as currently this role within the ash forming chemistry context has been completely omitted in the literature.

Table 37 introduces the metals most widely found in plastics along with their typical concentration ranges. For the minimum concentration value of the metal, it is assumed that only one additive compound containing this metal is used in the plastic. For the maximum concentration value of the metal, all additive compounds containing this metal, which in theory could be utilized in one particular plastic type, are present in the plastic. Therefore the information presented in the table has to be evaluated paying close attention to the various additive systems. In spite of the challenges in the evaluation of metal concentrations, the collected information clearly proves the wide-ranging use of metals in the plastics for various functions.

The compounds of Pb, Al, Sb, Ti, Sn, Zn and Fe are mainly used as stabilizers, flame retardants, fillers and pigments, and their element concentration ranges from several hundreds of mg/kg to as high as several thousands of mg/kg in the polymer. In particular the large amounts of Pb compounds used in PVC have to be taken into account when plastics are combusted alone or found mixed in wastes. Besides Pb, also the versatility of Ti, Sn, Al and Zn and Sb compounds is significant; in these cases metal residue can originate from several different sources. When comparing the metal concentrations of different plastic types, PVC is clearly in its own class; its total metal concentration can be up to several weight percent or even more, depending on the application (outdoor/indoor/flame retarded) and the heat stabilizing system (Pb/Sn/Ba/Zn/Cd) used. The compounds of Ni, Cu, Cd, Co, Cr and Mn, which are mainly used as pigments and catalysts, comprise the second category where elemental metal concentrations range from 10 mg/kg up to

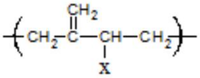
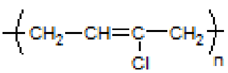
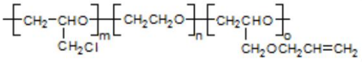
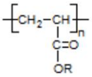
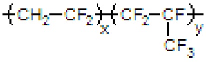
1000 mg/kg in the polymer. The last category involves the compounds of Ag and Zr, whose elemental concentrations in plastic polymers are lower than 250 mg/kg.

Table 37. Trace metal content in different type of plastics (mg/kg).

Metals in plastics	PVC	LDPE	LLDPE	HDPE	PP	PET	PBT	PS	ABS	PA	PC	PU
Pb (mg/kg)	300–35000	300–3000	300–3000	300–3000	300–3000	–	–	–	–	–	–	300–3000
Al (mg/kg)	80–200000	80–200000	80–5000	80–200000	150–37000	150–32000	150–32000	80–200000	150–32000	150–37000	150–32000	150–200000
Sb (mg/kg)	50–42000	50–42000	50–42000	50–42000	50–42000	150–42000	50–42000	50–42000	50–42000	50–42000	50–42000	50–42000
Ti (mg/kg)	100–30000	100–30000	100–30000	100–30000	100–30000	100–30000	110–30000	100–30000	100–30000	100–30000	100–30000	100–30000
Sn (mg/kg)	200–19000	–	–	–	2000–15000	2000–15000	2000–16000	–	–	2000–15000	–	100–900
Zn (mg/kg)	50–13000	50–3000	50–4000	50–4000	50–12000	50–12000	50–12000	50–3000	50–3000	300–12000	50–3000	50–5000
Fe (mg/kg)	200–4000	200–4000	200–4000	200–4000	200–7000	200–7000	200–7000	200–4000	200–4000	200–7000	200–4000	200–4000
Ni (mg/kg)	20–1200	120–1700	20–1200	20–1200	20–1700	20–1200	20–1200	20–1200	20–1200	20–1200	20–1200	20–1200
Cu (mg/kg)	30–600	30–600	30–600	30–600	30–600	30–600	30–600	30–600	30–600	30–600	30–600	30–600
Cd (mg/kg)	300–4500	300–3000	300–3000	300–3000	300–3000	–	–	300–000	300–3000	300–3000	300–3000	300–3000
Cr (mg/kg)	10–3400	10–3400	10–3400	10–3400	10–3400	10–3400	10–3400	10–3400	10–3400	10–3400	10–3400	10–3400
Ag (mg/kg)	1–50	1–50	1–50	1–50	1–50	1–50	1–50	1–50	1–50	1–50	1–50	1–50
Zr(mg/kg)	10–250	10–250	10–250	10–250	10–250	10–250	10–250	10–250	10–250	10–250	10–250	10–250
Co (mg/kg)	50–1500	50–1500	50–1500	50–1500	50–1500	50–1600	50–1600	50–1500	50–1500	50–1500	50–1500	50–1500
Mn (mg/kg)	20–1100	20–600	20–600	20–600	20–600	20–650	20–600	20–600	20–600	20–600	20–600	20–600

The concentrations of halogens in plastics and rubbers vary greatly according to the application. If the element is part of the repeating structure of the polymer, it is clear that the concentration of the element is high, usually several tens of percent by weight of the pure polymer. In the table 38, the most common chlorine, bromine and fluorine containing polymers are introduced in detail, beginning with the presentation of their repeating structure and evaluating the halogen contents of the polymers. In order to compare the usage levels of different polymers (and thus comprehend the major differences between the productions of different types of plastics/rubbers), the annual consumption of these polymers is also evaluated.

Table 38. Halogen containing polymers.

Name	**Repeating structure**	**Halogen content in the pure polymer (wt-%)**	**Annual consumption (10^3 tons)**
Polyvinyl chloride	$-(CH_2CHCl)-$	56–57	33500
Polyvinylidene chloride	$-(CH_2CCl_2)-$	~70	200
Halobutyl Rubber	 $-(CH_2-C(=CH_2)-CH(X)-CH_2)-$	0.5–2.5	>200
Polychloroprene	 $-(CH_2-CH=C(Cl)-CH_2)_n-$	~40	>200
Polyethers	 $-[CH_2-CH(CH_2Cl)O]_m-[CH_2CH_2O]_n-[CH_2CH(CH_2OCH_2CH=CH_2)O]_o-$	15–38	>20
Acrylic elastomers	 $-[CH_2-CH(C(=O)OR)]_n-$	0.5–2.0	>25
Polytetrafluoro-ethylene	$-(CF_2-CF_2)_n-$	76	90
Polyvinylidene fluoride	$-(CH_2-CF_2)_n-$	59–60	>10
Perfluorinated ethylene-propylene copolymers	$-CF_2-CF_2-/-CF_2-CF(CF_3)-$	75–76	>5
VDF–HFP fluoroelastomer	 $-(CH_2-CF_2)_x-(CF_2-CF(CF_3))_y-$	66–70	5
Fluorosilicones		30–40	3

Excluding halogen containing polymers and considering only chlorine, bromine and fluorine containing additive compounds, the comparison of the concentrations of each element in plastics is more convenient to visualize. Generally, chlorine containing compounds have the largest market share and they are used in numerous applications. Bromine compounds are used in niche applications, but in great volumes; flame retardants based on bromine are the dominant halogenated FR species in the market. Even though fluorine containing polymers are of great importance particularly in challenging environments, the variety of fluorine containing additive compounds is not so broad. According to the literature majority of halogen compounds in plastics are in an organic form; thus, due to the lower decomposition temperatures of organic species, both the formation of toxic halides and their reaction with heavy metals/organic substances present in MSW is very likely to occur during combustion.

The concentration ranges for chlorine, bromine and fluorine in plastics and rubbers are estimated in Table 39. The maximum and minimum contamination values of each element are evaluated by using the data introduced in the previous chapters. When the minimum concentration value is estimated, it is assumed that only one compound (with minimum loading level) has been used. Only rubbers with the largest global consumption are considered; in addition only stabilizers and flame retardants are involved in the rubber formulations.

Table 39. Total possible halogen concentrations in plastics and rubbers. *Only stabilizers and flame retardants are considered.

	Cl (mg/kg)	**Br (mg/kg)**	**F (mg/kg)**
PVC	–	60–3000	10–2000
LDPE/LLDPE	10–8000	60–205000	10–3000
HDPE	70–8000	60–180000	10–3000
PP	70–8000	60–210000	10–2000
PS	10–129000	60–113000	0–96000
PET/PBT	10–122000	60–105000	0–1000
ABS	10–29000	60–180000	0–1000
PA	10–117000	60–131000	0–1000
PC	10–5000	60–56000	0–1000
PU	10–227000	60–143000	0–96000
NR*	10–103000	0–100000	–
SBR*	10–103000	0–100000	–
BR*	10–103000	0–100000	–
EPDM*	10–103000	0–100000	–
IIR/HIIR*	10–103000	0–100000	–

One of the largest is the use of elemental sulfur and organic sulfur compounds is in rubber crosslinking. Vulcanizing agents such as elemental sulfur and accelerators for the vulcanization procedure are used in concentrations ranging from 0.2 wt-% to 2.0 wt-%, therefore the sulfur content in vulcanized rubber usually varies between 5000–15 000 mg/kg based on the weight of the rubber formulation. Inorganic pigments and fillers such as barium sulfate, sulfides of cadmium and zinc, and mixed metal pigments such as a combination of lead chromate and sulfate may be used in commodity plastics. The variety of organic sulfur pigments is broader: there are several pigments for yellow, red and orange coloration. Considering the usage levels of pigments, one can notice that the sulfur contamination caused by pigmentation is not high; typically it is in the range of 10–600 mg/kg for organic pigments and between 50–1000 mg/kg for inorganic ones. Besides pigments, sulfur compounds are widely used as antioxidants and light stabilizers, as well as antimicrobials in plastics. Phenolic type antioxidants and thiosynergists are used in elastomers and plastics requiring higher processing temperatures. Sulfur containing light stabilizers find use in LDPE films and in some PP formulations. Regarding the low loadings of stabilizer compounds, the sulfur content in plastics does not exceed the concentration limit of 500 mg/kg. In contrast to these, the use of heat stabilizers in PVC may result in higher sulfur contents: between 100–2500 mg/kg. The most important sulfur containing antimicrobial compounds are mostly used in PVC and PU, but may also be used in polyolefins and styrenics. The sulfur content in antimicrobial treated plastics is typically in the range of 100–1000 mg/kg. Sulfur compounds utilized as fluorescent whitening agents, blowing agents and antistatic additives are present in low volumes, sulfur content in treated polymers can be high, in the range of 100–6000 mg/kg.

The use of calcium in plastics and rubbers is very significant. The highest concentrations of calcium in polymers are obtained when calcium compounds, mainly calcium carbonate, are used as fillers in polymers. In this case the elemental calcium content in final products may be as high as 15 wt-% of the polymer. Calcium compounds are also utilized as stabilizers in PVC and widely applicable pigments; however when used for these purposes the elemental Ca content in products is not higher than 1000 mg/kg.

The targets of uses for barium compounds are very similar to those of calcium: barium compounds are mainly used as fillers, pigments and stabilizers in plastics. The most typical filler is barium sulfate, finding use especially in PP outdoor applications. Same compound is also used as white pigment, in this case the usage level is naturally lower. There are also some organic red and violet barium containing pigments, which are mostly used in PE, PP, PVC and PS. Barium containing organic stabilizer compounds, used typically in a combination with organic zinc salts, are still widely used in the stabilization of PVC.

Magnesium compounds are not that widely used in plastics and rubbers, but again there are some fillers and co-stabilizers which contain a significant proportion of magnesium. The most important filler is talc used mainly in PP applications among automotive industry. Other important compounds are magnesium hydroxide used as flame retardant additive in PVC, PP and PA, and hydrotalcite, which is a co-stabilizer compound used in the stabilization of PVC.

The concentration ranges for sulfur, calcium, barium and magnesium in plastics and rubbers are presented in detail in Table 40. The maximum and minimum contamination values of each element are evaluated by using the data introduced in this paper. When the minimum concentration value is estimated, it is assumed that only one compound (with minimum loading level) has been used. Only rubbers with the largest global consumption are considered.

Table 40. Total possible sulfur, calcium, barium and magnesium concentrations in plastics and rubbers.

	S (mg/kg)	**Ca (mg/kg)**	**Ba (mg/kg)**	**Mg (mg/kg)**
PVC	10–16000	100–200000	100–7000	250–250000
LDPE/ LLDPE	10–8000	10–160000	100–4000	10–40000
HDPE	10–7000	10–200000	100–4000	10–40000
PP	10–9500	10–200000	100–175000	3000–250000
PS	10–11000	10–55000	100–4000	3000–18000
PET/PBT	10–10000	10–55000	100–4000	3000–18000
ABS	10–11000	10–55000	–	3000–18000
PA	10–2000	10–55000	100–4000	3000–250000
PC	10–2000	10–55000	–	3000–18000
PU	10–9000	10000–200000	100–175000	10–40000
NR	10000-37000	10000–200000	30000–175000	3000–40000
SBR	9000–25000	10000–200000	30000–175000	3000–40000
BR	6000–32000	10000–200000	30000–175000	3000–40000
EPDM	6000–19000	10000–200000	30000–175000	3000–40000
IIR/HIIR	5000–20000	10000–200000	30000–175000	3000–40000

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Author(s)	Matti Ranta-Korpi, Pasi Vainikka, Jukka Konttinen, Antti Saarimaa & Milena Rodriguez
Abstract	Metals, alkali metals and halogens found in solid fuels cause various operational problems in boilers and furnaces: emissions, ash melting, ash deposition and corrosion. The role of ash-forming elements found in plastics have received little attention in the literature. All commercial plastics and rubbers, particularly polyvinyl chloride (PVC), polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polystyrene (PS) and polyurethane (PU) contain additives serving various functions. These additives may be utilized as catalysts, curing agents for rubbers, stabilizers, fillers, pigments and flame retardants. In many cases these compounds contain metal, halogen, sulfur and alkaline earth metal (i.e. magnesium, calcium and barium) atoms bonded to the structures of additive compounds. The usage levels of the additive compounds may be several percent of the weight of the polymer, leading to high elemental concentrations of metal, halogen, sulfur and alkaline earth metal. In this review paper, metals, halogens, sulfur and earth alkaline metal containing polymer additives and polymers most widely used are introduced separately. Starting from the evaluation of the chemical formula of the additive compound, going through its typical targets of use, and also estimating the concentration range of the elemental sulfur/metal/halogen present in the final polymer. The element concentrations of metal, halogen, sulfur and alkaline earth metal compounds vary significantly, ranging from several hundreds of mg/kg units up to several thousands of mg/kg in the polymer, depending on the application.
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Nimeke	**Tuhkaa muodostavat alkuaineet muoveissa ja kumeissa**
Tekijä(t)	Matti Ranta-Korpi, Pasi Vainikka, Jukka Konttinen, Antti Saarimaa, Milena Rodriguez
Tiivistelmä	Kiinteästä polttoaineesta löytyvät metallit, maa-alkalimetallit ja halogeenit, aiheuttavat kattiloissa ja uuneissa erilaisia ongelmia, kuten päästöjä, tuhkanmuodostusta ja syöpymistä. Tuhkaa muodostavien aineiden merkitys muoveissa on saanut vähän huomiota kirjallisuudessa. Kaikki kaupalliset muovit ja kumit, erityisesti polyvinyyli kloridi (PVC), polyetyleeni (PE), polypropyleeni (PP), polyetyleeni tereflaatti (PET), polybutyleeni tereflaatti (PBT), polystyreeni (PS) ja polyuretaani (PU) sisältävät lisäaineita, joiden tarkoituksena on toimia katalyyttinä, kumien kovettimina, stabilisaattorina, täyttöaineena, pigmenttinä tai palonsuoja-aineena. Monessa tapauksessa nämä lisäaineet sisältävät metalleja, halogeeneja, rikkiä ja maa-alkalimetalleja rakenteeseen sitoutuneena. Lisäaineiden käyttö saattaa olla useita painoprosentteja polymeerin painosta, mikä johtaa siihen, että muovien rakenteissa on merkittäviä määriä metalleja, halogeeneja, rikkiä ja maa-alkalimetalleja. Tässä julkaisussa esitellään yksitellen laajimmin käytetyt polymeerit sekä lisäaineet, jotka sisältävät metalleja, halogeeneja, rikkiä tai maa-alkalimetalleja. Kustakin yhdisteestä esitellään kemiallinen kaava, yleisimmät käyttökohteet sekä arvio konsentraatiosta lopullisessa polymeerissä. Käytöstä riippuen metallien, halogeenien, rikin ja maa-alkalimetallien määrä vaihtelee useista sadoista milligrammoista kilossa useisiin tuhansiin milligrammoihin kilossa.
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