Polyester Additives

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To achieve the desired final product quality most of the world-wide produced polyethylene terephthalates are meanwhile modified or process tuned by additives. Main targets of modification are crystallization behavior, melt temperature, dyestuff diffusion and bonding, light transparency and color, thermal and oxidative stability, flammability, gas permeation and many more. Unfortunately, some properties which are based on bulk effect of the polyester backbone like for instance glass transition temperature (Tg) or gas permeability are hardly to change in both directions. To reduce Tg is relatively simple but to increase Tg by means of additive is rather difficult. The same is valid for gas permeation.

Factoring out the process immanent catalysts and stabilizers we can distinguish between two general ways of additive application. The first category contains additives which are fed directly to the production process. This is necessary for either a very homogeneous distribution or the chemical reaction of the additives with the polyester matrix. The second category contains additives which are blended mostly as masterbatch to the polymer during further extrusion processing.

Observing the industrial developments of polyester in textile and packaging applications over decades there is common to both areas that the single plant unit production capacity is steadily increased. A plant size of 300 t/d was at the 90th of the last century of world scale. Today we recognize by fare larger units whereby bottle grade production is leading this development with single unit capacities of >1 500 t/d. But also, in textile polyester production the combined staple fiber and filament spinning lines exceed meanwhile the 600 t/d capacity limits. One clear consequence out of this unit capacity development is the increasing standardization and inflexibility concerning product and quality variations.
A diametrically opposed development is the steadily growing product diversity required by market and consumers. The solutions of this problem are providing polymer modifiers and additives which are developed and delivered by an established additive industry.

Considering the polyester additives and modifiers as part of the whole plastic additive market the market share is limited because the average total additive concentration in polyester is between 0,0005 % and 5% of weight with an average of about 0,2 – 3 % depending on final applications. At top of additive market shares are polymer modifier isophthalic acid for bottle grade production with an estimated consumption of 170 kt/a and titanium dioxide as dulling agent in nearly all textile grade polyester with estimated 90 kt/a. All other additives are whether low in concentration or limited to special applications only and it is rather difficult to get meaningful numbers of their market size.

Another trend especially for all additives of frequent use is their down-optimization of the average application concentration over the years. Semi-dull polyester contained between 0,45 and 0,40 % TiO_2 30 years ago. Over the last decades the concentration declined to 0,3% and even slightly lower at today. Reason is the economical pressure to the producer forced by the steadily declining margins and the steadily ongoing process optimization of polyester production and spinning. Similar development one can observe for the bottle polyester modifier IPA where cost pressure and improved solid state polycondensation processes as well as preform and bottle processing methods are the driving forces to reduce the average application concentration of co-monomers.

- Additives for textile polyester

Besides TiO_2 there is a number of specific polymer modifiers like Na-sulphoisophthalate for cationic dying, organic silicones for low pill fibers, phospinic acid compounds for flame retard fibers or PEG for deep dying fibers which all are to be added during the polymer synthesis process. The need to add these substances to the melt phase polycondensation is

minimizing the flexibility aspect and enforcing development efforts to find technical solutions for the addition of those modifiers as masterbatch prior spinning processes. Table 1 is providing a survey about the common additives for textile polyester. As one can see the frequency of application for most of the additives is at a lower level.

Table 1: Additives to produce textile polyester

Additive substance / property target	**Addition to process**	**Addition as masterbatch to extrusion**	**Market penetration high / med / low**
TiO_2 –(anatase type)/ Dulling agent, stretching aid	regularly addition as slurry in MEG	fiber grade masterbatch	high
5-sulpho-isophthlic acid, sodium salt NaSiP/ Cationic dying	regularly	No / trials ongoing	low (regionally medium)
diethylene glycol (DEG)/ DEG adjustment	Regularly	no	Medium
polyethylene glycol (PEG)/ Deep dyeing	Regularly	No /late addition in process	low
Siloxanes/ Low pill	Regularly	no	medium
Phosphinates/ Flame retardant	Regularly	masterbatch in development scale	medium (regionally)
Pentaerythrite/ POY-DTY modifier, melt viscosity modifier	Regularly	no	low (regionally medium)
optical brightener/ Color improvement , increasing L and adjusting b and a color	Possible	regularly	low
carbon black/ Coloring	possible as melt in melt blend after finisher	regularly	low
silver metal or silver ions fixed to ceramic carrier/ Antimicrobial	no	regularly	low
dyestuffs, PET insoluble as pigment or soluble/ Coloring	possible as melt in melt blend after finisher, limited applications	regularly	medium
$BaSO_4$/ Transparent spinning stretching aid	Possible	possible	low
H_3PO_4, H_3PO_3, P-ester of different kind/ Stabilizer, color improvement, especially in closed MEG loops	Regularly	possible, rarely applied for textile polyester	low
Polyacrylates-copolymers/ POY spinning speed increase	No	regularly	low

- Additives for bottle polyester

Similar to textile polyester the additives for bottle application are broadly diversified and only some of them are used in larger scale as standard recipes which are isophthalic acid, cyclohexanedimethanol, diethylene glycol, blue toner and P-based-stabilizer and in the last time increasingly additives to improve the IR-absorption and barrier. The addition to the process is apart from toner, IR-absorber and barrier additive directly to the polymer synthesis process to achieve the necessary homogeneous distribution and the chemical reaction with the polyester molecule. Toner and IR-absorber are added as well to the process as to extrusion. Table 2 is providing a survey about the common additives for bottle polyester. Similar to textile polyester the frequency of application for most of these additives is at a lower or medium level.

Table 2: Additives to produce bottle polyester

Additive Substance / Property	**Addition to Process**	**Addition as Masterbatch**	**Market penetration high / med / low**
Isophthalic acid (IPA)/ Reduce crystallinity	regularly	no	high
Cyclohexanedimethanol (CHDM)/ Reduce crystallinity	regularly	no	medium (locally)
Diethylene glycol (DEG)/ DEG adjustment Reduce crystallinity	regularly	no	medium - high
Blue toner red, blue, violet dyestuff or co-catalyst Cobalt/ Adjust b-color	regularly	possible	high
H_3PO_4, H_3PO_3, P-ester of different kind/ Stabilizer, color improvement, especially in closed MEG loops	regularly	possible, unusual application	high, nearly all bottle PET contains P
Pentaerythrite/ Melt viscosity enhancer like Pyromellitic anhydride	regularly	possible	low
C-compounds, Fe/Cr/Si/pigment-based (FHU)/ IR-absorption increased	regularly	frequently during injection molding	medium - high
Optical brightener/ Color improvement , increasing L and adjusting b and a color	possible	possible	low
UV-absorber additive/ Synthetic UV-absorbents like HALS-compounds	possible	possible	medium
Naphthalates/ UV-absorber modifier	regularly	possible	low
Amid- or imid-goups containing compounds, other functional groups reacting with AA/ AA-scavenger	possible as melt in melt blend after finisher, limited applications	regularly	
Dyestuffs, PET insoluble or soluble/ coloring	no	regularly	high

SiO_2/ Slipping agent	possible	regularly	low
Nylons like MXD6/ Oxygen barrier and acetaldehyde scavenger	possible as melt in melt blend after finisher, limited applications	possible	medium
Fe or Fe-compounds/ Oxygen scavenger	possible as melt in melt blend after finisher, limited applications	regularly	low
Chain extender/ IV build up, melt strength improvement	possible as melt in melt blend after finisher, limited applications	regularly	low
Polyolefins (small amounts) improved crystallization for hot fill application	After chips cutting	possible	Low / Japan

- Additives for film polyester

Both kinds of film - the biaxial oriented film (BOPET) and amorphous cast film (A-PET) do need special additives to modify the film surface roughness and adhesion. For BOPET are dominating the inorganic pigments like SiO_2, clay or $BaSO_4$ and for A-PET waxes in combination with those pigments are applied. During the time where BOPET-film was used for video-, audio-applications and floppy-discs a broad variety of more or less finely distributed inorganic additives has been used. But meanwhile this kind of film lost its importance and mainly packaging applications are left where different kinds of silica are added. The steadily increasing speed of BOPET stretching lines forced the development of additives which are adjusting the electrical conductivity of the polyester melt. Especially for the broad variety of A-PET applications nearly all kinds of additives which are listed under fiber and bottle application are applied additionally. Therefore table 3 is reduced to the film specific additives.

Table 3: Additives to produce film polyester

Additive Substance / Property	**Addition to Process**	**Addition as Masterbatch**	**Frequency of appl. high / med / low**
SiO_2, fumed or precipitated/ Surface roughness increase	for special products	regularly	high
Waxes/ Reduce adhesion	no	regularly	A-PET high BOPET low
H_3PO_4, H_3PO_3, P-ester of different kind/ stabilizer, color improvement	regularly	seldom	medium
Alkalin- and alkalin earth metal/ traces Electrical melt conductivity	regularly	no	medium

- Additives for other applications
Besides polyester for textile, bottle and film there is a number of further applications where additives are playing an important role which are engineering plastics, strapping, tire cord, foam resin, spun-bond, recycling and low melts. The variety of additives in these applications is again broadly diversified but the knowledge about actual recipes and ways of addition is rather limited.

- **Summary**
The provided survey about the broad range of additives used to modify the polyester intermediates and final products in the way the market demands for demonstrates the complexity and importance of this specific product group. Except for IPA, DEG and TiO_2 the market size of most polyester additives is rather limited. In many cases the additive application technology was developed and introduced as proprietary process know how of polyester producers and processors and access to economical data like market size and price level are confined.