



Additives for Plastics

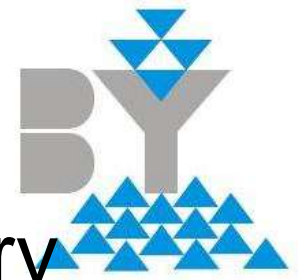
by

Dr. Yatish B. Vasudeo

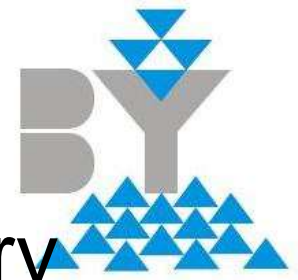
Innovation Consultant

Additives

Miracle Workers for Plastic Industry



Additives are rapidly becoming the miracle workers for the plastics industry, whether they are traditional favorites like plasticizers, impact modifiers and antioxidants or new technologies such as nanocomposites and antimicrobials; their importance is increasing all the time.



Additives

Miracle Workers for Plastic Industry

- Innovation is the ticket for suppliers who seek to stay competitive in a tough global market.
- From improved versions of workhorse grades to better service strategies and formulations, designed for new emerging polymers and inter-polymer competition, will be the rule of the additives business.

Additives - Introduction

- Additive
 - “A chemical added in minor amounts to a host plastic to improve the overall performance of the system”
 - Additives are categorized by the functions that they perform rather than their chemistry.
- Additive functions
 - Modifiers
 - Property extenders
 - Processing aids



Additives - Classes

- **Modifiers**
 - Plasticizers
 - Chemical blowing agents
 - Coupling agents
 - Impact modifiers
 - Organic peroxides
 - Nucleating agents



Additives - Classes

- **Property Extenders**
 - Flame retardants
 - Heat stabilizers
 - Antioxidants
 - Light stabilizers
 - Antistatic agents

- **Processing aids**
 - Lubricants
 - Mould release agents
 - Antiblock / slip agents

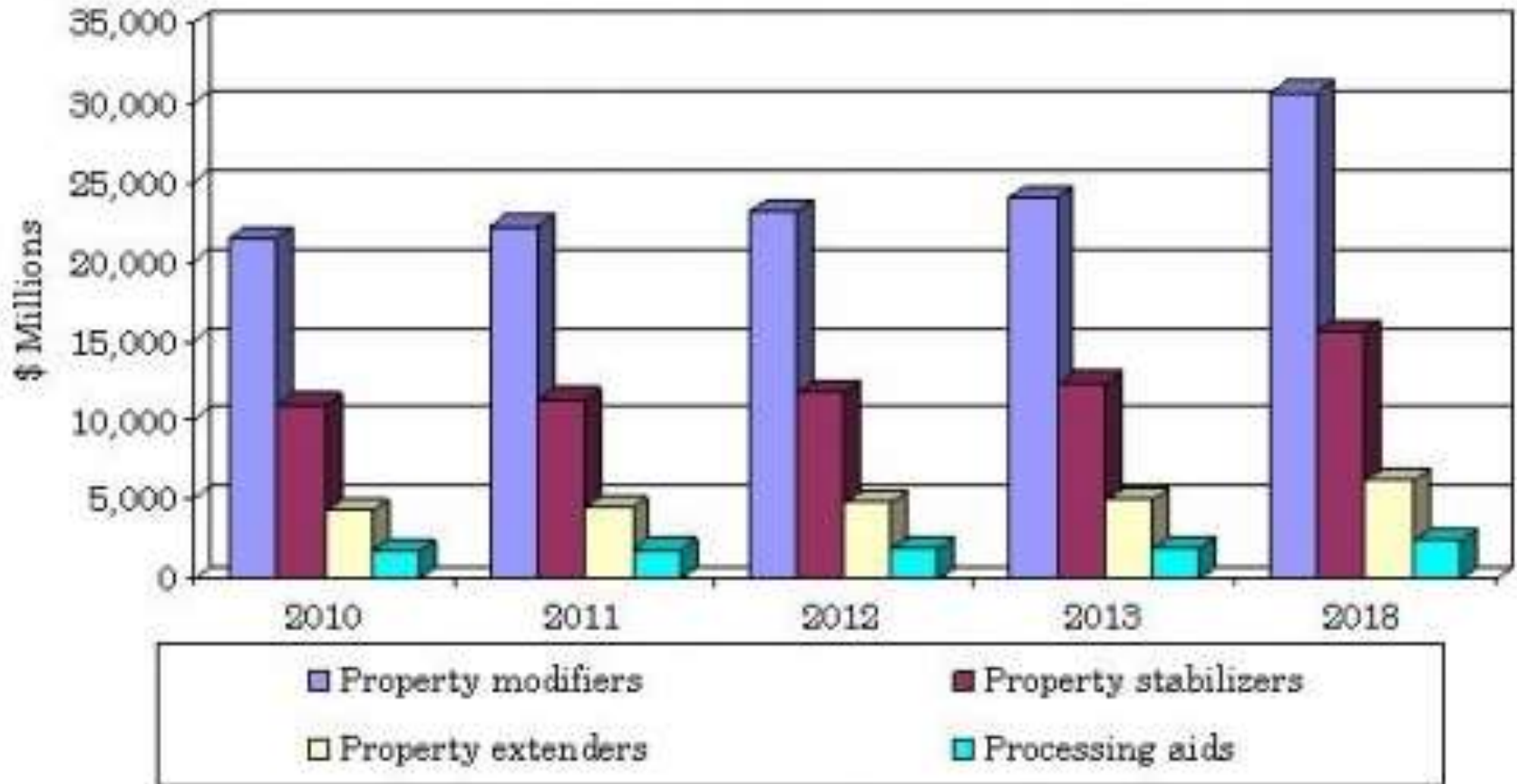
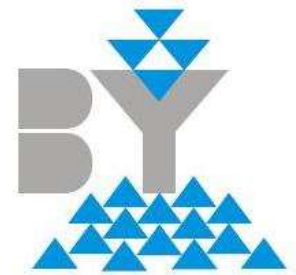


Additives – Global Market



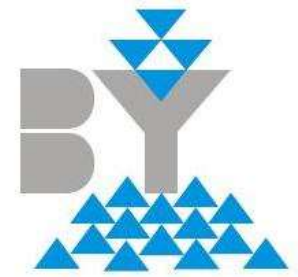
- The total market for plastics additives is projected to increase from \$39.6 billion in 2011, to \$41.3 billion in 2012, to more than \$43.1 billion in 2013, and to nearly \$54.7 billion in 2018 yielding a compound annual growth rate (CAGR) of 4.9% for a period of five years, from 2013 to 2018.
- The market for property modifiers was \$22.2 billion in 2011, which is expected to increase to \$24 billion by 2013. This segment is further projected to reach nearly \$30.6 billion by 2018, a CAGR of 5.0% over the last five years.
- The market for property stabilizers was \$11.2 billion in 2011, which is expected to increase to \$12.3 billion by 2013, a CAGR of 4.9% over the three year period. This particular segment is further projected to reach nearly \$15.6 billion by 2018, a CAGR of 4.9% over those five years.

GLOBAL MARKET FOR PLASTICS ADDITIVES BY TYPE, 2010-2018 (\$ MILLIONS)

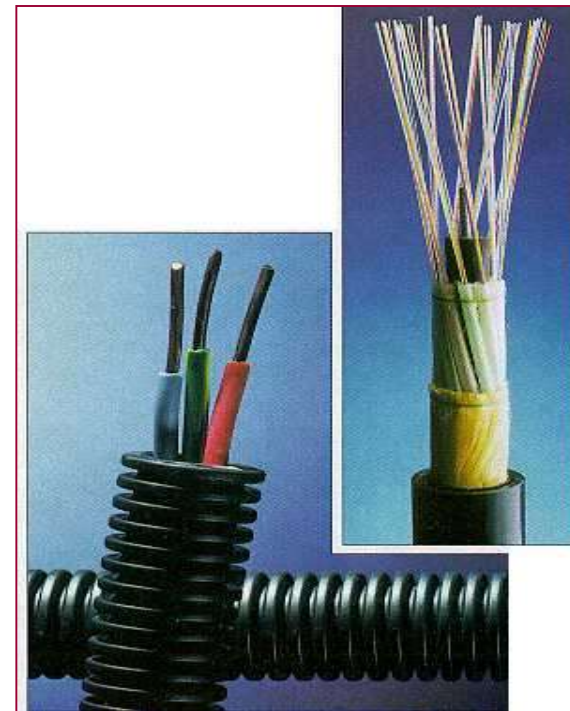


Additives : Business Perspectives

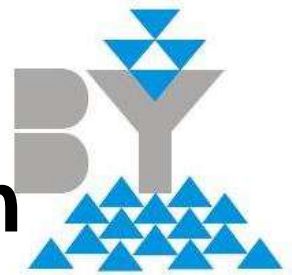
Worldwide Suppliers



- 350 companies of additive suppliers worldwide.
- 100 companies with annual sales over \$100,000
- Additives business has a high proportion of very small suppliers of specialty products.



Introduction to Polymer Stabilization



- Transformation of a polyolefin material on its way from the reactor fluff to the finished article usually comprise several steps, including processing operations at elevated temperatures.
- During these steps, the polymer suffers from various degradation processes caused by heat, shear & oxygen, which can affect the processing characteristics of the polymer melt & the final mechanical / aesthetic properties of the final article.
- Negative effects of these degradation processes can be restrained by use of stabilizers.
- All additives & co-additives used for the stabilization of a given polymer grade constitute an “additive package”

Essential Ingredients for Polyolefins Stabilization



As viewed from a raw material supplier's perspective

- Acid scavengers and lubricants
- Antioxidants
- UV stabilizers
- Slip agents
- Polymer processing aid
- Antiblocking agents
- Antistatic agents
- Nucleating agents and clarifiers

Salient Features of Antacids

Antacids serve several purpose in the additive formulation



- Presence of catalyst residues(from Zeigler – Natta catalyst systems) in a polymer matrix generates free acidity after the catalyst deactivation by steam stripping or solvent treatment. Antacids neutralize this acidity & prevent thereby many undesirable side effects such as corrosion of processing equipment, chloride stress-cracking.
- Stearate –type acid scavengers especially act like internal & external lubricants, which is important for the processing of HMHDPE & film production, in order to reduce shear forces during extrusion.

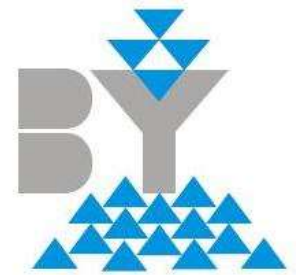
Salient Features of Antacids

Antacids serve several purpose in the additive formulation



- Certain Na & Ca salts of higher fatty acids (C28-C33), besides their acid scavenging property , influence the crystallization behavior of polyolefins.
- Improvement in the performance of HALS UV stabilizers as well as resistance to pesticides (for greenhouse films) can be achieved by acid scavengers as well.

Metallic Stearates



- Metallic stearates are highly versatile additives used in various applications and bringing numerous effects and benefits in polymer production.

We can distinguish three main effects:

Acid scavenging in polyolefin contributing directly to color stability and corrosion prevention

Lubrication/Process aid enhancing processability of polyolefins, polyamide, styrenics and rubbers in processes like extrusion (film, fibres, profiles) and calendering.

Mold release in thermoplastics, rubbers and thermosets like polyurethane foams and unsaturated polyesters

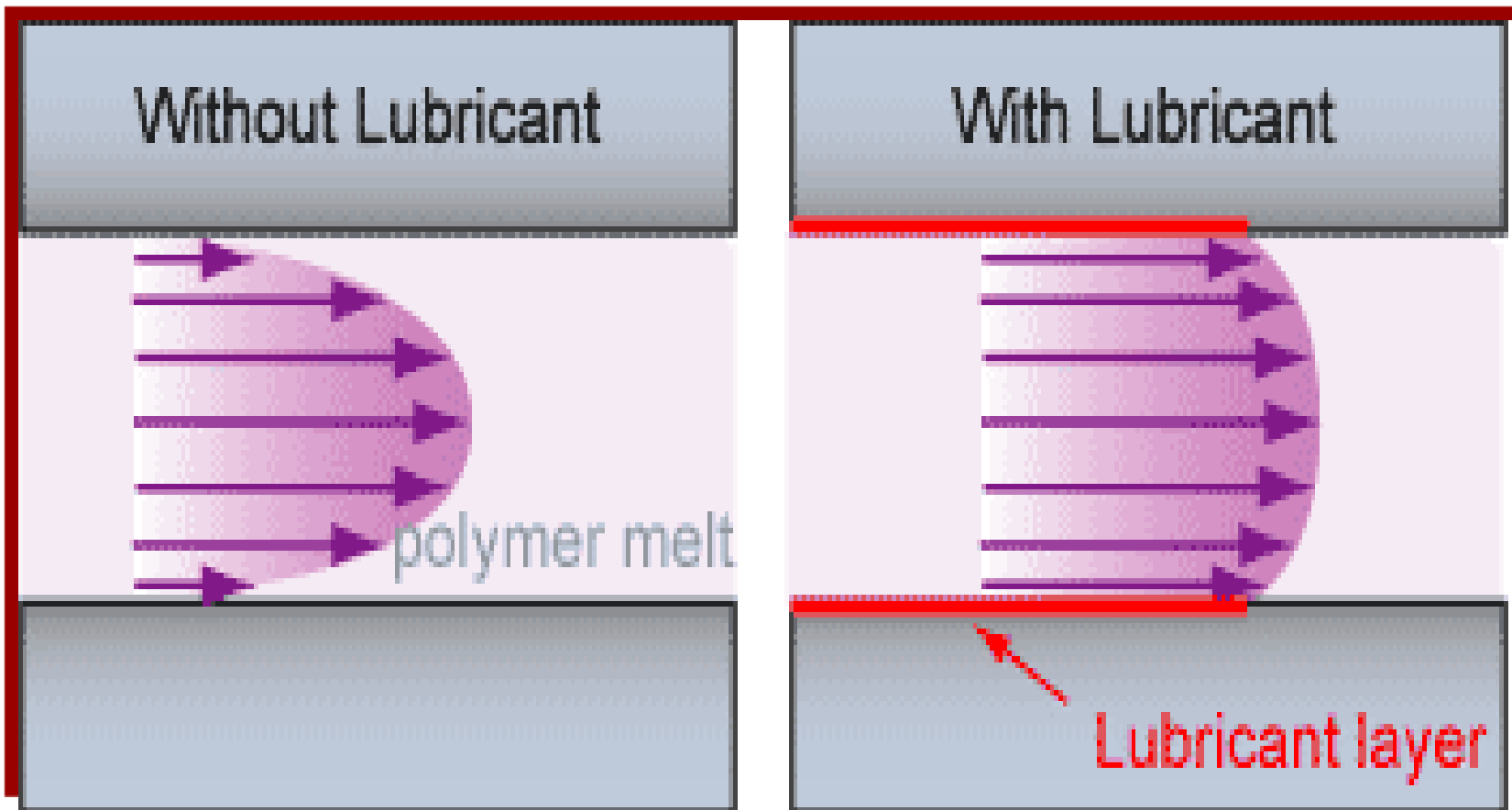
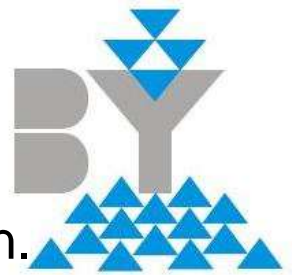


Metallic Stearates

Lubricating effect of stearates plays an important role in extrusion and calendering. In blown films, particularly in LLDPE films, the same properties prevent melt fracture. When stearates are used commercially for both neutralization and lubrication, the concentration can be several times greater than required for neutralization alone.

Influence of metallic stearates lubricity

in melt flow profile in a dies,
explaining melt fracture reduction in PE film production.





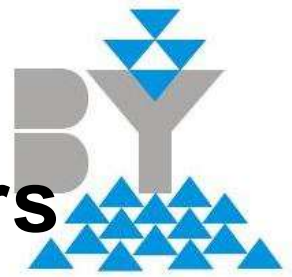
Antioxidants & Thermal Stabilizers for Polyolefins

Primary Antioxidants

Secondary antioxidants

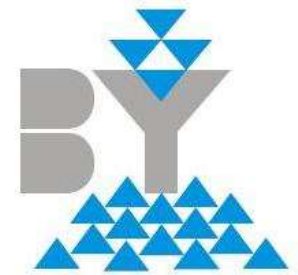
LTHA

Primary Antioxidants / Stabilizers



- Primary stabilizers are usually defined as additives that interfere with the oxidation cycle by reacting with the radicals formed & interrupting the cycle.
- Primary antioxidants perform well when used by themselves in their intended application.
- Both Hindered phenols & Hindered Amines function as primary antioxidants; both act as radical scavengers.
- Phenolic antioxidants protect the material both during processing (I.e. in its molten state) & during use.

Examples of Commercial Available HP



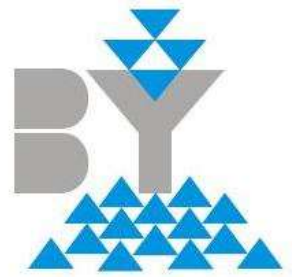
Trade Name	Manufacturer	MW	No. of Phenolics
BHT	various	220	1
Irganox 1076	Ciba	531	1
Irganox 1010	Ciba	1178	4
Irganox 3114	Ciba	784	3
Ethanox 330	Albermarle	775	3
Anox CA 22	Great Lakes	545	3
GA80	Sumitomo	741	2

Secondary Antioxidants



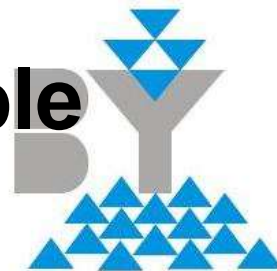
- Secondary antioxidants contain phosphites.
- Phosphites protect the material primarily during processing : at high temperatures they work faster & more effectively than phenolic antioxidants.
- Thus they prevent the primary antioxidant from being consumed during processing, preserving it for its subsequent function as long-term stabilizer during use.
- The phosphites themselves are largely used up during processing.

Secondary Antioxidants

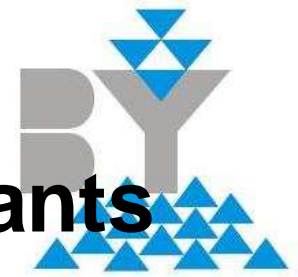


- This class of additives is termed “secondary” because their mechanism is not primarily radical scavenging. When used in a polymer resin by themselves, this class of compounds does not exhibit appreciable activity.
- The value of these compounds comes when they are combined with the correct primary antioxidant. When the correct combination is made at the proper ratios, a strong synergistic effect between the two results.

Examples of Commercially Available Secondary Stabilizers



Trade name	Manufacturer	Type	MW
Phosphites			
Irgafos 168	Ciba	Aromatic Phosphite	647
Ultranox 626	Crompton	Aromatic diphosphite	604
Weston 399	Crompton	Aromatic phosphite	688
Ultranox 618	Crompton	Aromatic diphosphite	732
Ethanox 398	Albemarle Corp	Fluoro phosphite	487

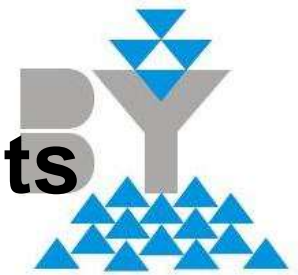


Synergism of Secondary Antioxidants

- **The best example of synergism is seen in the performance of a phosphite / phosphonite with a hindered phenol.**
- **Table illustrates the synergism.**
- **When used alone, the phosphite does not stabilize the melt well, while the HP does impart a relative good degree of stability.**
- **When used together, the HP / Phosphite combination exhibits a high degree of melt stability.**

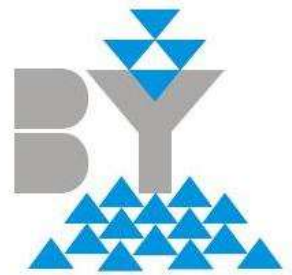
Synergism of Secondary Antioxidants

MFR Of Re-Extruded PP



Pass Number	Phenolic	Phosphite	Both *
1	4	3.9	2.5
3	6.3	6	3
5	10	16	6

Secondary Stabilizers



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Secondary Stabilizers

Thio Compounds

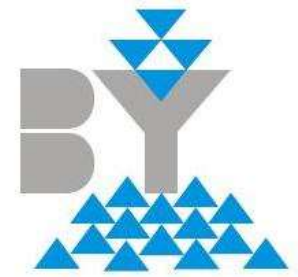
Trade Name	Manufacturer	Type	MW
DSTDP	Various	Thioester	683
DLTDP	Various	Thioester	514

- When used in a ratio of 1:4, the HP / thioester combination yields lifetimes of 80 to 100 days.
- Exact values of enhanced LTHA depends on HP/ thioester combination.

Effective Role of Additives



- Plastic generally ages rapidly under the effects of light, oxygen and heat, leading to:
 - ❑ Loss of strength, stiffness or flexibility
 - ❑ Discoloration
 - ❑ Scratching and loss of gloss
- Plastic has become an essential material in virtually every aspect of modern day life. Recent advances in plastic manufacturing, processing and enhanced knowledge of chemistry of additives, have led to ever more applications in which plastics replace other materials such as glass, metal, paper and wood.



Slip Additives

- Due to a high coefficient of friction, polyolefin films tend either to adhere to themselves or to the production equipment during film processing.
- Slip additives modify the surface properties of polyolefin films and reduce the film to film friction (e.g. on a roll) and the friction between the film and other surfaces with which they come into contact..

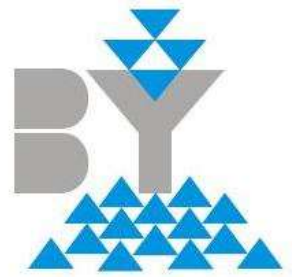
Slip agents therefore:

Facilitate increased line speed in the manufacturing process.

Enhance packaging machine operations due to reduced CoF (coefficient of friction) values.

Slip Additives

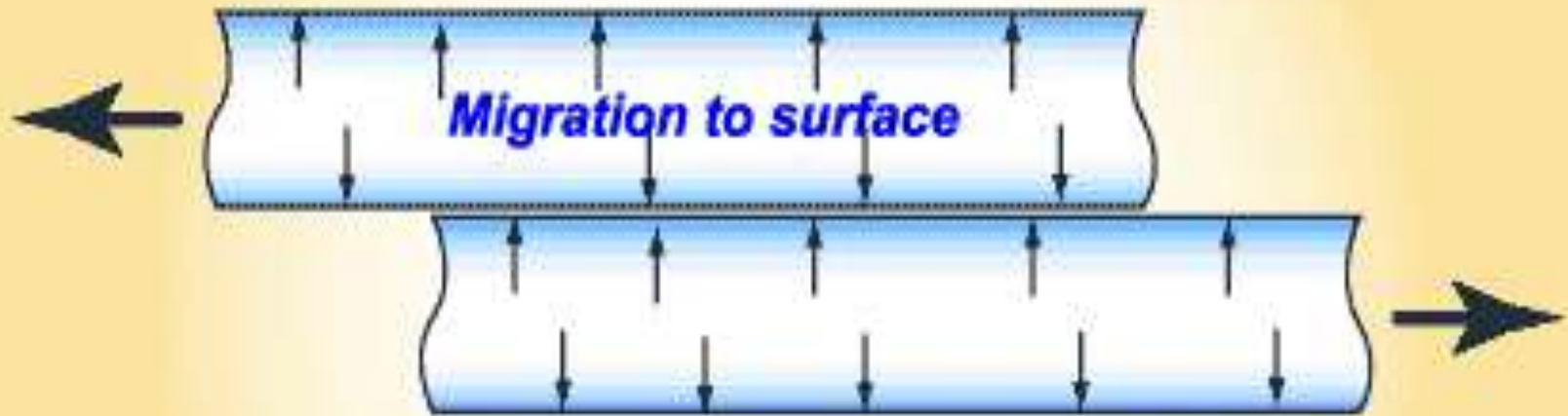
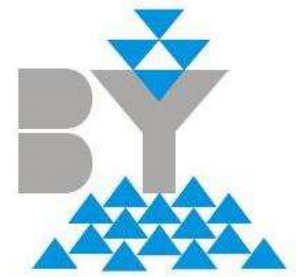
Principle of Action



- Slip Effect is a term used to describe the sliding of parallel film surfaces over each other or the sliding of film surfaces over substrates.
- Slip agents - such as stearamide, oleamide and erucamide - are added to polyethylene (PE) or polypropylene (PP) films during the extrusion process to decrease friction - both film-to-film friction and that between the film and production equipment - in order to increase the output of the line and to improve packaging line operations.
- Slip effect is measured as CoF (Coefficient of Friction).

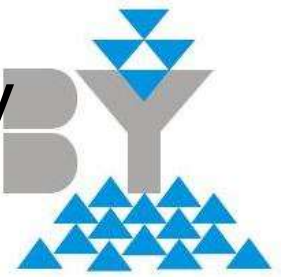
Slip Additives

Principle of Action

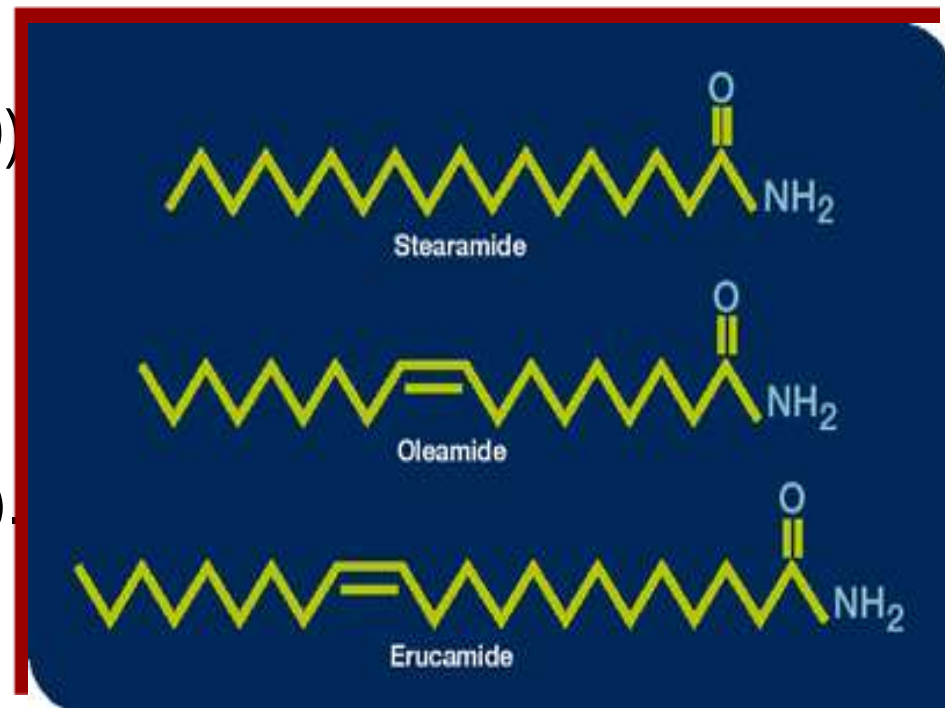


*Migration of slip additives to the film surface
reducing coefficient of friction*

Chemical Structures of Commonly Used Slip Agents

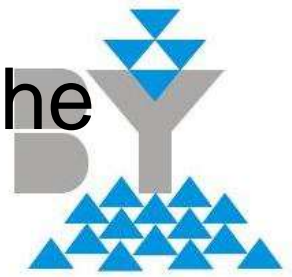


- Stearamide is prepared by amidation of stearic acid (C18:0)
- Oleamide is prepared by amidation of oleic acid (C18:1).
- Erucamide is prepared by amidation of erucic acid (C22:1).



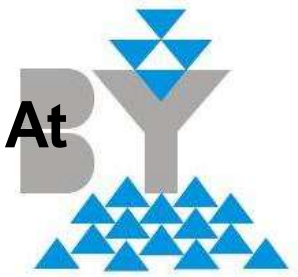
The most commonly used slip agents are oleamide and erucamide. Stearamide can also be added to provide antiblocking properties.

Effect of Oleamide and Erucamide on the COF of Polyolefin films

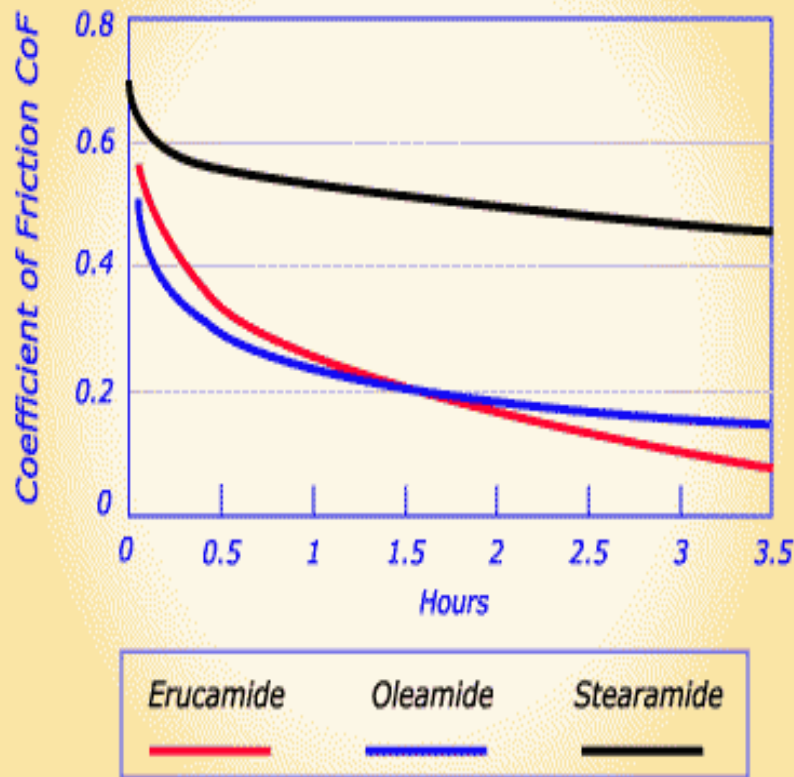


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- A method used quite often to determine slip performance of a plastic film is ASTM D 1894, Static and Kinetic Coefficients of Friction of Plastic Film and Sheeting.
- Slip agents such as erucamide and oleamide are in most cases used in concentrations between 500 and 1500 ppm.

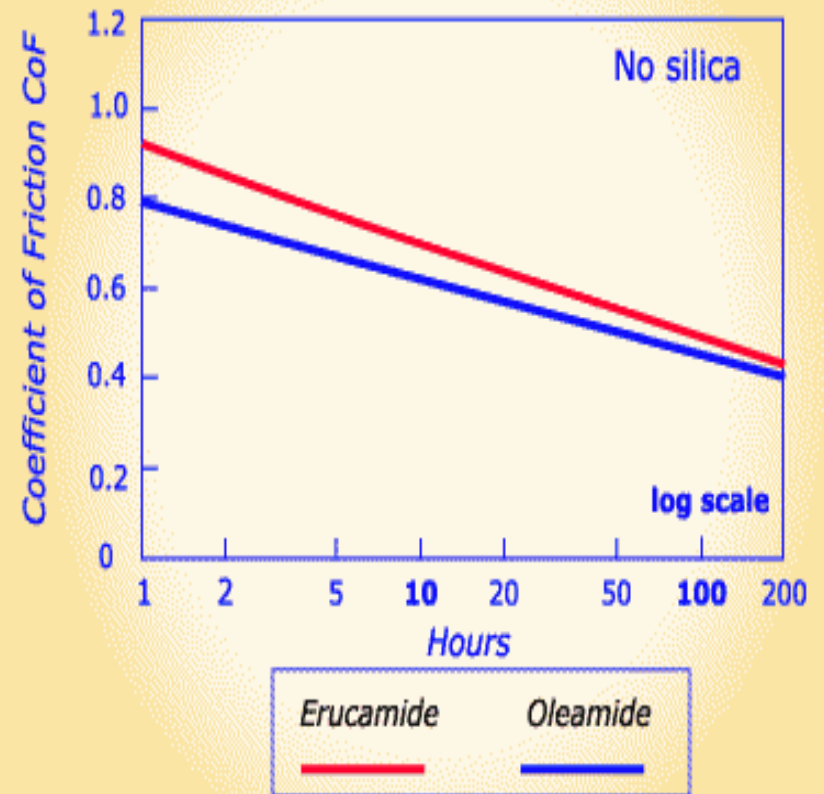
COF Of Polyolefin Films As a Function Of Time At Fixed Concentration of 1000 ppm Slip Level



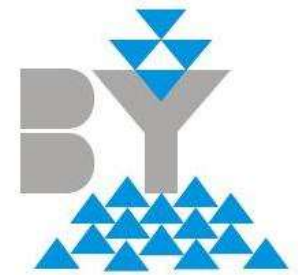
LDPE, 50 microns Film with 1000 ppm amide



PP, 50 microns Film with 1000 ppm amide



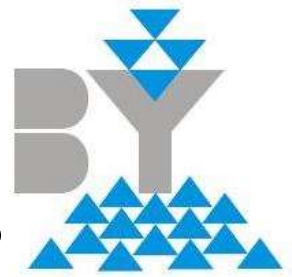
Some Observations on Slip Additives



- **Decreased CoF is a result of the migration of slip additive to the film surface due to the defined incompatibility of the slip additive with the polymer. The migration speed of slip agent to the surface is largely decided by the additive's chain length (compatibility with the polymer) and the crystallinity of the polymer. The larger the slip agent (more carbon atoms) the more compatible it is with the polymer and the slower it migrates. So oleamides migrate faster than erucamides.**
- **Erucamides are more heat stable than oleamides, more resistant to oxidation and create fewer volatiles during processing. This means that erucamides are more suitable for higher processing temperatures and processes with high output, which will result in high quality final products. Structurally, PE is less crystalline than PP, so encourages faster migration of the slip additive.**
- **Due to the migration of the slip agent to the surface of the polyolefins, primary amides are not only used as slip agents for polyolefin films but are also recommended for use as demoulding agents in injection molding applications.**

PPA (Polymer Processing Aid) :

A boost for many extrusions processes

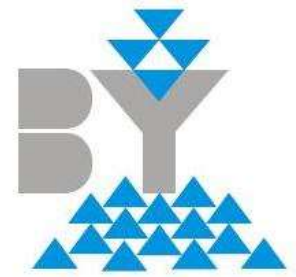


Problems during polymer extrusion

1. Melt fracture
2. Die build up
3. High pressure in the die
4. Limitation in cooling system
5. Limitation of output

Mechanism of PPA

Polymer Processing aids



- This additive is mainly acting during the extrusion process, and facilitates the extrusion process itself, even if there are some positive consequences on the extruded profile or film manufactured on the extrusion line. So, this PPA is an additive, but it is also a polymer.
- Depending of on manufacturer or extruding conditions, PPA can be fluoroelastomers (most of the time), or fluoroplastics. The fluorine content of PPA is typically around 60%wt.

Mechanism of PPA Action

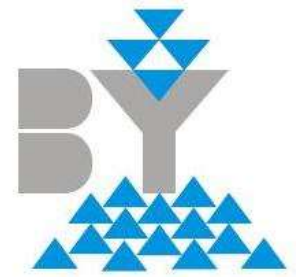
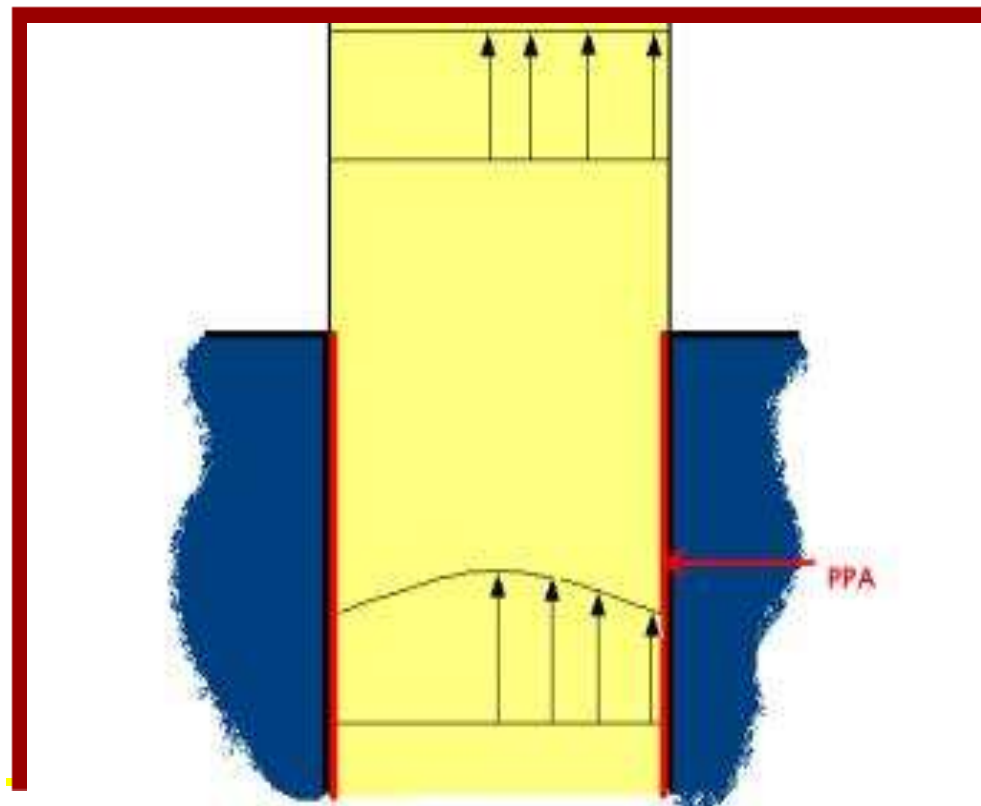
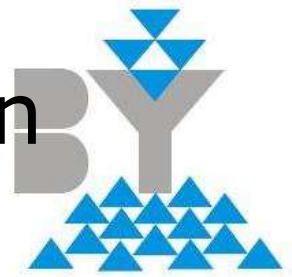


Figure illustrates the effect of adding 500 ppm of PPA's to a polymer. As fluoropolymers are not compatible with PE and have affinity with metal, it will naturally "migrate" at the surface to create a thin coating (Red in figure). This layer is very thin and count only few layers of macromolecules.

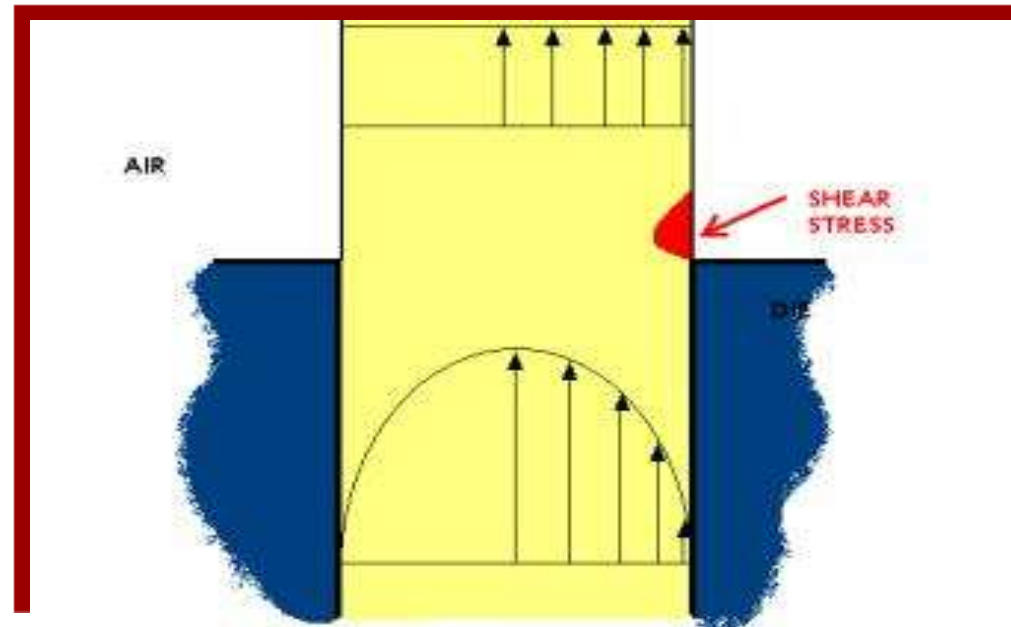


Problems during Polymer Extrusion

- Melt fracture



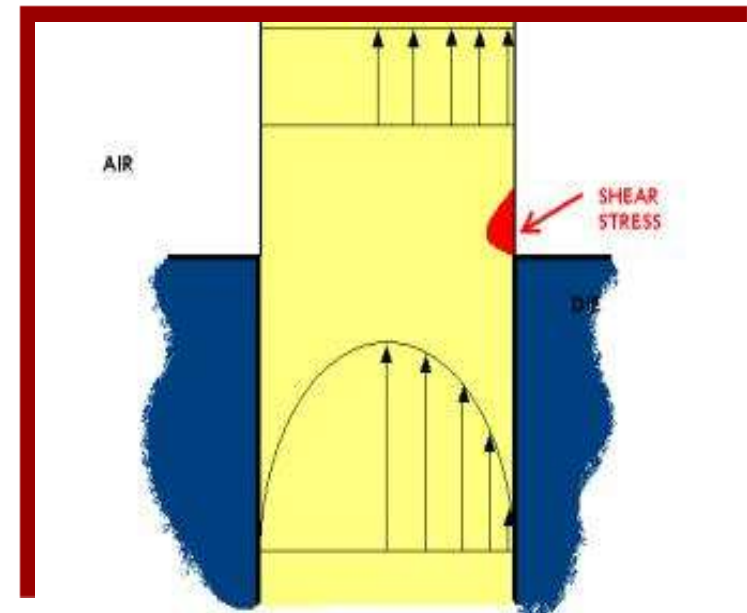
- Melt fracture is occurring mainly during the extrusion of rich blends of LLDPE ($> 50\%$ of LLDPE in the blend). The other resin can be LDPE or HDPE.
- The general behavior of a melted polymer flowing into a die is represented in Figure: Melted polymer is in Yellow and die walls (1mm gap) are in Blue.





Melt Fracture

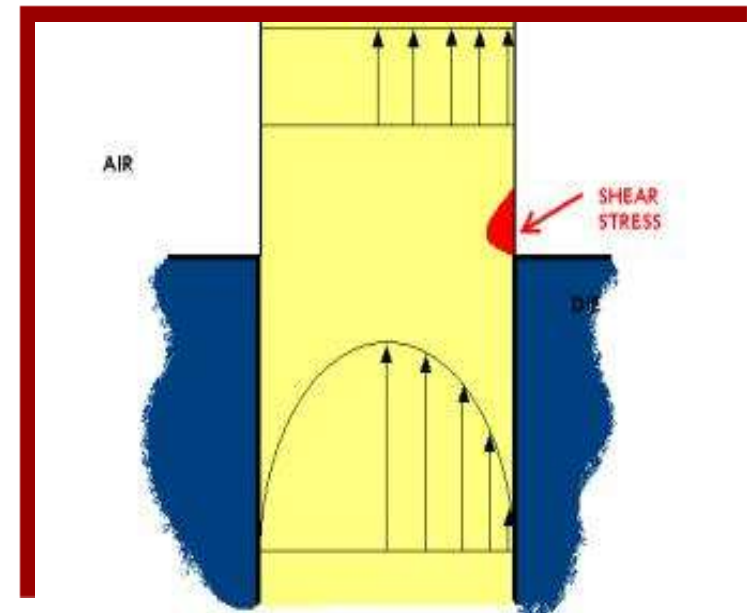
- Velocity profiles of the polymer have been reported inside and outside the die. As you can see, inside the die the speed of polymer's particles are not uniform.
 - Maximum velocity is observed in the middle of the gap and reach almost zero at the walls.
- When the polymer is out of the die, the velocity profile is becoming flat and all the speeds are equal to the average speed observed inside (few mm over the die).



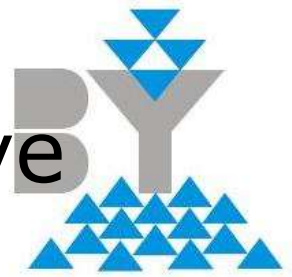


Melt Fracture

- On the specific point where the polymer is leaving the die, and for particles close to the wall, the speed is increasing rapidly from zero, up to average speed of the melt. This is creating an acceleration of the melt on short length equivalent of high shear stress. Elongation stress of LLDPE is over its possibility, and the melt breaks continuously at this place creating the melt fracture phenomena.



How processing aids can improve extrusion process



Melt fracture

As soon as the coating of PPA is created, the shearing zone at the die's outlet disappears. Melt fracture disappears a surface aspect improve significantly. Film gloss increase strongly and this phenomena is the first observed by the converters starting using PPA. The gloss can easily be measured with a glossmeter

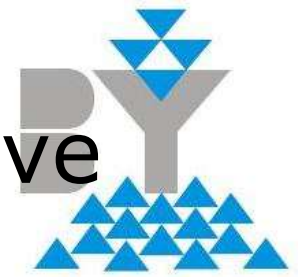
Problems during Polymer Extrusion

Die Build Up



Die build up is a deposit of burned polymers and fillers at the exit of the die. When this one has grown sufficiently it can be carried away by the extruded polymer leading to surface defects. This die build up becomes critical when the polymer contains fillers or fibers and also when extrusion temperature or pressure are too high (Most of the time, high pressure drives temperature up). The die build up can also be observed on the wall of the die due to material stagnation at zero speed. This phenomenon leads generally to undesired black spots or fish eyes.

How processing aids can improve extrusion process

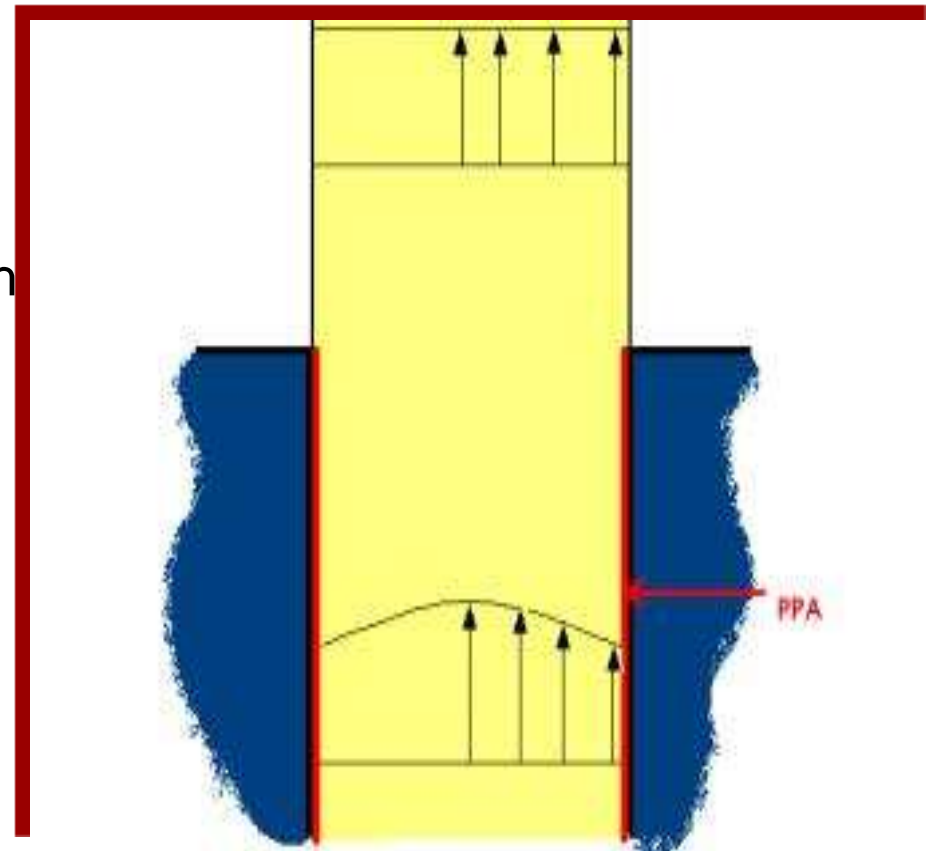


Die Build Up

- When the PPA coating is created in the die, the polymer particles speed on the wall is now relatively higher (due to the slippage on the wall). This means that particles at the wall have much lower residence time into the machine than previously, reducing significantly oxidations or degradation. As a result, extruded film or profile presents less oxidation spots or gels. Moreover, spots or gels slip on the PPA's coating and don't stick on the die's lips: Die build up is reduced.
- In the blown film industry, introduction of 100-200 ppm of PPA commonly increases time between two cleaning-up by ten or more.

Mechanism of PPA Action

Processing aids mechanism.
 Figure illustrates the effect of adding 500 ppm of PPA's to a polymer. As fluoropolymers are not compatible with PE and have affinity with metal, it will naturally "migrate" at the surface to create a thin coating (Red in figure). This layer is very thin and count only few layers of macromolecules.

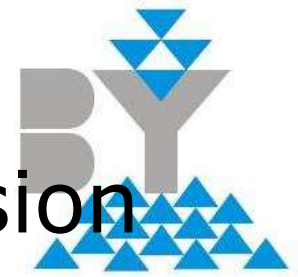


Problems during Polymer Extrusion

High Pressure in the Die



High pressure in the extruder and the die is the result of a too low melt index of the PE or of a too narrow gap in the die and/or an excessive compression ratio of the extrusion screw. Most of the time, result is an increase of melt temperature reducing significantly extrusion stability.



Problems during Polymer Extrusion

- Limitation in cooling system

Limitation in cooling system can be the bottleneck of lot of extrusions processes. This problem can be addressed by to ways : 1) Increase cooling efficiency (it is not possible every time) or 2. decrease the melt temperature.

- Limitation of output

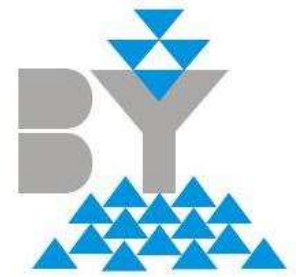
Bottleneck must be found.

How processing aids can improve extrusion process



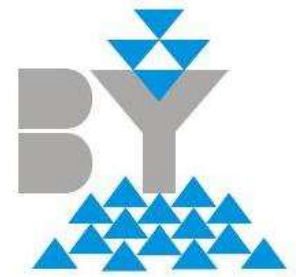
- As the polymer slips on the die surface, introduction of 500-600 ppm of PPA can reduce pressure to about 10 - 15%. Most of the time, this is interesting mainly to avoid self-heating of polymer in the die or in the metering zone of the screw (Compression ratio of the screw too high for the extruded polymer).
- This pressure reduction can be used to lower the melt temperature in order to get better cooling efficiency of the extrudate. Better cooling efficiency can also allow an increase of the output without affecting process stability.

Antiblocking Agents for Polyolefin Films



- Blocking is the tendency of polymer films to stick to themselves. This adhesion is termed “Blocking”
- Primary causes of blocking are pressures & temperatures that the film may encounter during extrusion, use or storage.
- The degree of severity of the blocking is a function of the film’s characteristics as well as the effects of outside forces acting on the film.
- Blocking affects the film’s entire life-cycle, from processing during manufacture of the film to its performance during end use.

Antiblocking Agents for Polyolefin Films



- In order to prevent film surfaces from blocking, small amounts of powdered materials called antiblocking agents , are incorporated into the polymers.
- These antiblocking agents create imperfections on the film's surface & prevent the total contact of the two film layers, reducing blocking

Antiblocking Agents for Polyolefin Films



- Blocking can have detrimental effects on the processing and performance of films, sometimes to the extent that films are unusable.
- To lessen the direct contact between layers of film & to counteract blocking forces, antiblocking and anti-slip aids are incorporated into polymers, creating a proper processing environment for the films.
- Antiblocking additives must be highly efficient & exhibit constant & dependable quality, with little or no effect over other film properties.
- Antiblocking additives must have FDA approval.

Antiblocking Agents for Polyolefin Films



Synthetic silicas such as

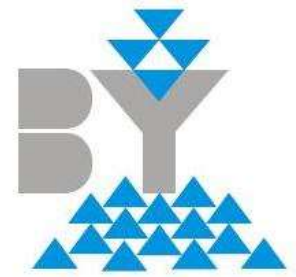
- fumed silica,
- silica –gel,
- zeolites

Naturally occurring silicas & minerals such as

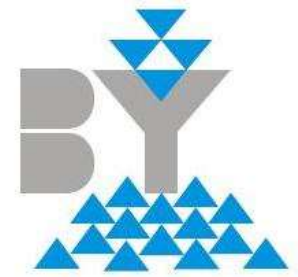
- clays,
- diatomaceous earth(DE),
- quartz or
- talc

Are used as antiblocking agents.

Antiblocking Agents for Polyolefin Films



- Among synthetic silicas (precipitated, fumed, gel) silica gel in micronized form have the greatest in antiblocking applications. In the micronizing process, the silica particle size & particle size distribution is closely controlled.
- The particle sizes of the silica can be adjusted with respect to film thickness ---- For example, a two micron particle size for very thin films & a ten particle size for thick films.
- The high porosity of the silicas is an additional benefit, with large quantity of available particles.
- Loading of antiblocking agents in any film is dependant on the film characteristics, the end-use and the efficiency of the antiblock.
- Loadings can vary from 1000 ppm to 5000 ppm.
- Combination of slip & antiblocking agents are also employed for synergistic effects.



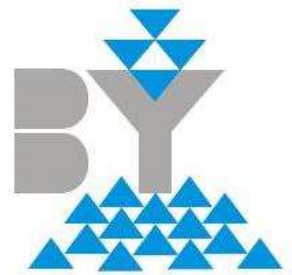
Antiblocking Agents

Factors affecting antiblock performance

- As antiblocking agents function by creating surface roughness, their performance is affected by size & shape. Properties such as particle size, particle size distribution, particle strength influence efficiency.
- In films such as LDPE or PP, the preferred average particle size is generally in the range of 6 to 20% of the film thickness. Three-dimensional particles, for example; DE, quartz, silica gel, are more efficient than two-dimensional platelet structures such as clays or talc. Synthetic silicas are found to be the most efficient antiblocking agents on account of their narrow PSD. The narrow PSD ensures that the largest number of particles are of the most efficient size.
- The strength of the antiblocking agent particles is important in order to retain size & shape during the high shear conditions encountered when the agent is incorporated in the polymer resin

Antiblocking Agents

Incorporation of Antiblocking Agents Into The Polymer



- Antiblocking agents may be incorporated into the polymer resin either by direct addition at the final concentration or via a concentrate or masterbatch that is added to a barefoot resin to achieve the final concentration
- As antiblocks must be well dispersed in order to have maximum efficiency, mixing equipment with good dispersive characteristics rather than distributive characteristics are necessary.
- Generally, antiblocks are dry blended with other additives & stabilizers in a carrier resin. The concentration of antiblock may range from 5 to 10 % for synthetic silica to 30 to 50% for DE & talc.



Antistatic Agents

High electrical charges on the surface of plastics can cause following problems:

- Antistatic agents act to reduce surface resistivities and hence dissipate high electric charge densities on the surface of plastics.
- handling problems during transport, storage and packing
- dust contamination, affecting both appearance and performance of end-products
- risk of electrical shocks to employees working at the machines
- risk of electrical discharge causing fire or explosion

Internal & External Antistats

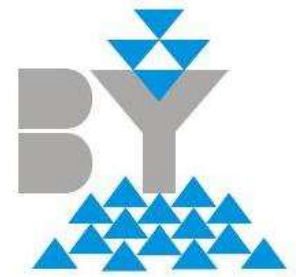


There are two types of antistatic agents:

- **Internal agents** are added to a polymer in the extrusion process. Internal antistatic agents are preferable to the external ones, because external agents are short-lived. External agents can be abraded easily from the polymer surface and migrate into the polymer. Although quick to apply and requiring low dosage levels, they are not suitable for high-quality applications, as they can cause printing and sealing problems because of a non-uniform coating
- **External agents** are applied to the plastic surface after the extrusion process by spraying or wiping.

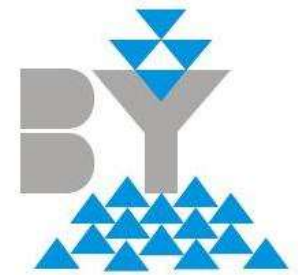
Internal Antistatic Agents

Mode of Action



- An internal antistatic agent is incorporated into the polymer matrix during the extrusion process. Upon extrusion, the additive migrates to the surface of the polymer - because of its defined incompatibility with the polymer - where the additive builds up a uniform layer on the polymer's surface. The hydrophilic end projects out of the polymer, the lipophilic end anchors in the polymer.
- The protruding hydrophilic end absorbs moisture from the surrounding air and builds up a conductive path, reducing the surface resistivity.
- Antistatic agents are hygroscopic and mainly too high concentrations of antistatic agents will have an influence on printing and sealing properties

Internal Antistatic Agents Mode of Action



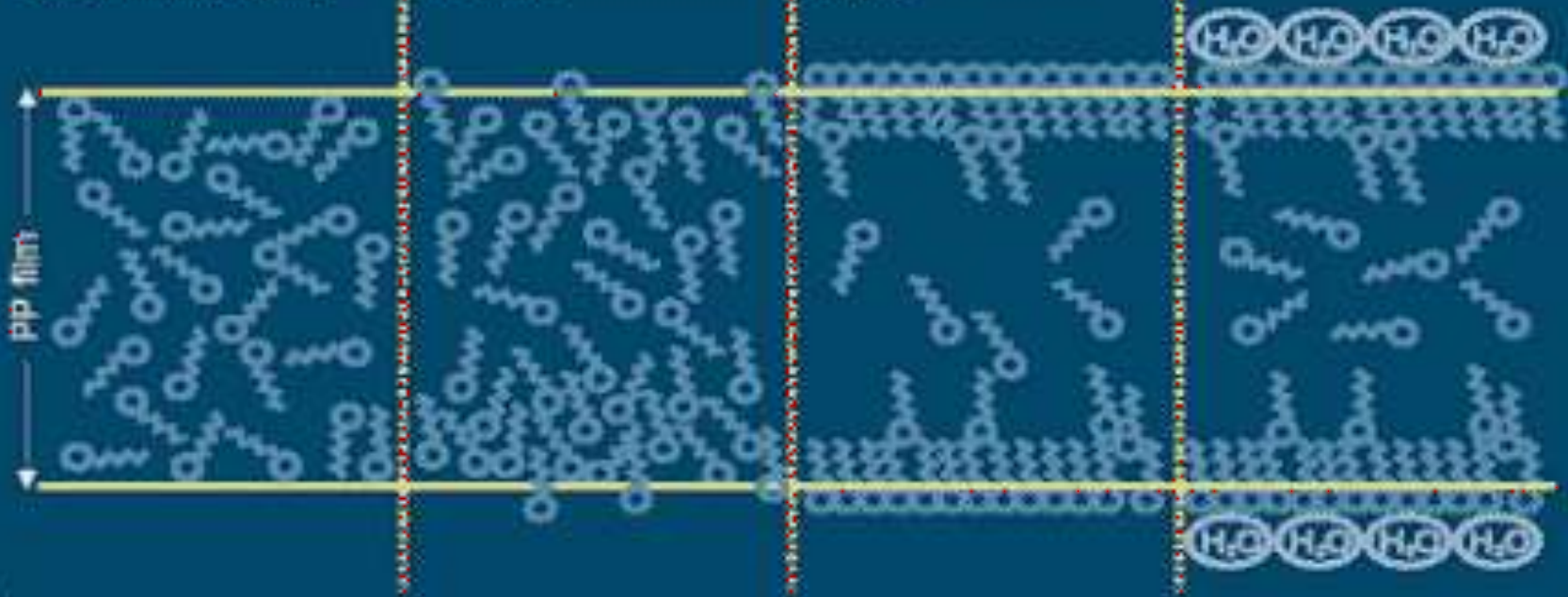
Mode of action

Phase 1:
Homogeneous distribution
of antistatic agent during
the extrusion process

Phase 2:
Antistatic agent begins to
migrate to surface after
extrusion

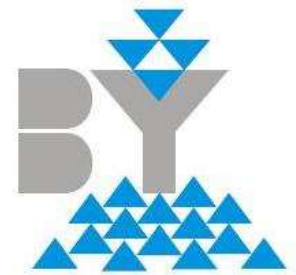
Phase 3:
Hours or days later
antistatic agent covers
surface

Phase 4:
Moisture pick up from the
surrounding air



Antistatic Agents

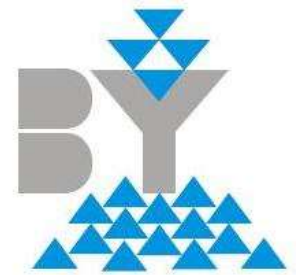
Rate of Migration



The migration rate of the antistatic agent from the bulk to the surface of the polymer depends from a number of factors. These include:

- **Relative compatibility** of antistatic agent and polymer
The less compatible an additive and polymers are, the faster the migration rate
- **Polymer Crystallinity**
The more crystalline a polymer's structure, the slower the migration rate is.
- Total **polymer additives** formulation
Certain additives absorb the antistatic agents
- **Concentration** of the antistat
Higher concentration = quicker migration
- **Temperature**-Higher temperature = increased migration.

Testing Antistatic Performance



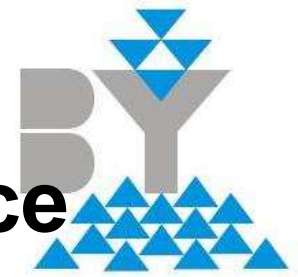
There are two main methods used in the industry to measure the performance of antistatic agents:

Half-charge Decay Time:

- is defined by the 'half-life' of a charge on a given specimen. A charge is applied (as in the diagram) and the time it takes the potential to be reduced to half the applied voltage (under specified temperature and humidity) is measured as the half-charge decay time. The shorter the half-charge decay time the better the plastic is at neutralizing surface charge

Surface Resistivity: (how poorly the polymer conducts electricity)

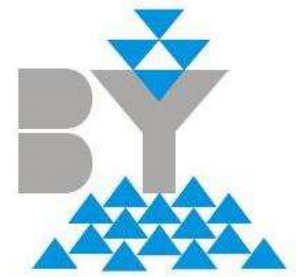
- is a measure of intensity of the current flowing over it. A potential is applied to the surface of a plastic via two electrodes and the smaller the surface resistivity the better the antistatic properties.



Testing of Antistatic Performance

Surface Resistivity (Ohms)	Half-Life Decay Time (Seconds)	Rating
Less than 10^{10}	< 1	Very Good
$10^{10} - 10^{11}$	1 - 10	Good
$10^{11} - 10^{12}$	10-60	Moderate
Greater than 10^{12}	> 60	Poor

Judging The Efficiency of Antistatic Agents



- The effectiveness of an antistatic treatment can be quantitatively assessed in a number of ways. Whichever technique is chosen, it is advisable to "condition" the sample at constant atmospheric temperature and humidity for at least 24 hours prior to testing and to carry out the test at that temperature and humidity.
- When it is necessary to compare the performances of different antistatic agents, it is essential that the same temperature and relative humidity is chosen for both the conditioning period and for all the tests.

Chemistry of Antistatic Agents



- Glycerol monostearate is a generic name encompassing various blends of glycol esters
- Manufacturing process determines whether GMS is almost pure monoglyceride, mixture of mono, di and triglycerides.
- Each of these glycol esters have different polarity, MW & size & hence different migration characteristics.
- Monoester is more hydrophilic, which means sufficient amounts of it must come to the surface for a good antistatic property to be achieved.
- GMS also imparts mold release properties to PP in IM
- Ethoxylated amines are also used as antistats for polyolefins



Nucleating Agents

Commercially available nucleators can be divided into two classes:

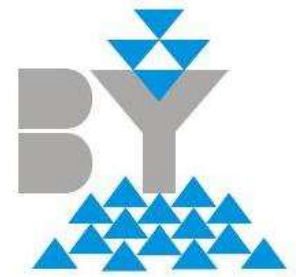
- **Melt Sensitive**

The melt sensitive nucleators have a melting point which is below or near the processing temperatures of PP based resins. These are made by Milliken Chemicals, USA

- **Melt Insensitive**

melt – insensitive nucleators do not melt at normal processing temperatures of PP based resins. These are made by ADEKA, Japan

Some Observations on Nucleating Agents



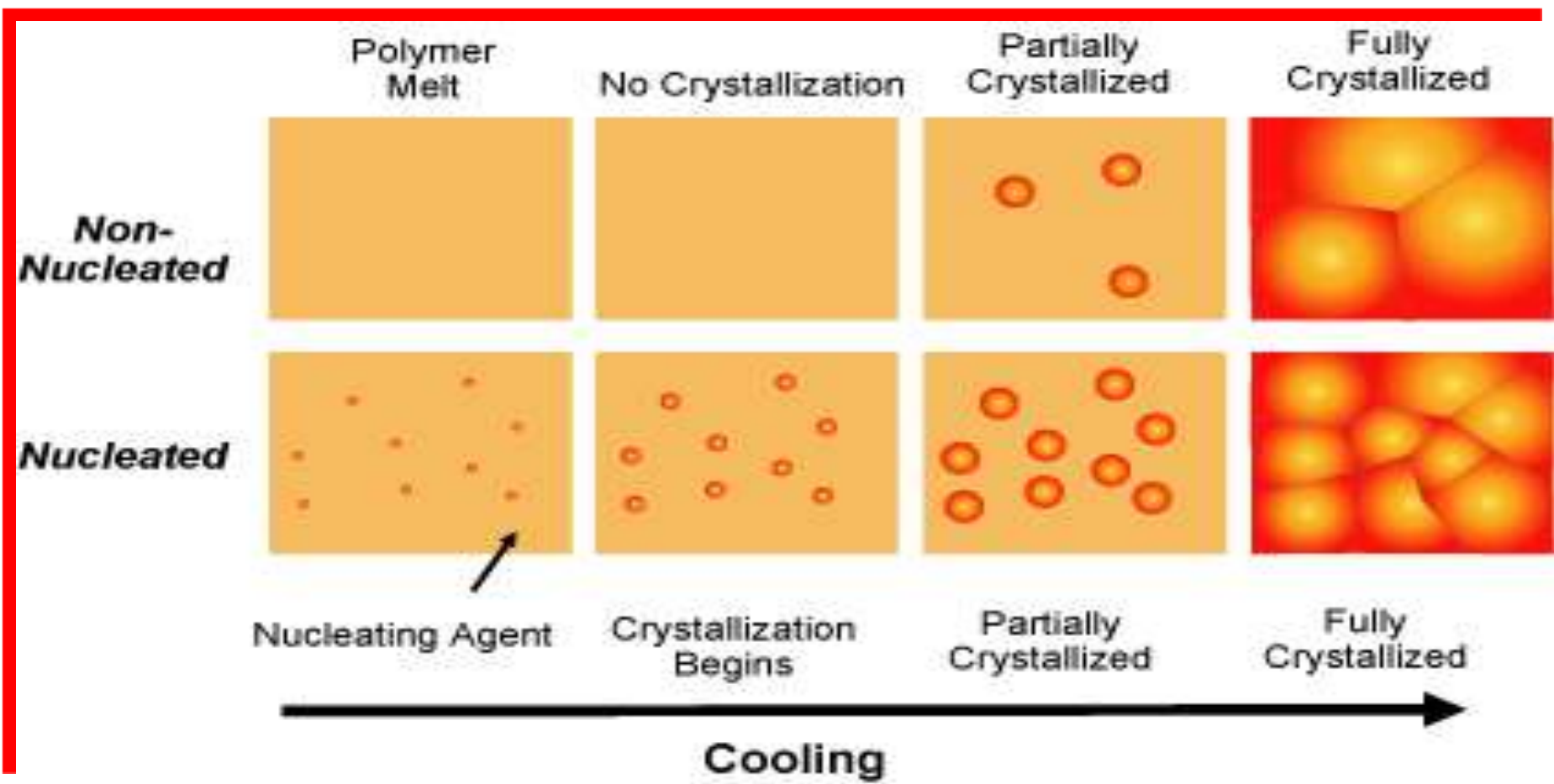
- **Melt Sensitive** Sorbitol based nucleators have discreet melting & boiling points.
- Organic based molecules may display solubility issues in a PP matrix.
- Plate-out of the additive can be a problem with sorbitol nucleators, which can get deposited on the metallic surface of the conversion equipment.
- The compounds are limited by thermal decomposition at elevated temperatures. This decomposition causes two distinct problems
 - Loss of Clarity in PP
 - Formation of aldehyde , which imparts odour to PP

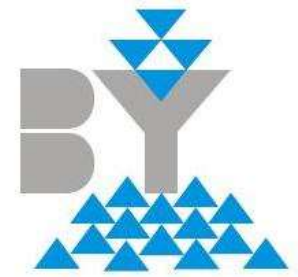
Melt in sensitive Phosphate esters do not have discreet melting points & are not prone to solubility issues in a polymer matrix.

- They are not prone to plate-out problems.
- They have no odour issue.



Mode of Action

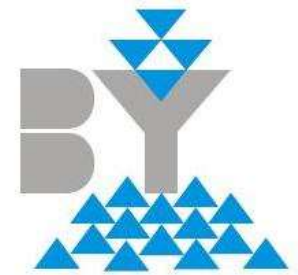




Cycle Time Reduction

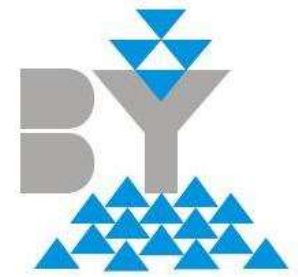
- Nucleating agents increase the temperature at which polypropylene begins to crystallize. The crystallization temperature of a polymer (denoted as "polymer T_c") is measured by differential scanning calorimetry (DSC). As shown in table, each of the nucleating agents increase the polymer T_c of the medium impact copolymer.
- Increases in polymer T_c result in decreases in the cooling time required for part solidification . This improves the overall cycle time of a molding or extrusion process and increases productivity .

Polymer Tc for Nucleating Agent In A Medium Impact PP Copolymer

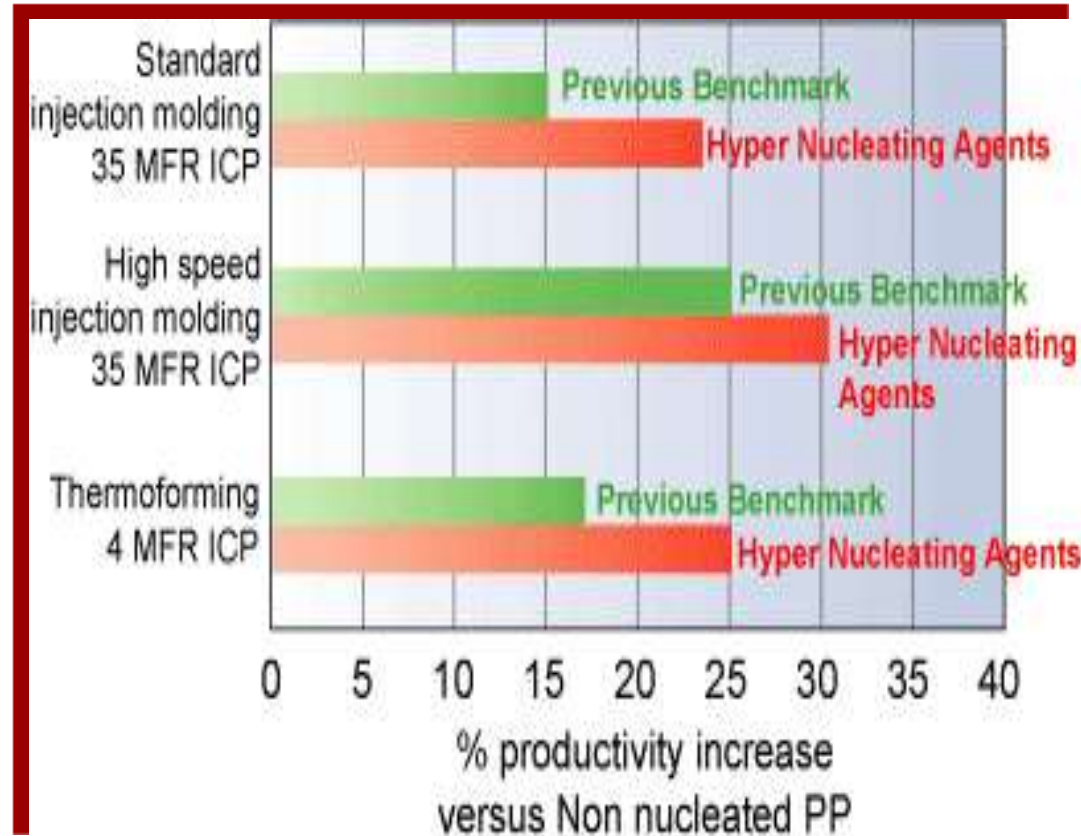


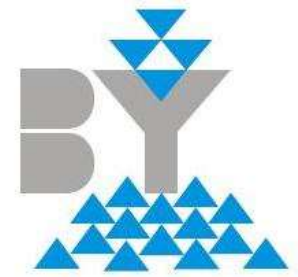
#	Class	Nucleating Agent	Polymer Tc Deg C
1	Control No Nucleating agent	---	109
2	Conventional nucleating agent	Sodium Benzoate	116
3	Hypernucleator	HPN 68 L	127
3	Advanced nucleator	Organophosphate salt (NA11 & NA18)	125

Figure shows typical % of productivity increase of various processes



Hyper Nucleating Agents provide significant cycle time reductions in both injection and extrusion processes. This allows increased productivity which ultimately lower manufacturing costs.

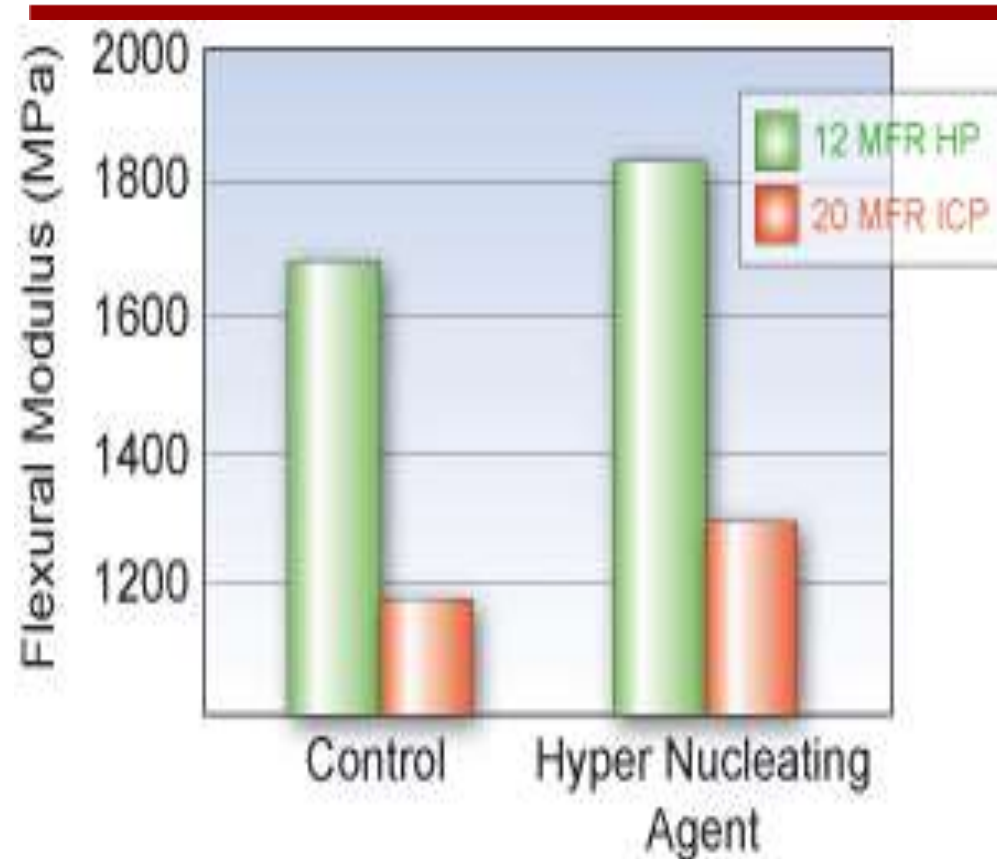




Mechanical Property Enhancement

Stiffness

Flexural Modulus (stiffness) of polypropylene can be improved by the addition of nucleating agents. Typically, nucleating agents increase the stiffness of polypropylene by 10-15% over a non-nucleated control. Data in a 12 MFR HP and a 20 MFR Medium Impact Copolymer are shown in Figure . Flexural Modulus: ASTM D790

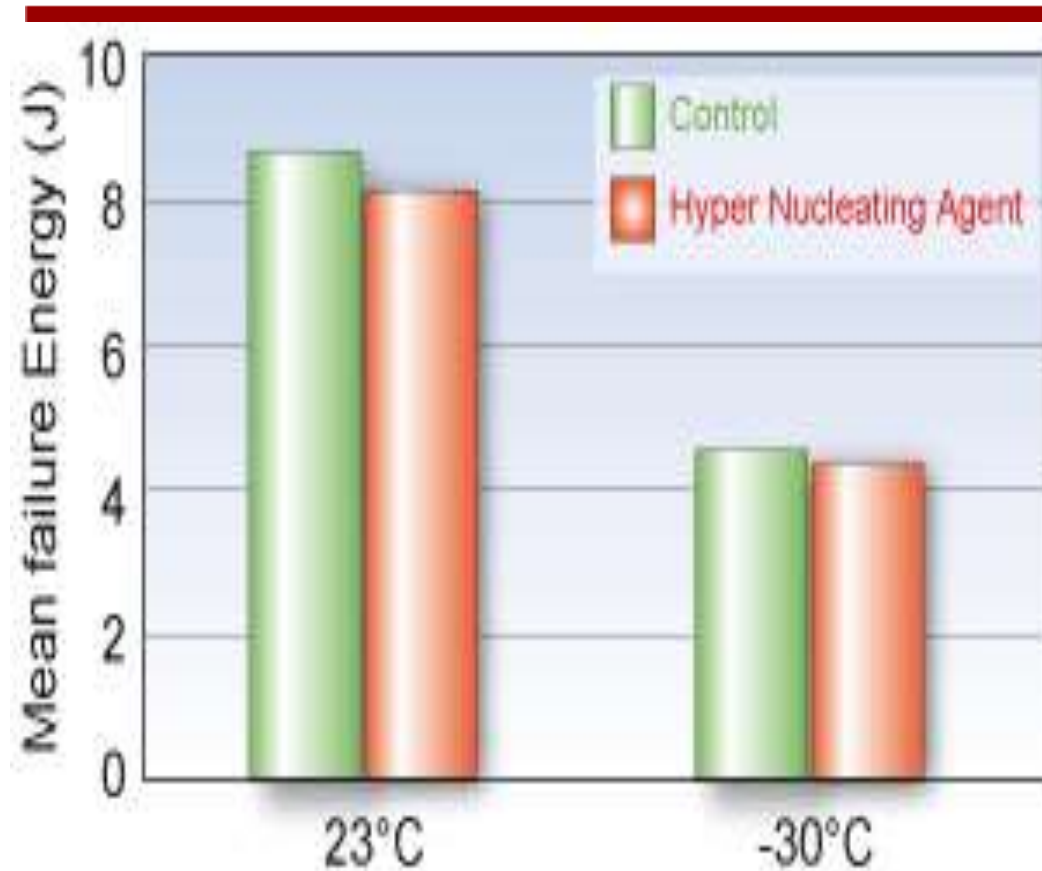




Mechanical Property Enhancement

Impact Resistance

The increase in stiffness due to the addition of nucleating agents is accompanied by a slight decrease in impact resistance. Gardner Impact data in a 20 MFR Medium Impact Copolymer is shown at 23°C and -30°C in Figure. Gardner Impact Resistance: ASTM D5420

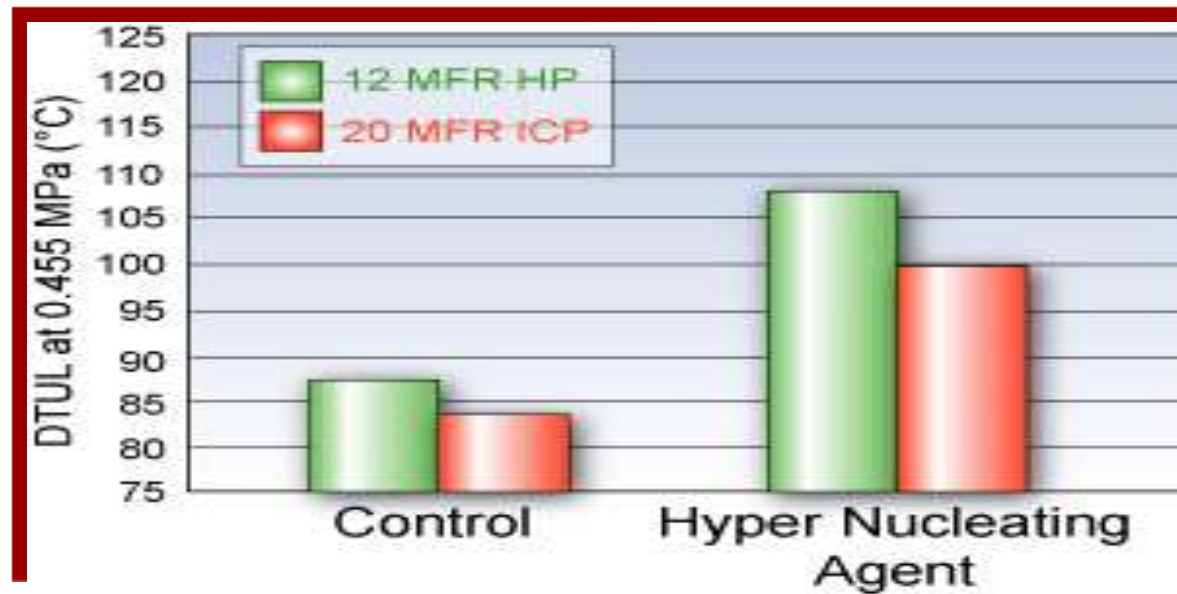




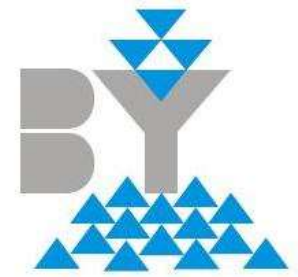
HDT Enhancement

- Hyper nucleating agents increase heat deflection temperatures (HDT) approximately 20 - 25% over a non-nucleated PP and allow to significantly improve polymer resistance to distortion at elevated temperatures.

ASTM D648



Clarifying Agents For PP



- Among the numerous possibilities of material selection in injection molding, blow molding or thermoforming, polypropylene provides a unique balance of benefits such as: low cost, easy processing, high stiffness and low density compared to other polymers or glass.
- As polypropylene is a semi-crystalline polymer, it is naturally translucent or opaque.
- The introduction of additives - called Clarifiers - can make PP highly transparent. The material is then referred to as Clarified PP.
- Clarified PP appears today as an outstanding alternative to other transparent polymers (generally amorphous) or glass. It allows the packaging and medical industries to develop new concepts with a unique combination of properties: transparency, gas barrier, chemical resistance and cost

Clarifying Agents For PP



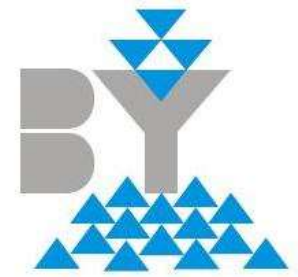
Commercially available clarifiers can be divided into two classes:

- **Melt Sensitive**

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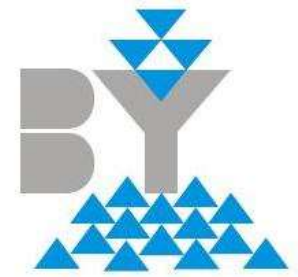


Mechanism

PP Crystallization and Haze

Polypropylene (isotactic PP) is a semi-crystalline polymer.

- The presence of this crystalline structure enhances the stiffness, as well as the mechanical, chemical and thermal resistance of the material.
- PP normally crystallizes slowly and forms relatively large complex crystal aggregates known as spherulites. The growth of these spherulites is generally initiated around microscopic "defects" naturally present in the material. This phenomenon is called nucleation.
- Without Clarifier, the size of these spherulites is generally larger than the wavelength of visible light resulting in light scattering and hazing of the material.

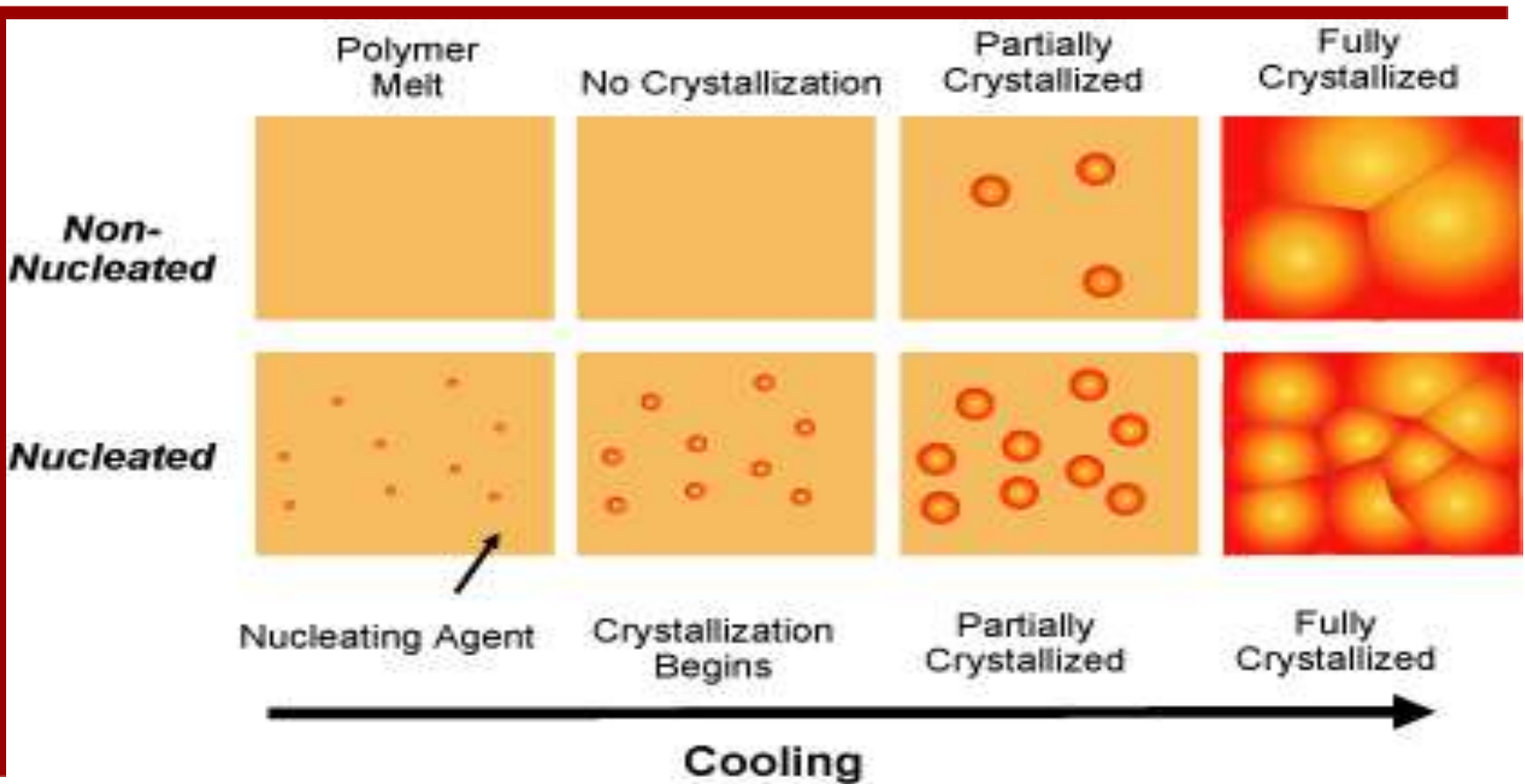
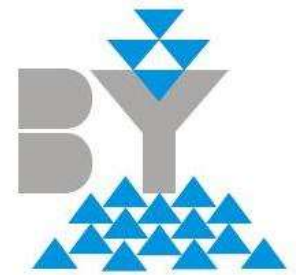


Mechanism

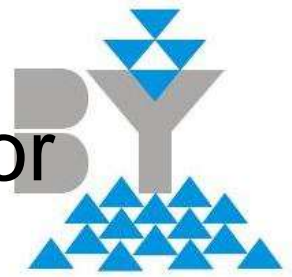
Nucleation and clarification

- Adding a clarifier to PP is equivalent to introducing "artificial defects" in which spherulites can initiate their growth. When PP is clarified, the rate of crystal initiation is increased by many orders of magnitude throughout the polymer. Because many more crystals are growing in the same amount of space, they are all much smaller in size. The result is crystals smaller than the wavelength of visible light that allow light to pass through, imparting enhanced clarity. Figure illustrates the principle of action of clarifier.
- The mechanism of nucleation is very complex and the effect of a clarifying agent depends on numerous parameters like the nature of the polypropylene (homopolymer, random copolymer, block copolymer), the melt index, the polydispersity index, processing conditions and even the polymerisation process.

How does it work?

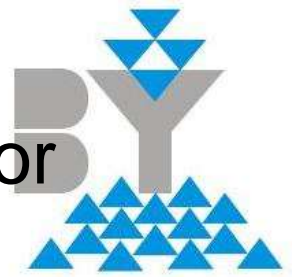


New Trends In Plastic Additives For Packaging Applications



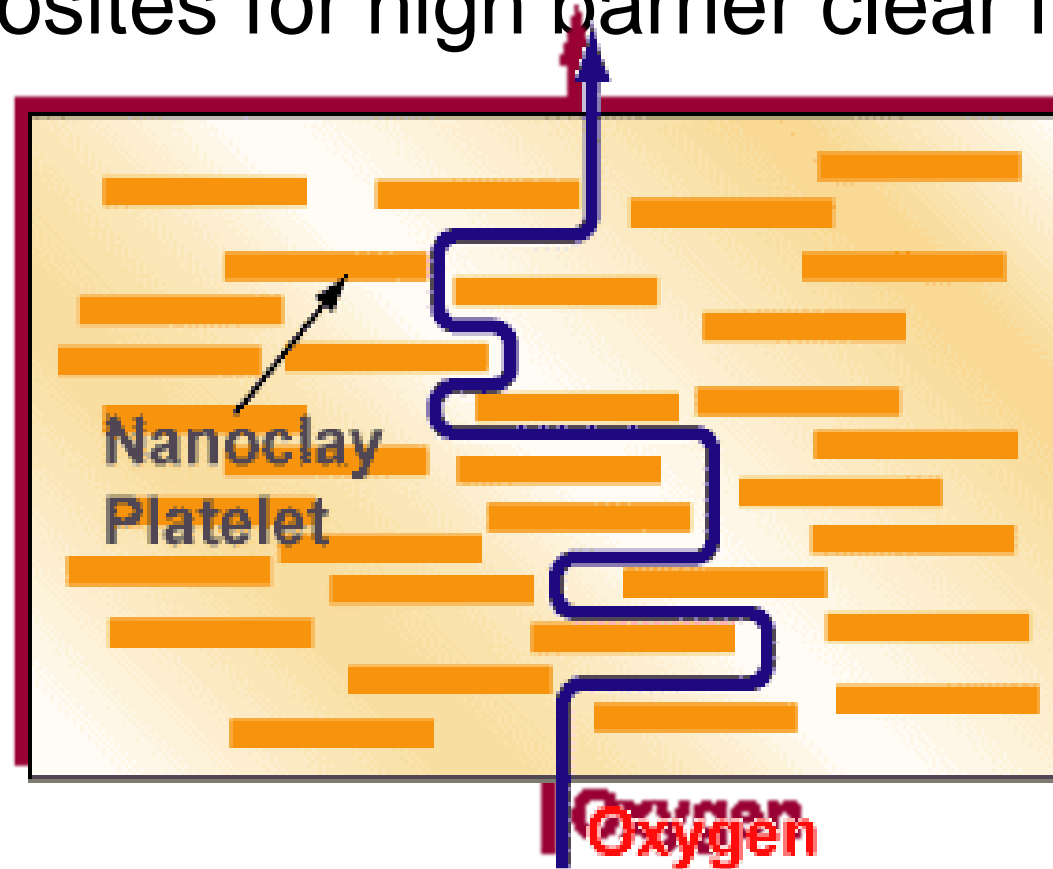
- Plastics additives industry is always looking for new effects and performance like :
 - Barrier properties at low cost
 - UV protection of goods to improve shelf-life
 - Improved shelf-life of foods
 - Permanent antistatic performance
 - Transparent PP products for aesthetic / price ratio
 - Smart and intelligent packaging

Solutions From New Generation Additives For Packaging Applications

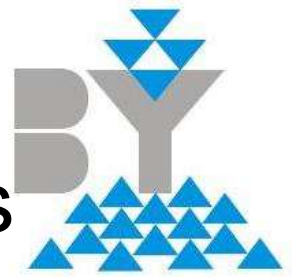


- UV filters for PET bottles
 - Polyether block polyamide copolymers (PEBA) as permanent antistats
 - High barrier properties with nanofillers
- Fresh Keeping Additives
 - Oxygen absorbers
 - Ethylene scavengers
 - CO₂ scavengers and emitters
 - Moisture regulators
 - Antimicrobials
 - Odour scavengers
 - Radical scavengers

Nanocomposites for high barrier clear films



Antimicrobial Additives In Plastics



Expected global growth rate 4% pa

- Applications
- Kitchenware
- Hosiery
- Carpets
- Hospital waste bags
- Refuse containers
- Packaging

PLASTICS IN AGRICULTURE !!

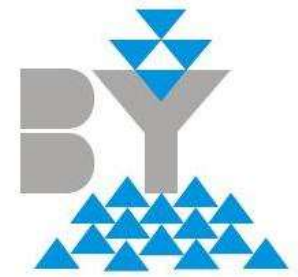


All applications are driven by additives incorporated into polyolefins to meet end use requirements.

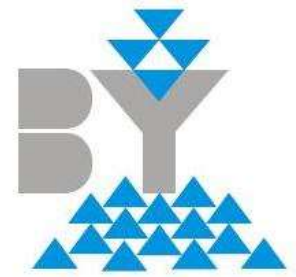
Opportunities in

- Mulch films
- Greenhouse films
- Packaging of fresh agricultural produce

Mulch Films from LLDPE



Mulch Film For Groundnut - Observations



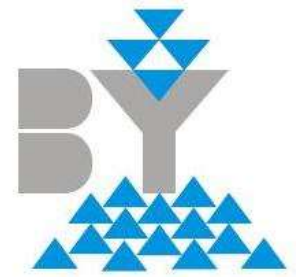
Without Mulch Film



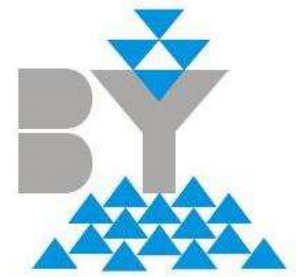
With Mulch Film



Specialty Greenhouse Films From LLDPE



Active Packaging Films Based On LLDPE



- For post-harvest packaging and protection of fresh fruits and vegetables



Looking Ahead !



- Strong additive-driven plastics applications
- Key areas for focus
 - Agriculture
 - Automotive
 - Appliances
 - Packaging



Additives – Truly Miracle Workers For The Plastics Industry !



Thank You