Chemical Primers

A Primer on Primers

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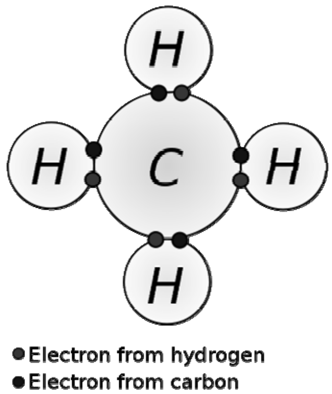
What is a Primer?

- Surface modifier
  - increases surface energy (polarity)
  - facilitates "wet-out" (polarity)
  - adds reactive sites (polarity)
  - cleans & removes contaminants
- Promotes adhesion between a substrate and coating (extrudate, inks, hot melts, etc.)
- Can enhance chemical resistance with certain polymer bases.

Classes of Bonding

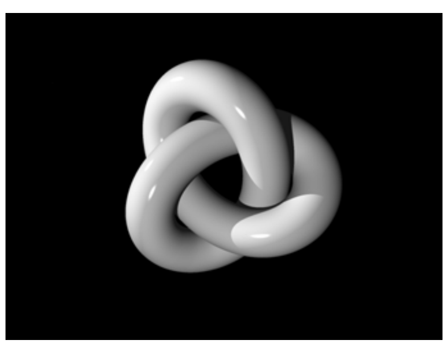
Chemical bonding relies on atomic attractions



Classes of Bonding

Mechanical bonding

(Mechanically-interlocked molecular architectures)

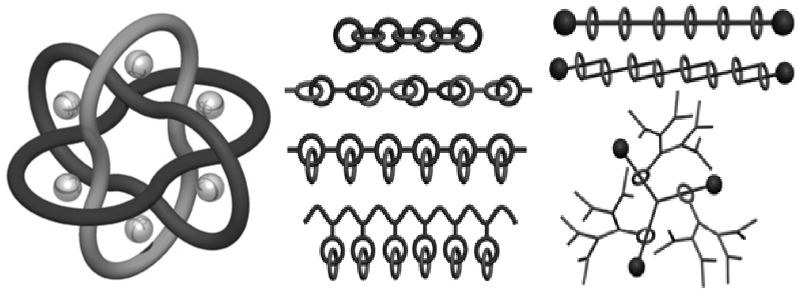


Classes of Bonding

Mechanical bonding relies on physical anchors

The molecules with this type of bonding are similar to a chain link fence.

The links are not directly connected to each other, but the molecules cannot be separated without breaking the loop/molecule.

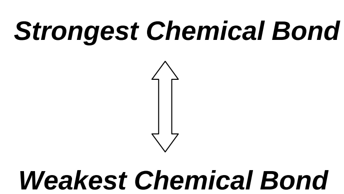


Three Types of Chemical Bonding

Ionic or Covalent Bond

Hydrogen Bonding

Van der Waals forces

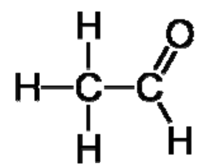


Types of Chemical Bonding

Ionic or Covalent Bond
Strongest Chemical Bond

Oxidation (Direct or Free Radical)

The addition of oxygen to a molecule and/or the removal of hydrogen from a molecule

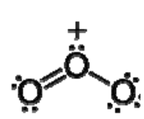
$(CH_2\text{-}CH_2)_n \xrightarrow[\Delta]{O\text{-}O}$ 

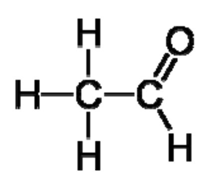
Polyethylene   Oxidized Polyethylene

Types of Chemical Bonding

Ionic or Covalent Bond
(Strongest Chemical Bond)

Ozone - Oxidation (Direct or Free Radical)

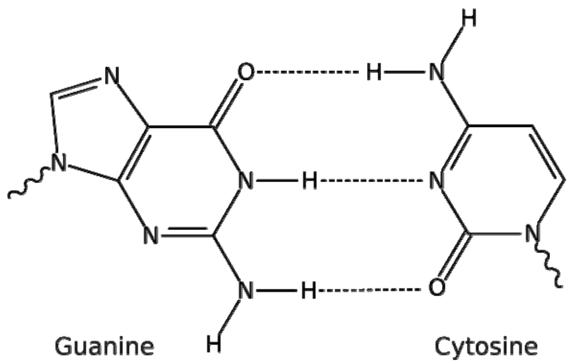


$(CH_2\text{-}CH_2)_n \longrightarrow$ 

Polyethylene   Oxidized Polyethylene

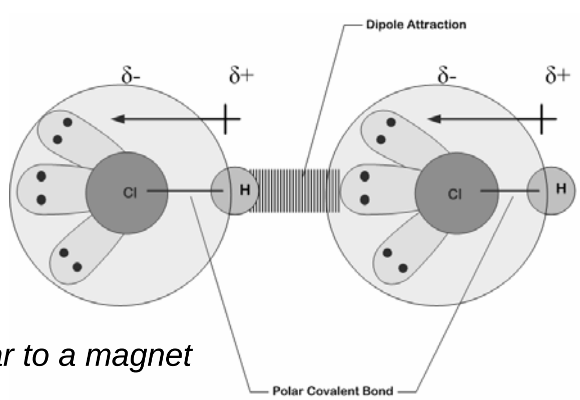
Types of Chemical Bonding

Hydrogen Bonding
(Second Strongest Chemical Bond)



Types of Chemical Bonding

van der Waals Force
Weakest Chemical Bond



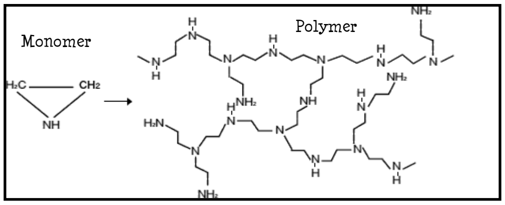
Similar to a magnet

Types of Chemical Bonding

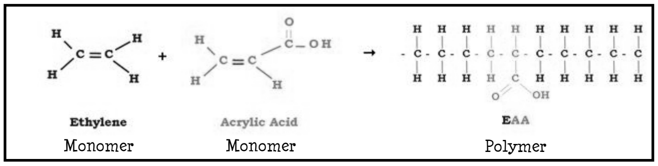
van der Waals Force

Polymers used as a Chemical Primer

Poly(ethylenimine) – PEI



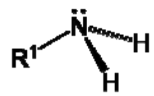
Ethylene acrylic acid copolymer – EAA



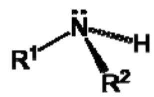
Polymers used as a Chemical Primer

Polyethylenimine (PEI)

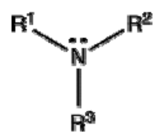
The polymer contains 3 types of amines;



Primary amine:
Polymer chain termination sites



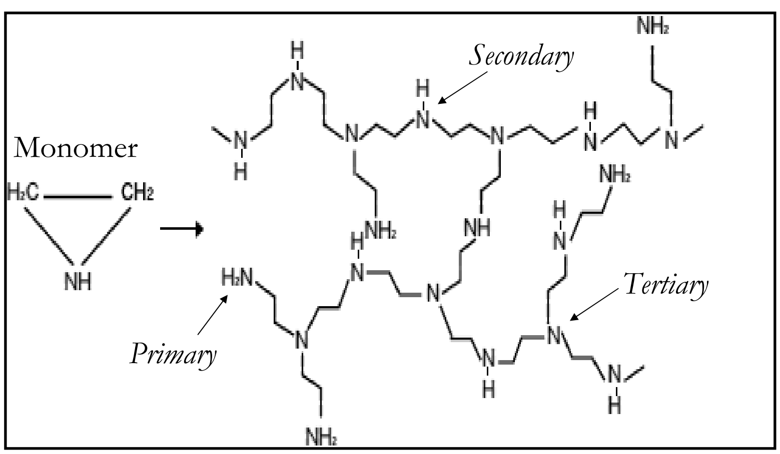
Secondary amine:
Polymer chain extender sites



Tertiary amine:
Polymer chain branching sites

Polymers used as a Chemical Primer

Polyethylenimine (PEI)

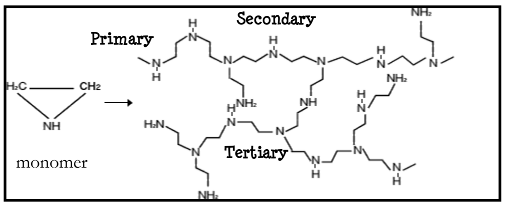


Polymers used as a Chemical Primer

Polyethylenimine (PEI)

The reaction sites for the polymer are the Primary and Secondary amines.

The Tertiary amines are the least reactive amines due to steric hinderance (blocked).



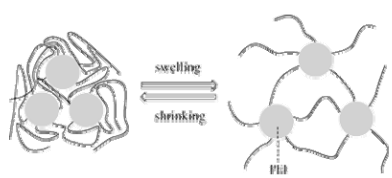
Polymers used as a Chemical Primer

Polyethylenimine (PEI)

Morphology is a Branched, Spherical, cationic polyelectrolyte

Properties include:

- water soluble (lower MW : greater solvent solubility)
- strongly attracted to anionic surfaces
  - i.e. promotes adhesion by creating a charged surface
  - i.e. promotes adhesion to charged surfaces (oxidation)
- pH changes cause polymer swell/shrinkage (steric hinderance)

Increase pH  Lower pH

Polymers used as a Chemical Primer

Ethylene Acrylic Acid Copolymer (EAA)

Form in an aqueous ammonium dispersion

$$R_1 - CH_2 - CH_2 - \underset{\displaystyle COO^-}{\underset{|}{CH}} - CH_2 - CH_2 - R_2 \qquad NH_4^+$$

Acid Form after drying

$$R_1 - CH_2 - CH_2 - \underset{\displaystyle COOH}{\underset{|}{CH}} - CH_2 - CH_2 - R_2 \qquad + NH_3 + H_2O$$

Polymers used as a Chemical Primer

Ethylene Acrylic Acid Copolymer (EAA)

Three important aspects of a high acid (>15%) content EAA:

1) Carboxyl groups (COOH) free to form bonds with any polar substrate (metal, glass, cellulose, polyamides).
2) Carboxyl groups (COOH) on adjacent chains can hydrogen bond with each other, this gives the polymer very good cohesive strength.
3) Carboxyl groups (COOH) bulkiness inhibits crystal growth, that improves optical clarity, reduces melting point and glass transition.

Polymers used as a Chemical Primer

Ethylene Acrylic Acid Copolymer (EAA)

Factors that influence adhesion:

1) Polymer coating can flow (wet-out) over substrate.
2) Polymer coating chemically interacts and attracts molecules on the substrate.
3) Surface condition of the substrate.

   Degree of oxidation

   Metals (aluminum, tin) with strongly bound oxide layers have high bond levels therefore have good resistance to moisture.

   Metals (nickel, copper) with weakly bound oxide layers are more water sensitive, due to the reduced bond level.

Polymers used as a Chemical Primer

Ethylene Acrylic Acid Copolymer (EAA)

Adhesion to various substrates:

- ☺ Excellent adhesion to metals, paper, paperboard, glass, leather, cellophane, nylon 6, nylon 66.
- ☺ Marginal adhesion to plywood and polyurethane.
- ☺ Poor adhesion to SBR, PVC, PVdC, PET, PMMA, PP, PE, PTF, PS, SAN.

Proper steps for Priming

☑ Pre-Treat Substrate

(Proper Surface Energy for specific substrate)

☑ Ensure Proper Coatweight

(PEI based primer: 0.02 – 0.03 dry lbs/ream)

(EAA based primer: 0.10 – 0.20 dry lbs/ream)

☑ Ensure Complete Drying

(Exit Web Temperature between: 140^{o}F– 180^{o}F)

Proper steps for Priming

Pre-Treat Substrate

Increase Surface Energy – ability of substrate to "wet-out", (i.e. evenly coat the entire surface of the substrate).

The Treatment Level should closely match the coating material (primer, ink, adhesives or extrudate) for uniform coverage.

Surface Treatment is especially important with Chemical Primers because it oxidizes the surface of the substrate.

Proper steps for Priming

Recommended Treatment Levels for Typical Substrates

Polyethylene, Polypropylene, Polyester	48-54 dynes
Aluminum Foil	72 dynes
Bi-axially Oriented Nylon	>50 dynes

Inherent Surface Energy Level of Typical Substrates

Polypropylene	29 dynes
Polyethylene (High, Low Density)	31 dynes
Polyester	43 dynes
Nylon	46 dynes

Proper steps for Priming

Watt-Density = Power /(area × time)

US Units: W/(ft^2/minute)

[KW setting × 1000] / [Line Speed (ft/min) × width (ft)]

Example:

Treater output = 3.0 kW; line speed = 450 fpm; Treater width = 5 ft

The watt-density is: (3.0 × 1000)/(450 × 5) = 1.7 W/(ft^2/min)

Important: You must determine optimum watt-density for each film and for each set of running conditions.

Some starting suggestions:

BOPP films: 3.0 – 4.0 WD
OPET films: 1.5 – 2.0 WD
BON films: 0.5 – 1.5 WD
(metric units are factor of 10 higher)

Proper steps for Priming

☑ Pre-Treat Substrate

(Proper Surface Energy for specific substrate)

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(PEI based primer: 0.02 – 0.03 dry lbs/ream)

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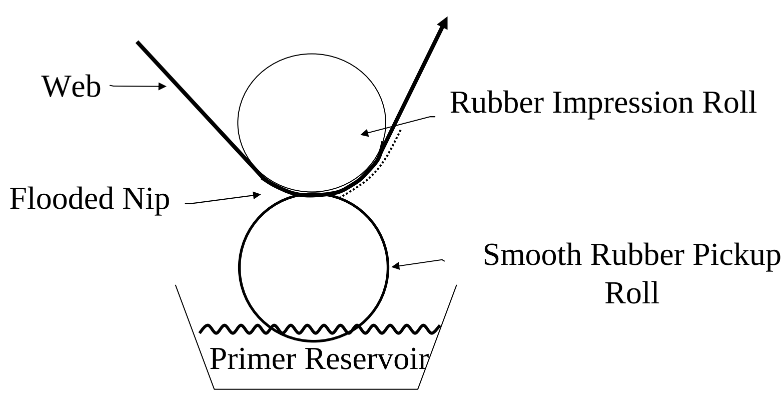
☑ Ensure Complete Drying

(Exit Web Temperature between: 140°F– 180°F)

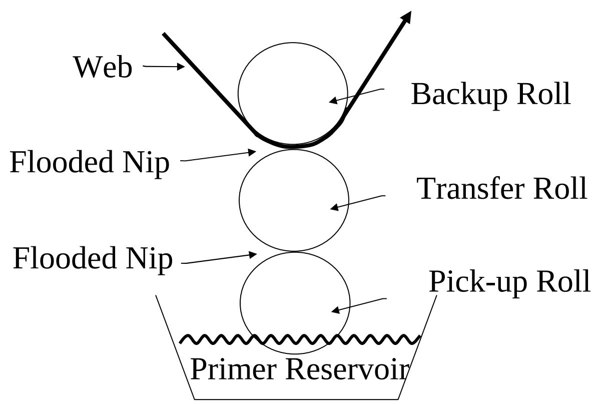
Coating Methods

Smooth Roll Applicator (Direct)



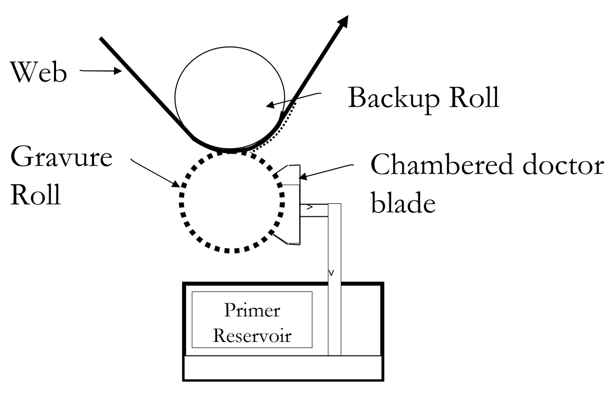
Coating Methods

Smooth Roll (3) Applicator (Indirect)



Coating Methods

Direct Gravure Applicator



Gravure Cylinder – Two types

Ceramic

» Long service life

» Prone to clogging

» Add 15 – 20% cell volume to compensate

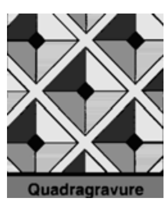
Chrome

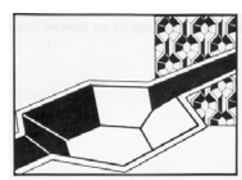
» Easier to clean

» Shorter service life

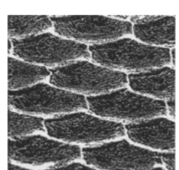
Gravure Cylinder - Cell Geometry

Chrome Roll

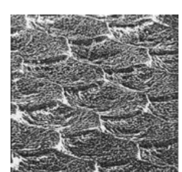




Ceramic
(SEM micrograph)



High Density Ceramic



Original Density Ceramic

Coating Methods

Gravure Cylinder Specifications

When determining the proper cylinder for a primer coat-weight specify the cell volume - not a line count.

Coating Cylinders now have a variety of lines per inch matched with a variety of cell volumes.

Example

PEI based primer for film application

Dilute primer 1:1

Apply 0.02 dry lbs/ream

Possible Gravure Cylinder configurations:

Direct forward gravure, 180 pyramid, 3.2 bcm

Direct forward gravure, 360 pyramid, 3.7 bcm

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(Proper Surface Energy for specific substrate)

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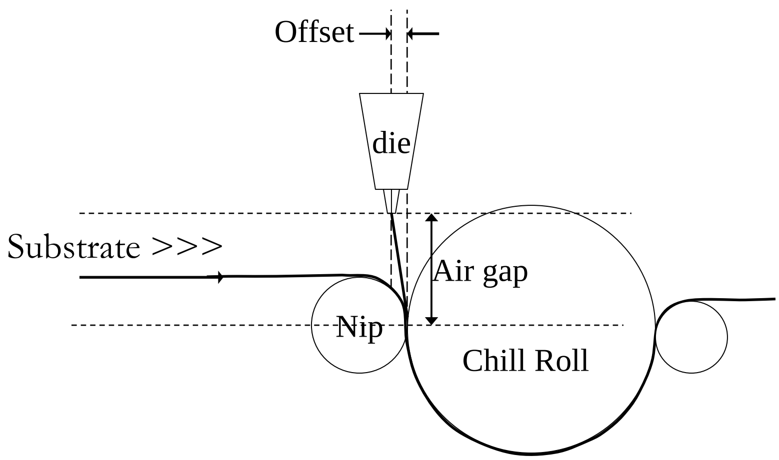
☑ Ensure Complete Drying

(Exit Web Temperature between: 140^{o}F– 180^{o}F)

Extrusion Conditions

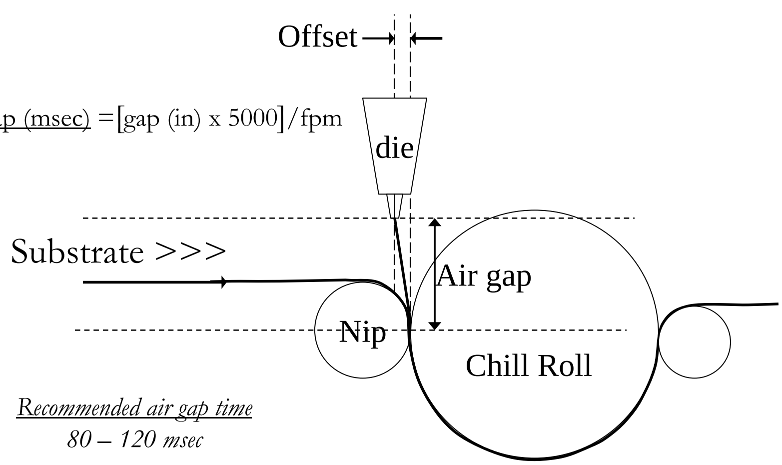
Films & papers; the offset should be ~1cm toward substrate.



Extrusion Conditions

<u>Optimizing Air Gap</u>

<u>Air gap (msec)</u> =[gap (in) x 5000]/fpm

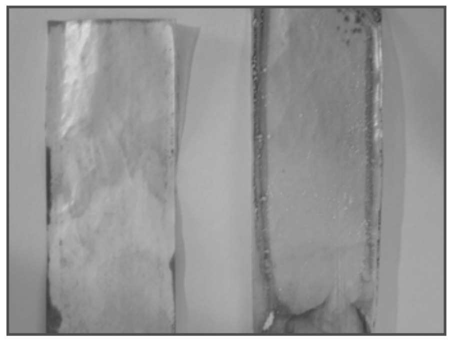


<u>Recommended air gap time</u>
80 – 120 msec

Oxidation Level of Extrudate

Time in the air gap: 60 msec 150 msec

LDPE @ 575ºF
0.918 density, 7 MI



Process Handling of Primers

Don't pump too quickly!

Don't stir too quickly

Watch for oxidation of primer bath (corona)!

Don't expose high pH materials to certain metals
such as; Copper,
Nickel,
Iron,
low quality stainless steel.

Aggressive Agitation and Excessive Air Exposure

Process Handling of Primers

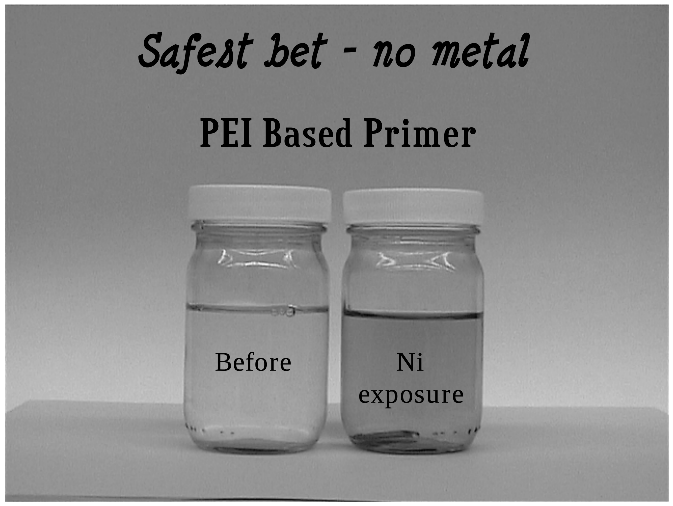
Don't pump too quickly!

Don't stir too quickly!

Watch for oxidation of primer bath (corona)!

Don't expose high pH materials to certain metals
such as; Copper,
Nickel,
Iron,
low quality stainless steel.

Pumps, Pipes, Fittings and Returns



Process Handling of Primers

<u>Corona Treatment precaution</u>:

Improper Corona Treatment can disrupt the film surface and/or cause the film additives to bloom to the surface.

These additives can poison the reactive sites of the primer thereby reducing it's effectiveness.

These film additives will wash off the film into the primer solution entering the recirculation system.

The concentration of these contaminates will increase over the course of a production run.

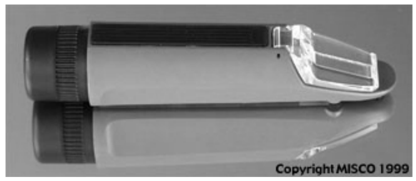
Troubleshooting

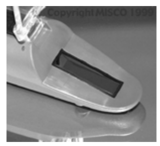
Capatch

The manufacturer of these strips is Steinhart.
For more information go to; www.steinhart.nl or www.capatch.com

Useful Tools

Handheld Refractometer





Problem Solving Session

Some Real World Examples

Problem Solving

Structure: Reverse Printed Polyolefin film/Poly laminate

Problem Solving

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Off-machine bonds: near destructive or very poor

Problem Solving

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Pre-treatment: Corona

Problem Solving

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Extrusion conditions: typical; product is in development stage, initial tests on manufacturing equipment.

Problem Solving

Structure: Reverse Printed Polyolefin film/Poly laminate

Off-machine bonds: near destructive or very poor

Pre-treatment: Corona

Extrusion conditions: typical; product is in development stage, initial tests on manufacturing equipment.

Problem: Bond strength is not consistent. Varies from near destructive to near zero. The ink is lifting off the printed film and going with the extrudate.

Problem Solving

Peel tests:

Sample 1 – poor bond strength

Sample 2 – near destruct bond

Eosin Stain: Stain is masked by the printing (Eosin stains ink).

Problem Solving

Closer look at the samplings;

- Bonds that are near destruct are in areas with little to no ink coverage.

- Bond strengths that are near zero are in areas with almost full ink coverage.

Problem Solving

Cause:

- The ink on the reverse printed film is being re-solvated during the primer application.

- There is too much water soaking into the printed surface and the drying oven conditions are not fully drying the surface.

- Moisture is trapped under the extrudate.

Problem Solving

Structure: Generic Polyester/Poly laminate

Problem Solving

Structure: Generic Polyester/Poly laminate

Off-machine bonds: destructive

Problem Solving

Structure:	Generic Polyester/Poly laminate
Off-machine bonds:	destructive
Pre-treatment:	Corona on pre-treated PET film

Problem Solving

Structure:	Generic Polyester/Poly laminate
Off-machine bonds:	destructive
Pre-treatment:	Corona on pre-treated PET film
Extrusion conditions:	typical; good product has been made for years using these conditions

Problem Solving

Structure:	Generic Polyester/Poly laminate
Off-machine bonds:	destructive
Pre-treatment:	Corona on pre-treated PET film
Extrusion conditions:	typical; good product has been made for years using these conditions
Problem:	After a couple weeks the bond strength is severely dropping off (sample easily peels apart).

Problem Solving

Peel test: less than 50 grams/inch peel strength

Eosin Stain Test:

Staining shows presence of primer

Stain is lifting off PET film and staying with extrudate

Problem Solving

Cause:

Over-treatment of PET film; corona treatment is decomposing film surface creating water-soluble oligimers.

Humidity is attacking the interface and water-soluble oligimers are causing delamination of PET film.

Problem Solving

Structure: Polyolefin film/Poly laminate

Problem Solving

Structure:	Polyolefin film/Poly laminate
Off-machine bonds:	near destructive or very poor

Problem Solving

Structure:	Polyolefin film/Poly laminate
Off-machine bonds:	near destructive or very poor
Pre-treatment:	Corona

Problem Solving

Structure:	Polyolefin film/Poly laminate
Off-machine bonds:	near destructive or very poor
Pre-treatment:	Corona
Extrusion conditions:	typical, except melt temperature is ~590°F; good product made with these conditions for years

Problem Solving

Structure:	Polyolefin film/Poly laminate
Off-machine bonds:	near destructive or very poor
Pre-treatment:	Corona
Extrusion conditions:	typical, except melt temperature is ~590°F; good product made with these conditions for years

Problem: Bond strength is not consistent. Varies from near destructive to near zero.

Problem Solving

Peel test: *Sample 1* - less than 50 grams/inch peel (gpi) strength

Sample 2 – near destruct bond (> 900 gpi)

Eosin Stain:

Stain shows presence of primer

Stain is staying on film surface lifting away from extrudate.

Problem Solving

Sampling:

Review of sampling – sample taken from entire web width and samples taken from operator side, center (2), machine side.

- Bonds near destruct on machine and center.
- Bonds near zero around operator side.

Problem Solving

<u>Cause</u>:

Bad thermocouple on die.

The poor bonding was isolated to one area on the web which was the location of the bad thermocouple.

The thermocouple was causing the heater on the die to drop below the temperature to give the poly proper oxidation in the melt curtain (cold spot).

Chemical Primers

Thank you

PRESENTED BY

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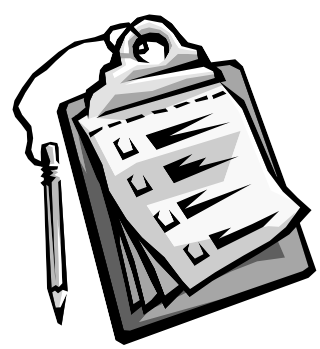

Please remember to turn in your evaluation sheet…