Clear Hard Coat Films via Hybrid Multi-layer (HML) Vacuum Deposition

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Abstract

Hard coat films of the type found in wide variety of applications are traditionally produced by spraying or casting solutions or emulsions onto a surface followed by evaporation of a solvent. Darly Custom Technology is introducing a technique to produce hard coatings on a number of film substrates, PET, PEN, PC, BOPP, etc, which does not require the use of water or solvents. This 100% solids process can duplicate the results of conventional wet chemistry processes at higher line speeds and therefore lower cost. The Hybrid Multi-Layer (HML) process involves vacuum deposition and curing of organic precursors on the surface of a substrate rendering the surface with anti-abrasion characteristics.

Introduction

A hard coat, for the purpose of this discussion, can be defined as a protective polymer applied to a substrate for abrasion, chemical resistance or other surface characteristics. The thickness of the hard coat typically ranges from about 1μ to about 20μ depending on the polymer and the application technique. Today’s hard coats and the substrates on which they are applied are becoming more end-use specific and in many cases, customer specific. Typically, hard coats are used for protection of surfaces in image display apparatuses such as LCD (liquid crystal displays), touch panels, CRT (cathode ray tubes), PDP (plasma display panels), EL (electroluminescence displays) and optical disks.

Traditionally hard coats of the type described above are deposited using solvent or water based formulations to first form a wet coating on the substrate. This wet coating is cured by either driving off the water or solvent thermally and/or curing the coating with a radiation source such as UV or e-beam. There are a number of known problems associated with the deposition and subsequent drying or curing of a solvent based hard coat. Some common defects include: Craters, Scratches, Blisters, Curl, Bénard–Marangoni Cells, Orange Peel, Picture framing, Air Bar Rubs, Mud cracking, Reticulation, Starry Night, Delamination, Cockle, Haze, Spots, Blooming, Drier Bands. Clearly, those that manufacture goods including hard coat films would welcome a replacement for processes creating defects having such colorful names. Also, from an environmental perspective, there is a desire for coating technologies that do not employ solvents, have minimal waste, and are safe to implement. Further, there is the matter of process cleanliness and dust
control that requires all atmospheric coating equipment to reside in a clean room environment.

Darly Hybrid Multi-layer (HML) Hard Coat and Tool

Darly Custom Technology is now introducing the Darly Hybrid Multi-Layer (HML) Vacuum Deposition process for producing hard coatings on various film substrates including, PET, PEN, PC, BOPP, etc, which does not require the use of water or solvents. The HML process, using 100% solids, provides custom designed hard coatings with improved precision and lower costs when compared with the results of conventional wet chemistry processes.

The Darly HML hard coat process involves vacuum deposition and curing of organic precursors on the surface of a substrate rendering the surface with anti-abrasion and other characteristics by design.

Competitive Advantages

The Darly HML process provides significant advantages over typical solvent based processes by producing high quality precision hard coatings at reduced production costs achieved through higher line speeds and without the environmental concerns of solvent based processes. The HML vacuum process provides high quality precision hard coatings without the costs typically associated with clean room environments.

Technology

The HML process is a major objective for the company’s continued growth in hard coat technology. Darly Technology’s work in the development of a hard coating vacuum process that will compete with traditional solution coated hard coats opens the door for Darly Technology for hard coat applications in a wide range of industries.

Following is an outline of some of the common concerns for hard coats and related processes in general. Thereafter, the Darly HML process is described as well as some key advantages of the HML hard coat products and coating process.

Thickness

In a traditional solution hard coat process the wet thickness of the coating is 6-80μ with a typical percent solids loading of 10-25 and the final thickness for solution coating is around 1-20μ. There a many reasons that dictate the need for such thick coatings for the traditional hard coats such as increased abrasion resistance, adhesion of the film to the substrate, control of defects like cracking, shrinkage and curling and control of optical properties. Following, is a brief description of a few of the reasons why the thickness of the hard coat layer is of importance in controlling certain properties of the resultant film.
Adhesion

With traditional solvent-cast hard coat formulations the adhesion between the substrate and hard coat layer can be insufficient due to the limitations imposed by sufficient wetting of the substrate by the solution. If there is a difference in surface energy between the substrate and the liquid coating material, the coating liquid will tend to bead and the uniformity of the coating will decrease. Non-uniformity in the coating thickness will tend to get worse as you try to deposit thinner layers of the wet coating. To overcome the non-uniformity caused by insufficient wetting on the surface, a thicker wet coating is required.

Another way to overcome surface energy ‘matching’ problems is to introduce an additive to the coating liquid that changes the wetting characteristics of the coating. However, additives that increase wetting properties will often reduce the overall abrasion resistance of the resulting hard coat product.

Cracking, shrinkage & curling

Typically organic materials that are hard and have abrasion resistant characteristics are very brittle. As such, cracking can be an issue when depositing these materials onto a flexible substrate. In contrast, soft and flexible organic materials are less prone to cracking defects but cannot supply the necessary hardness attributes desired for a hard coat. Thus, in order to overcome the effects of cracking it is necessary to balance the hard coating formulation using a blend of organic materials that offer good abrasion resistance with organic materials with that are soft and flexible. This blending, however, ultimately degrades the hardness performance of the resulting hard coat product.

Similarly, organic materials that exhibit increased hardness and abrasion characteristics are likely to have a large number of polymerizable functional groups which tend to shrink when cured. This shrinkage creates stress between the substrate and the coating material leading to defects including poor adhesion and curling. For example, a cured coating having good adhesion properties and well adhered to a substrate may tend to curl during a curing process or thereafter, as the substrate conforms to relieve stress between the substrate and the coating. Conversely, if stress from shrinkage is induced on a substrate/coating pair where there is poor adhesion, the coating will simply detach from the substrate. Again, the solution to defects caused by shrinkage is to dilute the coating formulation with precursors that contain fewer polymerizable functional groups. This dilution ultimately deteriorates the hardness characteristics of the final product.

Differential evaporation is another major concern with both organic and water-based solution carried hard coats. Differential evaporation is a phenomenon that occurs when the components of a formulation have different vapor pressures and evaporate from the surface of the film at different rates. This issue can create a number of defects in a finished hard coat film like pinholes, cracking, curling and poor adhesion. Most importantly, the problem of differential evaporation in solution carried coatings, leads to a reduction in critical hardness attributes because the coating formulation must be adjusted to compensate for the different evaporation rates.
Control of optical properties

Haze, transmission and reflection are also common problems associated with hard coat films used for optical applications. Haze is created when a hard coat film has surface roughness that causes light to scatter making it appear dull. Typically the transmission of light through an optical grade PET is between 88-94% VLT (visual light transmission), thus, it is critical that the hard coat layer does not reduce the light transmission of the base film. And finally, reflection of light back from the surface of the hard coat film also reduces the optical quality of the film by producing glare.

Advantages of the Darly HML Hard Coat Process

The Darly HML hard coat process including vacuum deposition of organic precursors directly on to a moving web can eliminate most of the problems described above and lessen the effects for others.

Thickness

The HML process which includes evaporation and deposition of 100% solids in vacuum results in hard coat films having thicknesses controlled to precise design specifications between about 0.1 μ to about 20 μ and within +/- 50 nm.

Adhesion

In the HML process an organic coating material is delivered to the surface of the substrate as a gas resulting in intimate contact between the coating material and the substrate. The interaction between the gas and substrate is affected less by the surface energy of the substrate resulting in a uniform coating formed by the condensing vapor. As the vapor condenses onto the substrate it is immediately cured and cross-linked by a radiation source (within nanoseconds depending upon the web speed). Thus, these two factors, gas interaction with the substrate, and speed of curing, alleviate many of the adhesion issues between the substrate and the coating layer often found in solution based coatings.

Cracking, Shrinkage and Curling

The HML process can also greatly reduce the above-identified problems of cracking, shrinkage and curling associated with solution coating. Using the Darly HML process, multiple individual layers can be deposited on a substrate to form a layered structure. The multi-layer hard coat film has the advantage of segregating the required characteristics of the hard coat into discrete layers each providing a specific functionality. For example, in one scenario a leveling/adhesion layer can be deposited on to the surface of the substrate. This leveling/adhesion layer is composed of a soft, conformable material that is better matched to the surface energy of the substrate thus providing better adhesion and surface wetting using a very thin layer. Also, the leveling/adhesion layer supplies a cushion on which a subsequent hard coat layer is deposited creating a mechanism to relieve the stress associated with shrinkage occurring from curing the harder, stiffer organic hard coating materials. In the Darly multi-layer hard coat film, the soft, pliable adhesion layer reduces
the stress between the substrate and the hard coating material thereby reducing or eliminating typical problems of shrinking and curling.

**Differential evaporation**

Unlike atmospheric coating processes that require the evaporation of a solvent, the HML process delivers 100% solids in unaltered formulations to the substrate surface without diluting the concentration of the formulation components. The Darly technique vaporizes all components equally and subsequently delivers them to the substrate surface without a change in the component ratio. This enables the chemist a greater range of formulation design flexibility and opportunities for custom blending of components to produce a stable hard coat product to avoid defects like adhesion, cracking, shrinking curling, etc…

**Control of optical properties**

In the same way the HML technique affords greater formulation flexibility for solving physical coating problems, greater control of optical properties can be achieved using this method. Reflection in a film, for example, is a result of poor refractive index matching between the base film substrate and the hard coating. By having a greater range of chemistry from which to choose to develop formulations, the chemist has the ability to match the refractive index of the coating materials and substrate. Also, it is know that alternating layers of high and low refractive index materials can reduce reflection in a film. Again the Darly HML method affords the use of a wider range of materials with high and low RI’s than the traditional solvent coating methods.

### Comparison of Atmospheric vs. HML vacuum coated HC’s

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Atmospheric</th>
<th>HML Vacuum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Use of silica or other inorganic particles</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Viscosity limitations</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Typical solids loading in a solvent</td>
<td>1-100%</td>
<td>100%</td>
</tr>
<tr>
<td>Wet coat weight</td>
<td>5-80μ</td>
<td>0.1-2μ</td>
</tr>
<tr>
<td>Final thickness</td>
<td>1-20μ</td>
<td>0.1-2μ</td>
</tr>
<tr>
<td>Average Line Speed</td>
<td>1-300 m/m</td>
<td>1-1000 m/m</td>
</tr>
<tr>
<td>Curing method</td>
<td>Thermal, UV &amp; E-Beam</td>
<td>UV &amp; E-Beam</td>
</tr>
</tbody>
</table>
The Darly HML Tool and Process

The Darly HML Vacuum Coating Tool includes the following specifications:

- Substrate width up to 36 inches with an available coating width of 34 inches
- Substrate roll diameter is 12 inches on a 6 inch core
- Dynamic speed range 1 – 1000 m/min
- Coating stations can be operated sequentially or independently
- Bi-directional web, coating sequence can be repeated for a multilayer structure
- Web system is designed to minimize contact of the coated surface
- Compatible with many flexible substrates

Process Schematic

The HML Deposition Process

A polymer film is fed from the unwind roller onto the rotating drum, which rotates in the direction shown by the arrow. As the film is unwound it passes through a plasma treatment unit to remove adsorbed water, oxygen, and any low molecular weight species before deposition of an organic coating material.

The rotating drum is cooled to a temperature that corresponds to the particular organic precursor being used to insure the condensation from vapor to liquid form. Typically, the drum is rotated at a speed equal to the film between about 0.1 to 1000 meters per minute.
The organic precursor(s) is then deposited on the film via a vaporizer which is supplied with liquid precursor where the monomer liquid coating material is instantly vaporized. The vaporized precursor(s) condenses on the surface of the polymer film positioned adjacent the cooled drum where it forms a thin organic film. The condensed liquid coating material is then radiation-cured using an electron beam gun (e-gun). The e-gun directs a flow of electrons onto the organic layer of the coating material curing the material to a cross-linked film. Subsequently, a second organic layer can be deposited on top of the first layer in serial stations of the HML tool, in the same manner described above.

Conclusion

Darly HML hard coatings deposited on various substrates provide a real alternative to conventional solvent and water based coating processes. The method provides custom designed hard coatings with improved precision and lower costs when compared with conventional wet chemistry processes. The completely enclosed vacuum chamber is environmentally friendly, inherently clean and does not employ solvents. Coatings can be applied at high speeds with a relatively low energy consumption that is cost competitive with mature liquid based coating technologies.