ABSTRACT

Blocking is a common problem encountered by manufacturers of polyolefin films and coatings. There is an array of antiblock types available. This overview covers the fundamental reasons for considering and using antiblock additives. A review of the most commercially important grades is offered with general guidelines relative to the user’s needs. Natural silica (diatomaceous earth) and talc prove to be of greatest interest for most commodity applications.

INTRODUCTION

Blocking is the adhesion of two adjacent layers of film. It is a problem most associated with polyethylene and polypropylene films (either blown or cast) and to a lesser extent in extrusion coated or laminated products.

It is thought that blocking of adjacent film layers occurs due to the presence of Van der Waal's forces between the amorphous regions of the polymer. These forces increase with reduced distance between the two layers, thereby increasing blocking when two layers are pressed together (e.g. winding onto a takeup roll or stacking of finished, converted films). Another possible reason for blocking is the presence of low molecular weight species (such as oligomers), which tend to migrate to the surface of the film.

The most effective method for combating these handling issues is to add an antiblock additive. An antiblock additive present in the resin microscopically protrudes from the film surface. This creates asperities (i.e. “little bumps”), which help to minimize the film-to-film surface contact, increasing the distance between the two layers, thereby minimizing blocking.

The blocking between adjacent layers results in increased friction (resistance to motion) and the addition of an antiblock generally contributes to a reduction in the film-to-film coefficient of friction (COF). COF is a measure of the relative difficulty with which one surface will slide over an adjoining surface. The greater the resistance to sliding, the higher the COF value (e.g. ‘low-slip’ or ‘no-slip’ film, sometimes referred to as ‘high COF’ film.)
Test Methods

The standard test method for testing blocking between layers of plastic film is ASTM 3354-89. By this method, the film-to-film adhesion is expressed as the load (in grams) required to separate two layers of polyethylene film. The test is limited to a maximum load of 200 grams. This is measured by a balance-beam type system similar to an analytical balance. One sheet of film is attached to a block suspended from the end of the balance beam. The other sheet of film is attached to a block fastened to the balance base. Weight is added equivalent to 90 ± 10 g/min to the other side of the beam until the two films fully separate, or until they reach 1.905 cm separation.

The standard test method for testing COF is ASTM 1894. This method covers the measurement of static COF, which is related to the force required to begin movement of the surfaces relative to each other, and kinetic COF, which is related to the force required to sustain the movement. Film-to-film values are measured by attaching a film to a stationary sled (a 200 gram weight), and attaching another film to a moving plane. These two films are then pulled across each other at a specified rate (6 inches/min). The force measured (in grams) is then divided by the weight of the sled to yield a dimensionless number between 0.0 and 1.0.

AVAILABLE MATERIALS

Commercially important antiblock additives can be broken down into inorganic and organic types.

Inorganic

These are non-migratory additives useful for high temperature applications since they melt at much higher temperatures than typical polyolefin extrusion temperatures. The particle size and shape of the additive (as well as quality of dispersion) play a key role in determining its antiblocking efficiency. Proper selection of additive type depends somewhat on the gauge (thickness) of the film. Inorganics are relatively inexpensive and best positioned for large volume, commodity-like applications.
Table 1 summarizes the variety of inorganic materials typically considered for antiblock use.

**Table 1. Commercially Important Inorganic Antiblocks**

<table>
<thead>
<tr>
<th>Type</th>
<th>Chemical Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Silica (DE)</td>
<td>Silicon Dioxide (SiO₂) - Mined</td>
</tr>
<tr>
<td>Talc</td>
<td>Magnesium Silicate - Mined</td>
</tr>
<tr>
<td>Synthetic Silica</td>
<td>Silicon Dioxide - Manufactured</td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td>Calcium Carbonate (CaCO₃) - Mined</td>
</tr>
<tr>
<td>Ceramic Spheres</td>
<td>Alumina-silicate ceramic - Manufactured</td>
</tr>
<tr>
<td>Kaolin/Clay</td>
<td>Aluminum Silicate - Mined</td>
</tr>
<tr>
<td>Mica</td>
<td>Aluminum Potassium Silicate - Mined</td>
</tr>
</tbody>
</table>

**Organic**

Organic antiblocks are migratory in nature and are thought to crystallize on the film surface, forming interfering layers between the adjacent film layers. Organic antiblocks are of interest in high clarity films and “release” applications (such as for rubber bales or sticky food items). Sometimes the terms “organic antiblock” and “release agent” are used interchangeably. As a general rule, organic additives are orders of magnitude more costly and therefore of greater interest in higher value-added applications.

Table 2 summarizes a variety of organic materials that can be considered for release applications.

**Table 2. Some Organic Antiblocks of Commercial Interest**

<table>
<thead>
<tr>
<th>Type</th>
<th>Example:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis-amide</td>
<td>Ethylene bisstearamide (EBS)</td>
</tr>
<tr>
<td>Secondary Amide</td>
<td>Stearyl erucamide</td>
</tr>
<tr>
<td>Primary Amide</td>
<td>Stearamide, erucamide</td>
</tr>
<tr>
<td>Organic Stearate</td>
<td>Glycerol monostearate (GMS)</td>
</tr>
<tr>
<td>Metallic Stearate</td>
<td>Zinc stearate</td>
</tr>
<tr>
<td>Misc.</td>
<td>Silicone, PTFE</td>
</tr>
</tbody>
</table>
Table 3 provides an overview of the sizes and shapes of inorganic antiblocks. It's important to remember that when dealing with particles, a distribution of particle sizes actually exists. The term “topcut” refers to the largest particles found within a given material's particle size distribution. For example, a typical antiblock grade of “DE” (diatomaceous earth or natural silica) can possess a topcut of 44 microns (µ). Consider that a commonly produced polyethylene film is often 25 µ. It’s not difficult to envision that a single DE particle can extend beyond the plane of both surfaces of the film.

It stands to reason that the more irregular the shape, the more effective an inorganic particle should be in affecting antiblock properties (given the need to create asperities.) The reverse argument would be that spherical shapes should be least efficient in maximizing the number of protuberances or microscopic mechanical surface imperfections.

Natural silica (or more specifically, diatomaceous earth/DE) and talc therefore appear to be best suited for efficient antiblocking given their irregular shapes.

<table>
<thead>
<tr>
<th>Type</th>
<th>Median Particle Size (µ)</th>
<th>Particle Shape</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Silica</td>
<td>4-8</td>
<td>Angular, irregular</td>
<td>yellowish white to grey</td>
</tr>
<tr>
<td>Talc</td>
<td>2-5</td>
<td>Platy</td>
<td>white to yellow</td>
</tr>
<tr>
<td>Synthetic Silica</td>
<td>4-5</td>
<td>Irregular sphere</td>
<td>White</td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td>2-3</td>
<td>Spherical</td>
<td>white to yellowish white</td>
</tr>
<tr>
<td>Ceramic Spheres</td>
<td>4-7</td>
<td>Spherical</td>
<td>white to gold to grey</td>
</tr>
<tr>
<td>Kaolin/Clay</td>
<td>2-4</td>
<td>Platy, hexagonal</td>
<td>White</td>
</tr>
<tr>
<td>Mica</td>
<td>&gt;10</td>
<td>Platy</td>
<td>yellowish white to black</td>
</tr>
</tbody>
</table>

Once cost, color, and availability of appropriate particle size distributions are applied to the above list of inorganic antiblock candidates; we discover that essentially 3 primary candidates remain for meeting most North American film applications: natural silica (SiO2), talc, and calcium carbonate (CaCO3).
Some key properties of these inorganics are found in Table 4.

Table 4. Chemical and Physical Properties of Potential Antiblocks

<table>
<thead>
<tr>
<th>Property</th>
<th>SiO2 (%)</th>
<th>Talc 60-63</th>
<th>CaCO3 &lt;1</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2 (%)</td>
<td>93</td>
<td>60-63</td>
<td>&lt;1</td>
</tr>
<tr>
<td>MgO (%)</td>
<td>&lt;1</td>
<td>31</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Fe2O3 (%)</td>
<td>1-3</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Acid Resistance</td>
<td>Good</td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td>Alkali Resistance</td>
<td>Good</td>
<td>Good</td>
<td>Fair</td>
</tr>
<tr>
<td>pH</td>
<td>10</td>
<td>9</td>
<td>9.5</td>
</tr>
<tr>
<td>Mohs Hardness</td>
<td>7-8</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.48</td>
<td>1.59</td>
<td>1.60</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>2.3</td>
<td>2.8</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Some of the more important properties to consider when encapsulating inorganics within a polyolefin film include: iron content (Fe2O3), hardness, refractive index and specific gravity (often referred to simply as “density” - not to be confused with bulk density, which is a measure of how particles and pellets pack together in a given volume).

High iron content can accelerate degradation of organic components (such as slip or antistat additives within the polyolefin) or eventually the polyolefin itself. Iron is a transition metal, which can act as a catalyst for various chemical reactions. In this area, talc and CaCO3 are expected to be least likely to participate in organic degradation. (For example, when an aged antiblock concentrate or combined slip/antiblock concentrate begins to exhibit odor or rancidity, it is generally believed that the iron component of DE has catalyzed some degradation reaction).

Hardness can have implications on machine wear. This is of primary concern to the concentrate (i.e. masterbatch) producers as it is their equipment that is exposed to the raw inorganics at very high levels. At typical film production levels, one might see minimal wear effects from the harder DE vs. talc and/or CaCO3.

Refractive index differences between inorganic particles and the surrounding polyolefin determine the additives impact on clarity or haze. For some film applications this may be of importance. Polyethylene has a refractive index of 1.5 and therefore DE should be almost ‘invisible’. (The topic actually becomes much more complicated when numbers of particles and particle size distribution are taken into account.)
Specific gravity can impact film yield for the film producer. As denser materials are added to a nominal 0.920 gm/cc polyolefin, apparent throughput is increased (kg/hr) meaning that if gauge is held constant, a given area of film will weigh more. Film producers are familiar with this concept as they are adept at calculating such yields on the basis of producing an almost infinite number of resin blends (e.g. HDPE w/ LDPE or medium density grades of LLDPE.)

A study was conducted to try and better understand which of the major antiblock candidates proved most effective in a common film recipe.

**EXPERIMENTAL**

Three concentrates were chosen for the study to be added to the film:

1. 20% DE in an LDPE carrier.
2. 50% talc in an LLDPE carrier.
3. 70% CaCO3 in an LLDPE carrier.

Films were blown on a Killion lab-sized film line adding these masterbatches at a rate to yield 2500, 5000, 7500, and 10,000 ppm of the antiblock in the final film. The CaCO3 was also evaluated at 20,000 ppm (2%).

The concentrates were let down in a blend of 75% 2 MI octene-LLDPE/25% 2MI LDPE. Both resins were barefoot. The films were all blown at an approximate thickness of 0.8 - 0.9 mils.

Blocking force was measured as described above using ASTM 3354-89.
RESULTS & DISCUSSION

Figure 1. Antiblocking Effectiveness as a Function of Antiblock Type and Level

As Figure 1 indicates, irregularly shaped DE and talc outperform the smaller, more spherical particles of CaCO3. While calcium carbonate proved to behave as an antiblock vs. the control film, it is apparent that much greater levels (250-300%) are required for performance equivalent to DE and talc. This would be expected to increase haze (reduce clarity) as well as possibly deter from physical properties of the film. More studies have been conducted to better understand the role of these inorganics in optical and physical properties of films. They are the subjects of another paper.

SUMMARY & RECOMMENDATIONS

Diatomaceous earth and talc prove to be the most efficient antiblocks currently available. Indications are that talc may be the antiblock of choice if the lowest cost/performance ratio is desired. DE appears to offer the most promise for minimizing total inorganic content and therefore potentially minimizing negative optical properties (i.e. haze.)

For more information, please contact Ampacet’s technical support team at 888-822-7546 or 812-466-9828.

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