Crodamide™
Easier processing & handling of polymers

Reasons to buy
• Optimum slip & anti-block performance
• Security of supply
• Consistent product quality

At the heart of better plastics

CRODA
Polymer Additives
Easier processing & handling of polymers

Today’s Crodamide additives for polymers offer processors and end-users more flexibility, greater performance and better quality plastics than ever. Croda is a world leading supplier of slip and anti-block additives, having over 30 years’ experience of production, applications and research in this area.

As a speciality polymer additives company, achieving tailored slip performance via the optimisation of product combinations has become one of Croda’s technical strengths, and is an exciting area of development for the polymer additives team. By understanding additives at the molecular level, from the seed growing stage onwards, we can offer a superior range of primary amides, secondary amides and secondary bis-amides with precisely controlled functionality.

From seed to plastics additive

Croda is a leading contractor of high erucic rapeseed oil (HERO) crops which are grown best in temperate climates. Croda’s crops are grown exclusively for industrial uses, thereby ensuring security of supply of this vital raw material for plastics. Long-standing commercial relationships with growers mean we are also able to specify the seed variety required to produce fatty acid amides with optimal performance benefits.

An ongoing multi-million Euro investment program puts Croda at the forefront of amide manufacturing technology. Our production infrastructure includes two Crodamide plants, allowing full integration of processes - from raw material to packaged finished product - and guaranteeing production volumes.

We offer a wide range of Crodamide products globally that have been optimised for the demands of individual application areas. The Crodamide range is subject to stringent quality control procedures during and after manufacture; SQC data on key variables can be provided on request.

“Croda’s HERO is grown under contract by reliable agriculturalists offering greater security of supply”

Understanding additives at the molecular level:

† Image: Rapeseed at very high magnification  
- Croda’s proprietary seed selection is specially grown for its particular fatty acid distribution & resulting slip properties
Product range

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Description</th>
<th>Physical form at 25°C</th>
<th>Raw material origin</th>
<th>Key effects &amp; recommended uses</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>High slip</strong></td>
<td></td>
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</tr>
<tr>
<td>Crodamide ER</td>
<td>Erucamide</td>
<td>Bead/Microbead/Pastille/Powder</td>
<td>Vegetable</td>
<td>Slip/release in polyolefins, also PVC and many other polymers. Crodamide OR is also used as a process aid in WPC</td>
</tr>
<tr>
<td>Crodamide VRX</td>
<td>Oleamide</td>
<td>Bead/Powder</td>
<td>Vegetable</td>
<td></td>
</tr>
<tr>
<td>Crodamide OR</td>
<td>Oleamide</td>
<td>Microbead/Pastille/Powder</td>
<td>Non-vegetable</td>
<td></td>
</tr>
<tr>
<td>Crodamide ORX</td>
<td>Oleamide</td>
<td>Microbead/Pastille</td>
<td>Non-vegetable</td>
<td></td>
</tr>
<tr>
<td><strong>Medium slip</strong></td>
<td></td>
<td></td>
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<tr>
<td>Crodamide 203</td>
<td>Oleyl Palmitamide</td>
<td>Bead</td>
<td>Vegetable</td>
<td>Medium or controlled slip in polyolefins, especially useful in laminated or co-extruded structures. Also slip in ionomers and other ethylene copolymers</td>
</tr>
<tr>
<td>Crodamide 212</td>
<td>Stearyl Erucamide</td>
<td>Bead</td>
<td>Vegetable</td>
<td>Medium or controlled slip in polyolefins, especially useful in laminated or co-extruded structures. Also slip/release for nylon (polyamides); process lubrication for engineering polymers</td>
</tr>
<tr>
<td><strong>Low slip &amp; anti-block</strong></td>
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<tr>
<td>Crodamide BR</td>
<td>Behenamide</td>
<td>Bead</td>
<td>Vegetable</td>
<td>Anti-block in polyolefins, also mold release. Crodamide SR is used as a process enhancer in WPC</td>
</tr>
<tr>
<td>Crodamide SR</td>
<td>Stearamide</td>
<td>Bead/Powder</td>
<td>Non-vegetable</td>
<td></td>
</tr>
<tr>
<td>Crodamide SRV</td>
<td>Stearamide</td>
<td>Bead</td>
<td>Vegetable</td>
<td></td>
</tr>
<tr>
<td>Crodamide S</td>
<td>Stearamide</td>
<td>Bead/Microbead/Powder</td>
<td>Non-vegetable</td>
<td></td>
</tr>
<tr>
<td>Crodamide EBO</td>
<td>Ethylene bis-oleamide</td>
<td>Bead</td>
<td>Vegetable</td>
<td>Anti-block and medium slip/release in polyolefin polar copolymers. Especially useful as a pellet anti-tack in EVA hot melt adhesives. Process aid in WPC</td>
</tr>
<tr>
<td>Crodamide EBS</td>
<td>Ethylene bis-stearamide</td>
<td>Microbead/Powder</td>
<td>Non-vegetable</td>
<td>Anti-block in polyolefins and process aid to improve dispersion of fillers. Also mold release in nylon and ABS, and lubricant for PVC. Process aid in WPC</td>
</tr>
<tr>
<td>Crodamide EBSV</td>
<td>Ethylene bis-stearamide</td>
<td>Powder</td>
<td>Vegetable</td>
<td></td>
</tr>
</tbody>
</table>

*Speciality slip agents for specific applications are also available under the tradename Incroslip™ for caps and closures, and IncroMold™ for molding applications.

**Product physical forms**

Crodamide products are available in up to four physical forms. Please check with your local sales contact for availability in your region. Typical particle sizes are given below under product images.

- **Pastille**: Size: 4mm dia x 1-2mm
  - Ensures 100% dosing; reduced potential for agglomeration

- **Bead**: Size: 1-2mm
  - Good general purpose form suitable for the majority of feeders

- **Microbead**: Size: 0.1-0.5mm (100-500µm)
  - Recommended for dry mixing with other granulates

- **Powder**: Size: 0.01-0.1mm avg (10-100µm)
  - Recommended for dispersion into liquids or other fine powders
Which Crodamide will work best in my application?

Polymer surfaces often exhibit high friction leading to problems during manufacture, processing and use. High friction can result in difficulties with winding of film rolls, bag production and packaging operations. There are several factors affecting the development of friction including:

- Polymer type (nature, polarity, crystallinity)
- Process temperature, process type (film, blown/cast, co-extrusion, etc)
- Film gauge & structure
- Other additives present (anti-fog, anti-static, pigment etc)

**Crodamide slip & anti-block agents**

Crodamide speciality additives are incorporated directly into the polymer during the extrusion process. They work by migrating to the surface as the polymer cools forming a solid lubricating layer at the surface. This acts to lower the friction or adhesion between contacting polymer surfaces and the polymer and other materials.

- Amide uniformly distributed in the polymer immediately after extrusion
- As the polymer cools, amide migrates to the outer surface and forms a partial layer. Friction drops rapidly
- Complete layers of amide on the surface, migration reaches equilibrium. Friction reaches a minimum
When selecting the correct Crodamide for your application you should consider a number of different formulating criteria, including:

**Slip/blocking performance required**

As a general guideline, unsaturated primary amides tend to have the best slip performance (CoF < 0.2). Secondary amides are excellent for the control of medium slip (CoF 0.3 - 0.5). Saturated amides exhibit poorer slip properties but improved anti-blocking performance (CoF > 0.5).

**Rate of slip development**

Generally the smaller the amide molecule, the faster it can migrate, especially in semi-crystalline polymers. Thus oleamide will cause a faster drop in CoF than erucamide. However, erucamide usually yields the lowest ultimate CoF.

**Volatility**

Lower molecular weight additives are more volatile and prone to cause smoking, chill roll plate-out and die fouling. An indication of the relative volatility can be gained by Thermogravimetric Analysis (TGA), see page 10. Erucamide is less volatile than oleamide and is therefore recommended for polymers requiring higher processing temperatures. Secondary amides are recommended for engineering polymers.

**Oxidative stability**

Unsaturated amides are more prone to oxidation due to the presence of the double bond. They may also have small amounts of polyunsaturates present which will significantly increase the rate of oxidation. The undesirable effects of oxidation include increased colour, odour, and loss of slip properties/increased blocking.

**Polymer type**

The performance and required inclusion level of the amide will vary depending on the type of polymer. Amide solubility is governed by the relative polarity of the polymer and the additive, and the crystallinity of the polymer. Slip molecules diffuse mainly through amorphous regions of a polyolefin, so with more crystalline polymers, such as PP and HDPE, migration of the amide to the polymer surface will be slower. In more polar polymers, eg PVC, amides exhibit greater solubility.

**How are Crodamide products incorporated?**

Products can be added directly to the polymer at the processing stage, pre-compounded or included via masterbatch. Experience has shown that Crodamide products can be easily incorporated into the polymer. Simple manual mixing prior to processing will normally give an acceptable dispersion, though mechanical means is preferable. The optimum dosage level depends on the polymer type and the degree of lubrication required. We recommend initial levels of around 500 – 2000ppm in film.
Applications

Slip
Crodamide products are effective at low levels, providing a cost-effective solution to friction related constraints in film production and conversion applications. The range offers various levels of slip performance, both in the initial development of slip and in the final slip characteristics, depending upon the application requirements, as shown in figures 1 & 2.

Slip - Polyethylene
At all concentrations Crodamide ER will give a lower ultimate CoF than Crodamide VRX in LDPE. Therefore, less Crodamide ER is required to give equivalent slip performance. To achieve an ultimate CoF of 0.1 only 850ppm Crodamide ER is required compared with 1200ppm Crodamide VRX, as shown in figure 3. A number of other processing variables and cost-performance benefits will also influence the final choice of slip additive.

Crodamide ER is recommended in LLDPE due to its excellent heat stability and lower volatility. Usage levels in LLDPE are typically higher than in LDPE as migration is slower and adsorption onto the higher loading of anti-block is greater (figure 4).

Figure 1: Comparative effects of Crodamide range on coefficient of friction in LDPE (40µm blown film, all additives at 1000ppm)

Figure 2: Comparative effects of primary amides on the slip (CoF) of LDPE vs time (35µm blown film, all additives at 500ppm)

Figure 3: Comparative effects of Crodamide ER & Crodamide VRX concentrations on the slip (CoF) of LDPE (35µm blown film)

Figure 4: Friction vs time for Crodamide ER at 500, 750 & 1000ppm in hexene LLDPE (40µm blown film, 3000ppm natural silica)
Slip - Polypropylene

Crodamide VRX is significantly faster migrating in hPP compared to Crodamide ER, however, Crodamide ER shows good migratory performance in coPP. Often blends of Crodamide ER and VRX are used to optimise overall performance, but care must be taken to ensure blocking force is not increased; see case study below.

In our own research work on optimising Crodamide combinations we have achieved very high slip in an impressively short time in polypropylene, as can be seen in figure 5.

The optimised Crodamide combination achieves a CoF of 0.25 after 35 hours approximately, whereas oleamide only reaches this CoF after 63 hours.

The effect of temperature when storing and/or transporting film can also significantly influence slip performance, and is a particular challenge in PP film. Whilst simulating cold weather conditions we tested the slip properties of PP film with various additives over seven days’ cold storage. The best performing additive was an optimised Crodamide combination which gave superior slip compared with both erucamide and oleamide (figure 6).

Case Study

Optimising slip in LLDPE/LDPE blend for packaging film

A customer processing a linear low/low density blend to produce packaging film encountered unexplained variability in blocking performance. It was noted that two different manufacturers’ grades of LDPE were being used. Although the properties of the two resins were found to be equivalent, analysis showed that one manufacturer was using oleamide as a slip agent and the other erucamide. The LLDPE contained only erucamide, such that some films had a mixture of oleamide and erucamide coming from the base polymer. When erucamide and oleamide are used in combination, the slip material on the polymer surface is softer than either of the two additives individually, resulting in a greater tendency to block. It was also noted that the slip performance was slightly poorer than erucamide alone.

Croda recommended that both the LDPE and LLDPE should contain Crodamide ER only to eliminate this problem. No further blocking problems were experienced after this change was implemented. Statistical analysis of the CoF post-change showed that less Crodamide ER could be used whilst still maintaining the desired CoF, resulting in further cost savings.

A project was initiated to look at the properties of erucamide and oleamide blends, and it was discovered that blending the two slip agents resulted in a softer, more greasy material than either additive on its own. Analysis showed that the blends had a lower melting point. This suggested that the blocking problem was related to the physical properties of the mixture of slip additives on the polymer surface. Blocking force was 20% higher where the two additives were blended, which was enough to cause serious problems during bread packaging.
Applications

Medium slip/control of slip
Secondary amides have a higher molecular weight than primary amides, and are less polar, allowing greater control over the slip properties of the film. For polyolefins medium slip of 0.3-0.5 CoF can be achieved with far lower variability than with primary amides. The use of a secondary amide such as Crodamide 203 or Crodamide 212 can also enhance the printability of film surfaces due to the lower level of slip additives present at the surface. In multilayer/laminated films stable CoF levels may be achieved with secondary amides as they are far less likely to migrate into adjacent polar layers.

Case Study

Medium slip solution for multilayer packaging film

A customer making a five-layer co-extruded packaging film required a stable CoF between 0.25-0.30 on the outside skin layer of the film structure. The customer had attempted to achieve this by adding 150ppm erucamide. Although the average CoF achieved was within the specification, there was unacceptable deviation throughout batches, typically between 0.1-0.4 CoF. The other layers consisted of two tie layers and a central barrier layer; the inner skin layer was LDPE.

The variability in slip performance was thought to be caused by the difficulty in dosing such a low level of additive accurately, and the tendency of erucamide to migrate into adjacent layers, especially if they are of high polarity, such as tie layers and adhesives. It was suggested to the customer to replace the erucamide with Crodamide 203, a medium slip additive, and produce a trial batch using 750, 1000, and 1500 ppm of Crodamide 203. The skin layer also contained 1500 ppm of an inorganic anti-block. The CoF performance of the films produced was measured over 21 days. Within three days of production a stable CoF was achieved at all levels of Crodamide 203, with 1000 ppm achieving the required level 0.25-0.3 CoF, with a variability of +/-0.05.

Over the same period erucamide at 500 ppm achieved a CoF of 0.1 within one day, which remained stable for two weeks with a slight upward trend in the third week. Erucamide at 150 ppm achieved the required CoF during the first week but with a larger variability in excess of +/-0.1. After the first week the CoF steadily rose up to 0.5 in the third week.

Figure 7: Comparative performance of Crodamide 203 & Crodamide 212 as medium slip additives in LDPE (35µm blown film, various concentrations)
Anti-block
Most Crodamide additives will improve blocking when used in combination with inorganic materials. Crodamide BR is the most effective, migrating to form a continuous non-sticking layer. This allows lower levels of inorganic anti-blocking agent to be used, resulting in improved clarity. Crodamide BR can be used in combination with Crodamide ER, without increasing the total amide level, to give combined slip and anti-block performance.

Benefits
- High film clarity
- Low use levels (500 - 2000ppm)
- Slipping or non-slipping solutions
- Synergy with inorganic anti-block additives

Anti-blocking schematic

The customer selected 950ppm of Crodamide 203 for all future production, and over the following year achieved almost 50% reduction in out of spec film, and almost 100% reduction in film considered unsuitable for sale. An added benefit was the ability to formulate differential slip on the inside and outside of the film structure. It was also noted that Crodamide 203 showed less tendency to off-set from one side to the other when the film was wound up on reels. A similar approach was taken when formulating a multilayer laminate film, and in this case Crodamide 212 was found to give the most stable CoF.

Film with low molecular weight polymer at the surface. Surface layer may comprise polymer and low molecular weight oligomers.

Low molecular weight material covered by a layer of amide

Film surfaces separated by inorganic anti-block

Film with amide and inorganic anti-block. Used in combination the level of inorganic anti-block can be reduced, thus improving film clarity.
Applications

Blocking in film

Figure 8 shows induced blocking whereby two pieces of film are placed together between two pieces of glass (100 x 100mm) with a load of 7kg. The samples are held at 50°C or 70°C for 24 hrs, cooled to room temperature for 24 hrs, and the force required to separate the two layers tested according to ASTM D3354. It can be seen that at 50°C Crodamide ER gives quite a good anti-block performance, but Crodamide SR is best overall. However, when the temperature is increased to 70°C, only Crodamide BR gives a good result. Whilst good performance is seen with amides alone in film, we recommend that organic anti-blocking agents should be used to reduce the level of inorganic anti-block, rather than replace it entirely. The inclusion of an inorganic anti-block gives time for the organic anti-block to migrate to the surface.

Thermal stability of the Crodamide range

Based on the graph below we recommend that oleamides and stearamides are used up to 230°C, erucamides and behenamide are used up to 260-270°C and secondary amides may be used up to and in excess of 300°C. These recommended maximum processing temperatures are for guidance only and alterations may be necessary to compensate for residence time during processing.

Questions?

To find out more about Croda products and optimising Crodamide combinations please contact your nearest regional office or visit www.croda.com/pa
Pellet anti-tack additive solves agglomeration problem in Asia

A customer was using a combination of primary and secondary amides to improve the flowability of high vinyl acetate content EVA pellets (VA greater than 20%). The product worked well under normal conditions. However, at elevated temperatures in less temperate regions, such as Asia, they experienced numerous problems with polymers stored in silos or when transported in railcars. It became impossible to discharge the pellets due to excessive agglomeration. It was theorised that the amides resolubilised in the polymer surface and thus were rendered ineffective as surface lubricants.

Croda recommended the use of 0.2-0.5% Crodamide EBO to enhance the flow of the pellets and reduce pellet blocking under the widest range of conditions. This allowed continuous discharge from silos and railcars even after prolonged storage at temperatures in excess of 35°C. It was noted that there was no detrimental effect on the adhesive properties of the EVA in the end user application. The customer was able to optimise the additive level to use a lower quantity than in the original combination product. Crodamide EBO can also be used in combinations with other additives to optimise pellet flow properties for polymers of differing compositions.

Crodamide EBO acts as an effective pellet anti-tack for high VA content EVA. EVA uses include solar panel manufacture & hot melt adhesives.
Further information

Croda sales and distribution are coordinated through an extensive worldwide network of associates and agents. For details of your local representative please contact your nearest Croda regional office. Visit our global website at www.croda.com/pa

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