IMPROVED HIGH TEMPERATURE MOLDING WITH MONTAN WAXES

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Abstract

With the increase in demands for light-weighting and rapid, economical production of automotive and equipment parts, polymers which can withstand the high temperatures of under the hood applications have been replacing metal. In order to produce these parts rapidly and consistently, molders have reported needing the following to produce such parts consistently: easier flow, better mold release, consistent color without black specks, a “resin-rich” surface in filled polymers, faster cycles times, maintenance of physical integrity, reduced mold cleaning and reduced vent plugging. This paper provides data which shows how these improvement targets may be reached with montan waxes as the major process lubricant.

Introduction

To achieve the target effects requested by molders of high-temperature polymers – namely PA’s, PET, PPA, PC, PEEK – both filled with minerals, glass, etc., and unfilled, one must look at the causes of the common complaints; i.e. blacks specks, color shifts, mold and vent deposits, and loss of the polymers’ physical integrity. In many cases the causes has been identified as one, or all, of the following: char of incumbent wax due to insufficient heat stability, high volatility, and/or exusion from either low molecular weight or incorrect polarity.

Looking at the waxes and lubricants in the market, the most common ones sold into the high temperature market have been [C18] stearic acid-based; either metallic stearates [i.e. calcium, zinc or magnesium stearate] stearamide esters [i.e. EBS] or fatty acid complex esters [i.e. polyol stearate complex esters].

While these aforementioned lubricants have been workhorses of the industry, the need for reduced volatility and reduced charring after long heat histories, while still providing both internal and external lubrication of the high-temperature polymers, encouraged the developments of the higher molecular weight [C28] montan esters, which may be made (The Gersthofen Process) from polyols such as ethylene glycol or 1,3 butanediol for the simpler esters or other polyols like glycerol, sorbitol, or erythritol to produce complex montan esters. Additional saponified grades (either Na\(^+\), or Ca\(^{2+}\)) also have the processing and lubricating attributes of a classical “soap” while still having the long, aliphatic, hydrophobic “tails” which reduce the chance of water attraction and provide for a larger, more complex intertwinement between the polymer chains, improving flow. The resulting esters and complex esters should now show a higher molecular weight, and hence reduced tendency to char or volatilize.
As an added benefit, the saponified grades would be expected to increase the rate of nucleation of the crystalline polymers such as PET or PA, causing them to form spherulites more rapidly and with more regularity during the cooling stage of injection molding, much like a saponified acid such as sodium benzoate will nucleate PP.

Testing to Theory

To verify the performances of the various grades of montan waxes against the hypothesis, a series of tests were performed on the montan esters, and some other common waxes used in high temperature applications, such as metal stearates, ethylene-bis-stearamide and fatty acid ester (typically stearates) waxes for comparison. The following tests were performed:

1) Spiral Melt Flow – to show actual increase in flow (internal lubrication).
2) Capillary – Viscosity – to show maintenance of polymer integrity
3) Differential Scanning Calorimetry (DSC) – to quantify $H_c$ shifts and cycle reduction
4) Injection Molding Cooling Reductions – for cycle time tests
5) Injection Molding – Mold Release Force – to quantify reduction of mold sticking.
6) Heated Air Draft Oven – To demonstrate volatility and char or discoloration potential or resistance at elevated temps
7) Thermo-Gravimetric Analyzer (TGA) – to quantify volatility as heated and at elevated isothermal conditions

The above-listed test apparati and testing conditions will be explained individually with the data.

Materials

The names and characteristics of montan waxes tested:

<table>
<thead>
<tr>
<th>NAME</th>
<th>CHEMICAL CHARACTERISTICS</th>
</tr>
</thead>
<tbody>
<tr>
<td>LICOWAX E</td>
<td>Ester wax on the basis of montanic acids</td>
</tr>
<tr>
<td>LICOWAX OP</td>
<td>Partly saponified ester wax on the basis of montanic acids</td>
</tr>
<tr>
<td>LICOWUB WE 4</td>
<td>Ester wax on the basis of montanic acids</td>
</tr>
<tr>
<td>LICOWUB WE 40</td>
<td>Complex ester of montanic acids</td>
</tr>
<tr>
<td>LICOWUB WM 31</td>
<td>Montanic acid and long chain aliphatic acid based ester wax</td>
</tr>
<tr>
<td>LICOMONT NAV 101</td>
<td>Na salt of the montanic acids</td>
</tr>
<tr>
<td>LICOMONT CAV 102</td>
<td>Ca salt of the montanic acids</td>
</tr>
</tbody>
</table>

The other lubricants tested are labelled in each graph. The polymers used for comparison are also identified in each data table or graph.

PA Test Results Examples

Spiral Flow Test 1: PA 6 – MFR = 130g/10 min. @ 275°C/5 Kg – ASTM D1238. Samples were produced in a Haake-Kneader, Banbury rotors, at 265°C, 40 rpm rotor speed.
Spiral Flow Test 1 results:

**Waxes for Polyamide 6**  
- Flow Improvement (Spiral Flow Test)

Spiral Flow Test 2: PA 6:6 – MFR = 80g/10 min. @ 275C/5 Kg – ASTM D1238. Samples were produced in a Haake-Kneader, Banbury rotors, at 295°C, 40 rpm rotor speed.

Discussion: Both PA 6 and 6:6 showed the greatest increase in flow from the calcium saponified montan ester (Licomont CaV 102). The partially saponified (Ca²⁺) Licowax OP and long chained aliphatic:montan ester Licowax WM 31. Showed the next best flow.

**Capillary Viscosity**

Viscosity was also determined for the PA 6; comparing montan waxes to metal stearates.

**Waxes for Polyamide 6**  
- Influence on Polymer Degradation

**Molding Cycle Time Example**

**Example of cycle time reduction with Licomont CaV 102 in Polyamide 6.6**

**PA 6 Release Properties Data**

The integrated Release Quantifying Force (N) was determined on a Kistler 6827 A unit attached to an Arburg Allrounder 320 (locking Pressure of 50 N), with a Charge amplifier model 5007 using
piezoelectric pressure transducers model 9331 (sensor for release/ejector force) and model 6157 (sensor for cavity pressure).

**Example PA 6 Demolding (Release) Force Results:**

![Graph showing performance of montan wax in polyamide 6 compared to standard lubricants - measurement of release force](image)

**EXAMPLE PET RESULTS**

**Materials:** A 22 MFR PET (injection molding grade) was used.

**Differential Scanning Calorimetry**

Differential Scanning Calorimetry (DSC) was conducted on PET samples prepared in the Haake-Kneader, at 40 rpm and 285°C. The DSC was run from 50-300°C, and then cooled from 300 – 50°C, at 20°C/minute. The PET contained varying amounts of a sodium saponified montanic acid ester (Licomont NaV101).

**Cycle Time Reduction** correlation to \( H_c \) shift from nucleation:

![Graph showing cycle time reduction](image)

**Flow Property and Demold (Release) Data in PET**

![Graph showing flow property and demold (release) data in PET](image)

**EXAMPLE PC DATA**

**Additional Property Data: PC Demolding**

![Graph showing additional property data](image)
AIR DRAFT OVEN TESTING

Long-term heated oven testing results show the resistance to char and discoloration. Tests performed at 250°C / 30 min., with 1 L air flow/min. on various montan waxes and metal stearates.

TGA TESTING – VOLATILITY

Montans vs. EBS: The TGA was run from 50-300°C at 120K/h, then held at isothermal conditions at 300°C with 1 L air / min. Multiple montan waxes were compared to EBS wax (Licowax C). data was plotted at 20°C and 10 min. intervals.

Montans vs. Other Lubricants: Weight loss percentages plotted versus temperature.
CONCLUSIONS

The data suggests that the montan ester waxes show a reduced tendency to char after prolonged heat exposure and show less volatility than the standard waxes used in high temperature molding. These traits would lend themselves to less color shift and less mold and vent build-up under aggressive molding conditions. The melt flow increase and maintenance of polymer viscosity suggests that the flow increase is from internal lubrication of the polymer, and not from polymer degradation. This would be beneficial when filling in thin-walled parts and reducing the need for preventive cleaning, which consumes time and money. This would also improve the likelihood of resin-rich surfaces with filled polymers, which are sought in many automotive applications, and generally render better impact physicals than a rough surface. The increased temperature of crystallization (H°c) in PET and PA when using saponified montan waxes suggests that nucleation is occurring more rapidly. The increase in nucleation rate can lead to shorter injection molding cycles and better physicals in injection molded parts.

REFERENCES

C. Lechner, Clariant Corp., Improved Pigment Dispersion with Micronized Waxes, AMI-Masterbatches 2009, Germany


