FROM DOMESTIC WHEELIE BINS AND LARGE MOBILE CONTAINERS TO POLY TANKS AND PLAY EQUIPMENT, COLOURED PLASTICS CERTAINLY BRIGHTEN MANY EVERY DAY OBJECTS. BUT HOW DO THE PIGMENTS USED IN COLOURED ROTATIONALLY MOULDED POLYETHYLENE (PE) PRODUCTS REALLY AFFECT PERFORMANCE?

To get an overview of this question from industry, qenos conducted a study using data collected from members of the Association of Rotational Moulders Australasia (ARMA). The purpose of the survey was to ask manufacturers for their experiences of goods moulded from different coloured PE resins. Questions related to: cook time; impact strength; shrinkage; warpage; mould sticking; fade resistance; tendency to crack; and life span.

FIRST: A CLOSER LOOK AT THE PIGMENTS USED IN PE

Pigments used to colour plastic moulded products can be naturally occurring minerals or synthetic compounds. In practice, relatively few pigments can be used in PE for rotational moulding purposes. The range is limited to those pigments that exhibit certain properties during moulding and final application including:

- Retention of colour at high moulding temperatures
- Colour fastness to prevent colour bleeding onto the mould
- Low cost
- Effectiveness at low addition rates
- Outdoor fade resistance
- Suitability for food and water contact where required
- Free of heavy metals
- Have minimal environmental impact when the article has reached the end of its useful life

Table 1. Some of the pigments commonly used in rotationally moulded PE products and typical colours they are used in.

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Colour range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium dioxide (white)</td>
<td>White, beige, smooth cream, grey</td>
</tr>
<tr>
<td>Carbon (black)</td>
<td>Black, grey, Monument</td>
</tr>
<tr>
<td>Iron oxide (red)</td>
<td>Heritage Red</td>
</tr>
<tr>
<td>Phthalocyanine (blue)</td>
<td>Mountain Blue</td>
</tr>
<tr>
<td>Ultramarine (blue)</td>
<td>Storm Edge</td>
</tr>
<tr>
<td>Chrome titanate (brown)</td>
<td>Bronze Olive, Jasper, Monument</td>
</tr>
<tr>
<td>Chrome (green)</td>
<td>Mist Green, Rivergum</td>
</tr>
<tr>
<td>Phthalocyanine (green)</td>
<td>Heritage Green</td>
</tr>
</tbody>
</table>

Linear low density polyethylene (LLDPE) is widely used for rotational moulding applications because of its outstanding physical properties and ease of processing.

PE can be readily pigmented to provide a wide range of colours, however, the choice of pigment has the potential to influence the performance of rotationally moulded items.

In a recent study, data was collected from Australian rotomoulders on the differences experienced when moulding PE of different colours. This data, combined with field and laboratory testing, reveals the ways in which different pigments affect the rotational moulding process and the performance of moulded items.
Since many of the thousands of products that are produced using rotational moulding of PE resins are designed for outside use, the final product needs to be tough, durable and UV resistant. However, the addition of pigments to the PE resin certainly impacts some of the physical properties of the material, as highlighted in this paper.

A SUMMARY OF THE SURVEY RESULTS

To gain more information about colour performance, ARMA conducted a survey of Australian moulders on behalf of Qenos. The results given in Table 2 show that white, off-white and light coloured plastics take a long time to cook, have poor impact strength and can tend to stick to the mould. However, they shrink, warp and fade less relative to other colours, have a low tendency to crack and a long lifespan. In contrast, the Heritage colours tend to fade more quickly, and along with blue, tend to have shorter life spans. Overall, respondents agreed that beige, black and lighter greens generally perform better than other colours.

HOW DO DIFFERENT PIGMENTS AFFECT PE?

To investigate in detail how different pigments affect a range of physical properties of PE, a series of tests was conducted in the Qenos Technical Centre. Samples were prepared by mixing powders of Qenos Alkatuff LL711UV PE and pigment at a rate of 0.3% (1.5% for titanium dioxide) and compounding them with an extruder. The PE resin contained thermal and UV stabilizers. The coloured compounds were then compression-moulded into 5 mm thick plaques for testing.

For the purposes of the testing, no other additives were included. In practice, rotationally moulded products often contain extra ingredients such as mould release additives and thermal stabilisers.

Melt flow index

The Melt Flow Index (MFI) is an important characteristic of PE; a higher MFI ensures ease of flow that aids production, while a low MFI leads to better toughness and environmental stress crack resistance. As can be seen in Figure 1, phthalocyanine blue and iron oxide red both increased the MFI of the PE material relative to the unpigmented (natural) sample.

Crack resistance

To test the crack resistance time of the PE samples, a full notch creep test (FNCT) was conducted in a 2% Igepal solution at 50°C. As shown in Figure 2, some of the pigments had a major effect upon crack resistance with black and white (0.3% pigment) showing the most resistance and phthalocyanine green the least resistance.
**Melting and freezing temperatures**

Figures 3 and 4 show that phthalocyanine blue and green increased both the melting and freezing temperatures of the PE samples. These organic pigments increase the crystallization rate by acting as nucleating agents, which may contribute to warpage and brittle behavior. The nucleation effects were further investigated by blending materials with different freezing points. A 50:50 mix of natural and green (phthalocyanine) powder was prepared. The high magnification image of the internal surface of the moulding containing the mixed powder shows an “orange peel” type effect on the inner side of the moulding (Figure 5). The image indicates that the natural PE shrinks later than the green to form valleys.

**Surface oxidation**

PE will degrade when it is exposed to excessive heat in an atmosphere containing oxygen. The polymer undergoes chain scission, where the chains are broken into smaller fragments which contain oxygen end groups.

To test how surface oxidation is affected by the choice of pigment, each PE sample was heated above the melting point and exposed to pure oxygen. The time to the onset of oxidation was then measured. As shown in Figure 6, the pigments had a major impact on the rate of surface oxidation when the PE samples were exposed to heat. The ultramarine blue PE sample provided the best thermal resistance, while iron oxide red and phthalocyanine blue offered the least resistance to surface oxidation.

**Thermal properties**

Testing identified that different pigments absorb light (and heat) to different degrees, see Figure 7. Figure 8 shows the variation in field performance of a variety of coloured moulded plaques during a typical summer’s day in Melbourne. The products clearly operate at different temperatures with carbon black absorbing the most sunlight and white (1.5%) the least.
Field testing of thermal properties

To understand the performance of some actual moulded products, a number of thermal imaging tests were conducted in the field. The maximum wall temperature of three water tanks located in Melbourne was measured at 10am, 1pm and 4pm. The temperature variation across the day was significant with the side walls getting quite hot in the morning and afternoon, as shown in Figure 9. Overnight the temperatures dropped dramatically. Temperature was also dependent on whether the tank was full or empty, with water having a cooling effect on the wall temperatures.

Table 3. Working temperature of PE pigments

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Working temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unpigmented “natural” PE</td>
<td>40</td>
</tr>
<tr>
<td>Titanium dioxide (white)</td>
<td>40</td>
</tr>
<tr>
<td>Carbon (black)</td>
<td>63</td>
</tr>
<tr>
<td>Iron oxide (red)</td>
<td>55</td>
</tr>
<tr>
<td>Phthalocyanine (blue)</td>
<td>55</td>
</tr>
<tr>
<td>Ultramarine (blue)</td>
<td>50</td>
</tr>
<tr>
<td>Chrome titanate (brown)</td>
<td>50</td>
</tr>
<tr>
<td>Chrome (green)</td>
<td>55</td>
</tr>
<tr>
<td>Phthalocyanine (green)</td>
<td>55</td>
</tr>
</tbody>
</table>

The expansion of the samples from laboratory conditions (23°C) to working temperature was measured. As shown in Figure 10, the degree of expansion varied considerably across the different colours.

To better understand likely performance of the pigments in the field, some of the earlier physical property testing was repeated.

Rigidity was found to reduce for all colours at working temperature, as shown in Figure 11. (Rigidity testing at 23°C had shown no impact between the different coloured samples).

A repeat of the crack resistance testing found a significant shortening of the time to failure, especially for non-white pigments, as shown in Figure 12.

In all cases, the results show that solar heating in combination with pigmentation leads to a change in PE performance.
OBSERVATIONS AND CONCLUSIONS

Based on the experiences of moulders surveyed through ARMA and testing conducted in the Qenos Technical Centre:

- There are a limited number of pigments that are suitable for rotational moulding applications
- Some pigments can change the melting and freezing temperatures of PE
- Pigments can change the thermal stability, crack resistance and shrinkage rate
- Pigments can affect the properties of PE exposed to solar heating

The long-term performance of a rotationally moulded article is dependent on many factors including the:

- Selection of a high-performance resin
- Choice of pigment and additives
- Physical design
- Manufacturing process

Qenos Alkatuff LL711UV was used as the base PE for the test protocols in this study. Since its introduction in the 1990’s, Alkatuff 711 has demonstrated superior long-term performance under both laboratory and field test conditions. Alkatuff 711 contains a high level of UV protection, uses a C6 comonomer to achieve high stress crack resistance, and has a broad processing window enabling the manufacture of articles with long-term high performance across a wide range of processing conditions.

The technical team at Qenos is available to support rotational moulders in the development of new and high-performance applications for rotational moulding.

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THE CHOICE OF PIGMENT CAN PLAY AN IMPORTANT ROLE IN THE PERFORMANCE OF MOULDINGS

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Figure 11. Rigidity at working temperatures

Figure 12. Crack resistance at working temperatures
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