Edward Bartholomey, Kobo Products Inc, discusses the synthetic resin, hydrogenated polycyclopentadiene for use in cosmetics and personal care

Hydrogenated polycyclopentadiene, a resin for long wear

For cosmetics and personal care products, the term resin is applied to a group of substances obtained as gums from trees or those that are manufactured synthetically. The term, synthetic resins, dates from the years when synthetics began to replace natural resins. Synthetic resins are polymeric materials, which are better known as plastics. There are two important classes of synthetic resins: thermostetting resins and thermoplastic resins.

A thermostetting resin is a high molecular weight polymer that solidifies irreversibly when heated. Thermoplastic resins are polymeric materials that can be softened and resoftened indefinitely by the application of heat and pressure, provided that the heat that is applied does not chemically decompose the resin.

Hydrocarbon resins are based on a petroleum feedstock, i.e., a synthetic source. Hydrogenation is primarily used to improve color and stability of the resin by removing vulnerable double bonds. Partial and selective hydrogenation are methods used to produce resins with broad compatibility and good stability.

HPCP FOR COSMETICS AND PERSONAL CARE

Hydrogenated polycyclopentadiene (HPCP) resin is a very light colour cycloaliphatic hydrocarbon resin. (Figure 1). Like other low molecular weight resins, it is an amorphous polymer. Amorphous molecules are arranged randomly and are intertwined. The polymer has a glass-like, transparent appearance. For this article, we have explored specific grades of HPCP resin with a weight-average molecular weight range (Mw of 400g/mol to about 430g/mol) and with glass transition points, Tg of 50–64.

Hydrogenated polycyclopentadiene is an excellent alternative to many resin based materials, such as tall oil glycerides or pentaerythritol rosinate which are widely used within the cosmetic industry.

Rosins have wider variability of properties as a result of their natural origin and structure. High odour and colour changes are sometimes associated with rosins and derivatives. Rosin resins, unlike hydrocarbon resins are not polymers. They are a blend of different molecules.

In many cases the cosmetic and personal care industry prefers to avoid the use of resin and derivatives due to their allergenic profile.

We have found that HPCP resin has excellent properties that translate to the cosmetic and personal care industry. Its low molecular weight accommodates the production of concentrated solutions that allow formulators to easily incorporate HPCP resin into the batch making process.

Volatile petroleum solvents that are widely used within the cosmetic industry, such as petroleum distillate, C10-13 isoparaffin and isododecane solubilise the resin. When the volatiles evaporate from solution within a formulation, the resin will form an hydrophobic film on the skin, hair, nails or lashes. Other cosmetic oils and esters, such as caprylic/capric triglyceride, octyl palmitate and vegetable squalane can be used as carriers for the resin as well. Non-volatile liquids will form resin films with excellent gloss and adhesion, however, the rub-resistance will not be the same level as the resin dispersed in the volatile carrier since it will be plasticiised.

US Patent 8,679,464 describes an HPCP composite that is a solid having additional advantages because it softens and melts more readily than the HPCP resin itself. It expedites the manufacturing process for large batches where additional liquids may not be necessary. In addition, it also has excellent gelling capacity due to the high viscosity of HPCP when combined with polyethylene. The composite forms a matrix, which envelops and stabilises the surrounding oil components of a formulation.

TESTING AND APPLICATIONS

The HPCP resin is now currently used in more than 100 products in the marketplace including lipsticks, mascaras, sunscreens, eye shadows, foundation make-up, etc. Its recommended level of use in formulations is 5–20% solids.

The addition of fine particles of silicone resin, poly(methylsilsequioxane), will reduce the amount of tack that is inherent in all types of resins.

KOBOGUARD® HRPC, as defined by US Patent 8,679,464, is a composite of hydrogenated polycyclopentadiene and polyethylene and carnauba wax and tocopherol. The polyethylene wax has high viscosity and impact strength, which are

Table 1. Comparison of the physical properties of a number of waxes tested as possibilities for inclusion in the HPCP composite

<table>
<thead>
<tr>
<th>Waxes</th>
<th>Impact strength ft bs/in</th>
<th>Viscosity Saybolt Furol Sec</th>
<th>Penetration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>4.8</td>
<td>90</td>
<td>3.0 – 6.0</td>
</tr>
<tr>
<td>Microcrystalline wax</td>
<td>0.3</td>
<td>11</td>
<td>4</td>
</tr>
<tr>
<td>Oxidised microcrystalline wax</td>
<td>0.6</td>
<td>18</td>
<td>7</td>
</tr>
<tr>
<td>Carnauba wax</td>
<td>0.3</td>
<td>14</td>
<td>1</td>
</tr>
</tbody>
</table>
related to flexibility of the film and the tough, long wearing properties in formulations containing polyethylene. [Table 1]. A base formulation that did not contain any resin was compared to one that contained HPCP resin and then to one that contained the composite Koboguard HRPC. [Figure 2].

Rub-resistance testing was performed by creating a film of the finished cosmetic product, allowing it to dry and then applying force in a circular motion for a period of 60secs. The amount of product that was transferred on to the substrate was then scanned and the results were calculated from image analysis. The composite material, Koboguard HRPC, improved the rub-resistance of the formulation (in blue) significantly vs the other two control formulations.

We had successfully blended the HPCP resin with individual, binary and ternary blends of waxes, such as:
1. Hydrocarbon-based (such as paraffin, ozokerite, microcrystalline and synthetic waxes, polyethylene, etc).
2. Hydrocarbon waxes modified with silicone (such as alkyl silicone waxes) or fluoro moieties.
3. Silicone or fluoro waxes.
4. Natural waxes that contain high levels of hydrocarbons (such as candelilla, beeswax, carnauba, etc).

Table 2. High melting point waxes that are compatible with hydrogenated polycyclopentadiene resin

<table>
<thead>
<tr>
<th>Resin-waxes</th>
<th>Melting point</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPCP resin - Hydrogenated</td>
<td>104.5°C</td>
</tr>
<tr>
<td>Polycyclopentadiene</td>
<td>101°C</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>85-92°C</td>
</tr>
<tr>
<td>Microcrystalline wax</td>
<td>68.5-72°C</td>
</tr>
<tr>
<td>Candelilla wax</td>
<td>78-82°C</td>
</tr>
<tr>
<td>Rice bran wax</td>
<td>81.5-86°C</td>
</tr>
</tbody>
</table>

5. Hydrogenated natural waxes or modified versions. For the final and most successful versions of the composite product, it was found to be necessary to use higher melting point waxes that were compatible with the HPCP resin. [Table 2]

The methods of processing to produce these blends played an important part in the outcome of the development. We developed these new composite materials by:
1. Recrystallisation from a molten mixture of solid wax or waxes and a solid hydrocarbon resin.
2. Recrystallisation from a molten mixture of solid wax or waxes and a partially solvated hydrocarbon resin.
3. Recrystallisation from a molten mixture of solubilised wax or waxes and a fully solubilised hydrocarbon resin. The inclusion of tackifiers, such as HPCP resin, can improve the adhesion of cosmetic and pharmaceutical formulations but they adversely affect the sensory properties. Low molecular weight, tackifier polymers, such as HPCP form hard, non-breathable films when the solvent completely evaporates because their Tg temperature is often higher than body temperature and due to crystallisation packing. The amount of tack can be modified for formulations with volatile and non-volatile solvents or liquids. Modifying HPCP resin with either an individually selected wax or a blend of solid, compatible waxes creates a better balance of flexibility and breathability of the film. It improves the sensory application of the polymer to the skin.

**SUMMARY**

Our laboratory testing has shown that the resin, HPCP, has the following benefits for formulations:

- Adhesive film-forming properties improve long wear for decorative cosmetic, sunscreen and skin care products.
- Substantivity
- Water-resistance;
- Improves rub-resistance;
- Imparts gloss;
- Reduces process time on the bench and in manufacturing;
- Helps to suspend pigments;
- Low odour and colour.

Kobo Products Inc prepares liquid solutions of HPCP, known as Koboguard 5400 and markets them for use in cosmetics, personal care and pharmaceutical preparations. Kobo also uses HPCP to prepare solid composites, such as Koboguard HRPC, since many applications do not require the need for additional liquids in their formulations. In many cases, customers prefer to choose and add their own liquids and blends.

The HPCP resin, hydrogenated polycyclopentadiene, has proven to be an excellent material to extend longer wear for formulations in the cosmetic and personal care industries.

**Bibliography**