New Natural and Biodegradable Wax Additives

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Wax Technology

Wax additives are an essential part of any ink and coating formulator's toolkit. Micronized wax powders, dispersions and emulsions can improve the durability of all types of surface coatings, imparting slip, abrasion and scratch resistance, anti-blocking, and rub resistance. Most commercial wax additives are based on synthetic materials including polyethylene and polypropylene. In the last few years, there has been a growing trend to develop formulated systems that contain higher percentages of materials that are bio-based, renewable, and/or biodegradable.

Classical Bio-based Waxes

Historically, the only commonly used wax additive that qualifies as bio-based and renewable would be carnauba wax. This natural wax, derived from the Brazilian Palm, is freshwater biodegradable based on OECD 302 testing. Dry powders based on carnauba wax can provide slip and lubricity with good film clarity. Emulsions of carnauba wax can improve water beading in high gloss coatings with slip, anti-blocking and mar resistance.

Another class of wax additive that offers significant biocontent would be ethylene bis-stearamide, or EBS wax. This material typically contains around 90% stearic acid, which can be derived from both animal and plant sources. Most formulators prefer an EBS that is based on plant-derived stearic acid, especially for food packaging applications. EBS can be used as the sole was powder but is often more effective when contained in a composite wax powder, where multiple components are melted together and homogenized prior to milling into an ultrafine powder.

Beyond carnauba wax and EBS, there have been limited options available to formulators looking to increase the natural content of an ink or coating.

Micro Powders, Inc.

New Bio-Based Wax Technologies - Nanocomposites

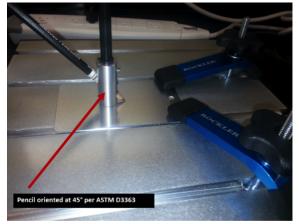
Micronized carnauba wax powder is a useful wax additive, but due to the softness and lower melting point of the wax, the performance attributes can be limited. However, this flaw can be overcome by modifying the natural wax with other more durable materials. Floor coatings are one of the most demanding end uses that require maximum resistance to scratching and surface damage caused by foot traffic, furniture movement, and even pets. Many high-performance floor coating formulations utilize a protective wear layer that is fortified with hard inorganic particles. Aluminum oxide has been used to impart a highly durable surface that resists wear, abrasion, and scratching. The Mohs Scale is a measure of mineral hardness, ranging from 1 (talc) to 10 (diamond). Aluminum oxide (also known as alumina or corundum) measures a 9 on the Mohs Scale, making it an extremely hard and durable substance. With alumina at the surface of a floor coating, dramatic improvements in wear resistance can be achieved.

The structure of fumed aluminum oxide is a complex morphology of tightly fused aggregates of nano-sized alumina particles, which subsequently attach to each other into agglomerates that are held together by weak interactions. These agglomerates can be broken down with sufficient shear energy into individual particles that can approach 300 nanometers. Aluminum oxide is also a very heavy material, with a density on the order of 3.8 - 3.9 grams g/cc. Since the particles are heavy, they could settle in low viscosity coating systems, leading to potential inconsistencies in performance when applied. These particles have a very high specific surface area (SSA) and can be extremely difficult to efficiently disperse into coatings. Additionally, they are dusty, difficult to handle, and could present health effects if lab or production workers are exposed to airborne dust particles.

Since aluminum oxide particles are so heavy, they will require extra energy to get them to a coating surface. Following a common wax design concept where HDPE/ PTFE composite wax particles are used to get the heavy PTFE to the surface of a coating more efficiently, the heavy alumina can be combined with molten carnauba wax in a high energy extrusion process, and then micronized to a precise particle size. The result is MicroKlear 418AL, an alumina/carnauba wax nanocomposite powder:

Property:	MicroKlear 418AL
Chemistry	Carnauba wax, aluminum oxide
Mean particle size (µm)	6.0 - 8.0
Maximum particle size (µm)	22.0
Melting point (°C)	81 - 86
Density at 25 °C (g/cc)	1.04

To compare the improvement in scratch resistance, the carnauba/alumina nanocomposite product was tested against a conventional carnauba wax powder. The wax was dosed at 1% on total formula weight in soft water-based PUD coating and applied to aluminum panels. The dried panels were tested for pencil scratch hardness using a Taber linear abraser per ASTM D3363.



The results show that the nanoalumina-modified carnauba wax powder (MicroKlear 418AL) shows significantly improved scratch resistance when compared to the conventional carnauba wax powder (MicroKlear 418):



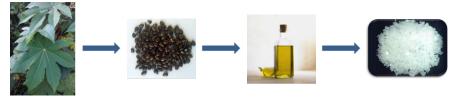
New Bio-Based Wax Technologies - Novel Materials

Natural powders are frequently used in the formulation of cosmetics and personal care products, where naturality is a highly desired consumer attribute. Three different materials were considered and evaluated for use as an industrial wax additive:

- Hydrogenated castor oil
- Rice bran wax
- PHBV

1. Hydrogenated Castor Oil Powder

NatureFine H325 is a micronized powder based on hydrogenated castor oil. Castor oil is commercially extracted from castor beans (*Ricinus communis*) and is a liquid at room temperature. When fully hydrogenated, castor oil is transformed into a hard, waxy material.



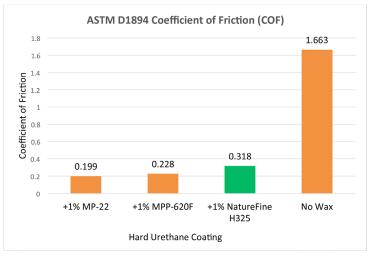
Hydrogenated castor oil is a 100% naturally derived, biodegradable, renewable and sustainable material. NatureFine H325 was evaluated as a functional alternative to MP-22 and MPP-620F synthetic-based waxes:

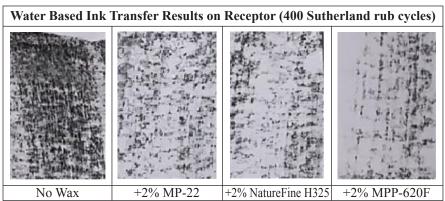
Property:	NatureFine H325	MP-22	MPP-620F
Chemistry	Hydrogenated castor oil	Synthetic wax	Polyethylene
Mean particle size (µm)	8-12	7-10	7-9
Maximum particle size (µm)	31.0	31.0	31.0
Melting point (°C)	82 - 87	102 - 106	114 – 116
Density at 25 °C (g/cc)	0.99	0.93	0.96

Tests were conducted to compare the level of lubricity (COF) and abrasion (Sutherland Rub) resistance in printed materials between NatureFine H325, MP-22 and MPP-620F.

- For the COF test, coatings were drawn down with a 3 mil (75 μm) Bird Film Applicator to produce approximately 1 mil (25 μm) DFT coatings.
- For the Sutherland Rub test, a wax-free black ink was dosed with 2% of each test wax. The ink was drawn down with a #10 wire wound rod to apply a 1 mil (25 μm) wet film thickness to a coated Leneta card.
- All test panels were cured for 7 days at room temperature at ~50% humidity.

COF reduction (slip and lubricity) for the hydrogenated castor oil powder was found to be similar to the synthetic-based waxes:





Ink transfer (printed surface to unprinted surface) was assessed by Sutherland rub:

The rub resistance of the hydrogenated castor oil powder was found to be superior to MP-22 (Fischer-Tropsch wax) but not as good as MP-620F (polyethylene wax). SGS GmbH was engaged to conduct a biodegradability study on hydrogenated castor oil according to OECD 302C (Ready Biodegradability). Under OECD 302C, a material is considered "Inherently Biodegradable" if 60% of the organic carbon in the material is converted to CO2 within 28 days. The mean results show that hydrogenated castor oil achieved a percent biodegradation of over 60% within 28 days. As a result, hydrogenated castor oil (NatureFine H325) can be categorized as Inherently Biodegradable in freshwater.

2. Rice Bran Wax Powder

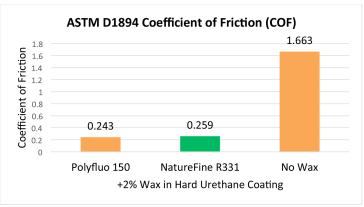
NatureFine R331 is an ultrafine powder derived from sustainable Oryza sativa (Rice) bran wax. The wax component is extracted from leftover rice husks after rice kernels are processed for food consumption. What was once a waste product has been repurposed as a natural micronized wax powder that can add functionality and natural content to inks and coatings.



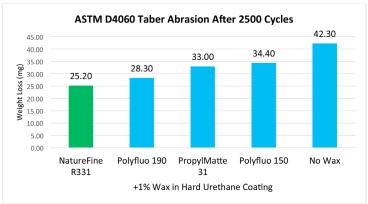
Rice bran wax is a 100% natural, biodegradable, renewable and sustainable material. It can be evaluated as a functional alternative to synthetic-based wax powders:

Property:	NatureFine R331	PropylMatte 31	Polyfluo 150	Polyfluo 190
Chemistry	Rice bran wax	Polypropylene	PE/PTFE	PE/PTFE
Mean particle size (µm)	6.0 - 10.0	8.0 - 12.0	3.5 - 5.5	9.0 - 12.0
Maximum particle size (µm)	31	31	15.56	31
Melting point (°C)	78-82	160 - 170	113 - 116	121 - 132
Density at 25 °C (g/cc)	0.96	0.89	1.04	0.98

Micronized rice bran wax provides similar slip and lubrication properties when compared to a polyethylene/PTFE wax powder such as Polyfluo 150:



The ability of micronized rice bran wax to improve surface abrasion resistance (Taber) was found to be superior to many other classical synthetic wax powders, including PTFE-modified waxes:



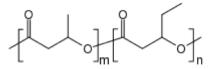
SGS GmbH was engaged to conduct a biodegradability study on rice bran wax according to OECD 302C (Ready Biodegradability). Under OECD 302C, a material is considered "Inherently Biodegradable" if 60% of the organic carbon in the material is converted to CO2 within 28 days. The mean results show that rice bran wax achieved a percent biodegradation averaging 70% within 28 days.

As a result, rice bran wax (NatureFine R331) can be categorized as Inherently Biodegradable in freshwater.

3. PHBV

NatureMatte 31 is a micronized ultrafine powder based on poly-(hydroxybutyrateco-hydroxyvalerate) or PHBV. PHBV is a member of polyhydroxyalkanoate family and is synthesized by bacteria as storage compounds under growth limiting conditions. PHBV can be commercially produced in a bio-fermentation process using selected bacteria and natural vegetable sugars.

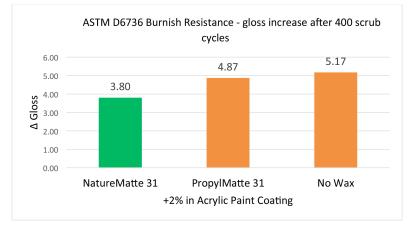
PHBV derived products are attractive because they are both marine and fresh water biodegradable. PHBV is one of the most common type of polyhydroxyalkanoates, having the following generic structure:

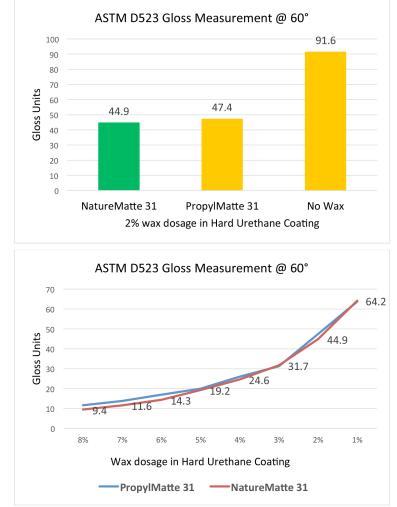


PHBV is a 100% natural, biodegradable, renewable and sustainable material. It can be evaluated as a functional alternative to PropylMatte 31:

Property:	NatureMatte 31	PropylMatte 31
Chemistry	PHBV	Polypropylene
Mean particle size (µm)	7.5 - 10.5	8.0 - 12.0
Maximum particle size (µm)	31.11	31.11
Melting point (°C)	170 - 180	160 - 170
Density at 25 °C (g/cc)	1.25	0.89

Micronized PHBV shows improved durability and resistance to burnishing, or "gloss-up" after a mattified surface is abraded:





Micronized PHBV shows a similar matting efficiency profile when compared to a synthetic-based wax:

SGS GmbH was engaged to conduct a biodegradability study on PHBV according to OECD 302C (Ready Biodegradability) and OECD 306 (Marine Biodegradability). Under OECD 302C, a material is considered Readily Biodegradable if 60% of the organic carbon in the material is converted to CO2 within 28 days. The results show a percent biodegradation of 68%. As a result, NatureMatte 31 can be categorized as Inherently Primarily Biodegradable in freshwater.

Under OECD 306, a material is considered biodegradable in seawater if 60% or more of the organic carbon in the material is converted to CO2 within 28 days. The

results show that the test sample achieved a percent biodegradation of 70-80%. As a result, NatureMatte 31 can be categorized as biodegradable in seawater.

Future Developments

Several new products are in development to expand the portfolio of natural additives for inks and coatings, including:

- Rice bran wax emulsion
 - Initial data shows water beading (contact angle) higher than paraffinbased emulsions
- Naturally derived, biodegradable texture additive series

Conclusions

Using a combination of novel particle design and natural raw materials, a broader range of wax additives is now available to the ink and coating formulator when developing products with higher bioderived content. These products provide:

- High natural content
- Biodegradability
- Superior functional performance when compared to synthetic-based waxes