Novel Natural Additives

FOR SURFACE COATINGS

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Many additives used in the coatings industry are based on synthetic petroleum-derived raw materials. As concerns grow regarding the sustainability, naturality, and biodegradability of coatings, formulators are beginning to consider replacing non-renewable formula ingredients with alternate additives based on natural and sustainable chemistries.

This article reviews several new developments in natural additive powders and emulsions that offer a more favorable environmental profile while also demonstrating excellent performance properties.

WAX ADDITIVE 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 past few years, there has been a growing trend to develop formulated systems that contain higher percentages of materials that are biobased, renewable, and/or biodegradable.

CLASSIC BIOBASED WAXES

Historically, the only commonly used wax additive that qualifies as biobased 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 is ethylene bis-stearamide, or EBS wax. This material typically contains approximately 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 wax 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.

NEW BIOBASED WAX TECHNOLOGIES: NANOCOMPOSITES

Micronized carnauba wax powder is a useful wax additive, but the performance attributes can be limited because of the softness and lower melting point of the wax. 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 nanosized 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. They are also dusty, difficult to handle, and could present health effects if lab or production workers are exposed to airborne dust particles.

Because aluminum oxide particles are so heavy, they require extra energy to get them to a coating surface during the drying process. 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 an alumina/carnauba wax nanocomposite powder, as shown in *Table 1*.

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 (*Formula 1*) and applied to aluminum panels. The dried panels were tested for pencil scratch hardness using a Taber linear abraser per ASTM D3363 (*Figure 1*).

TABLE 1—Carnauba Wax/Alumina Powder

PROPERTY	
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

FORMULA 1—Soft Urethane (PUD) Coating

Anionic Aliphatic Urethane (40% Solids)	89.6
Diethylene Glycol Monoethyl Ether	5.0
Polyether Modified Siloxane	0.5
Defoamer	0.3
Water	4.6

FIGURE 1—Taber Linear Abraser

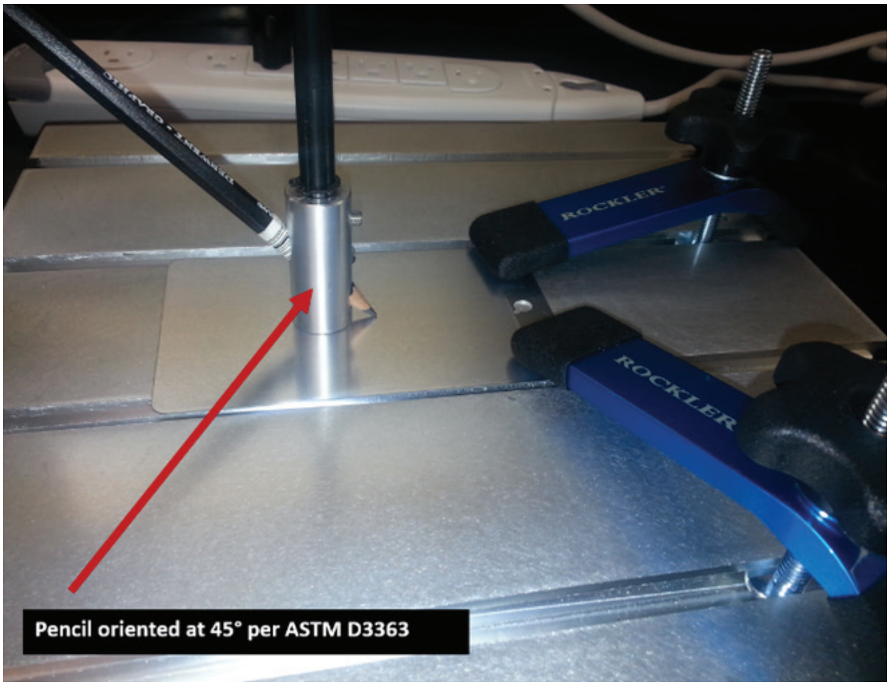

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CHART 1—Pencil Scratch Hardness (soft PUD)

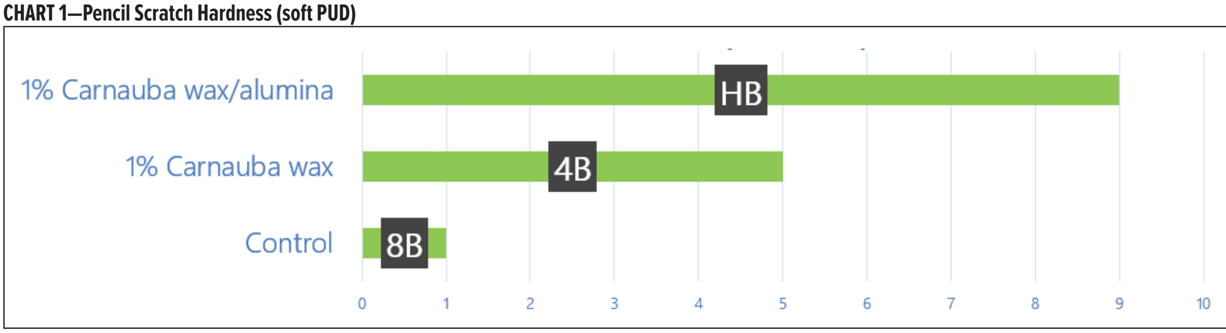
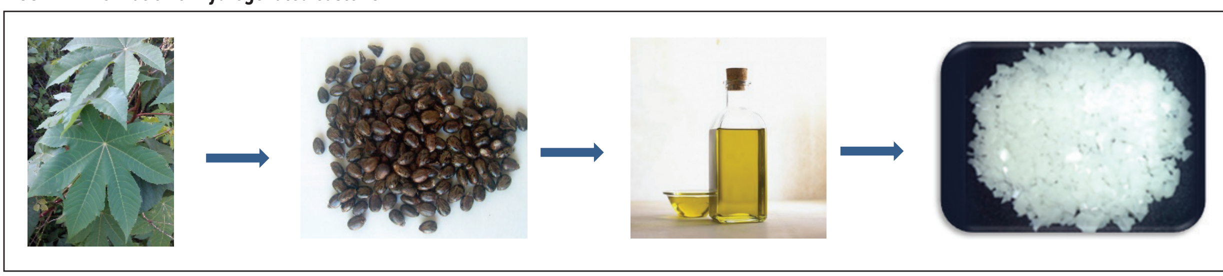


FIGURE 2—Derivation of Hydrogenated Castor Oil



The results in *Chart 1* show that the nanoalumina-modified carnauba wax powder shows significantly improved scratch resistance when compared to the conventional carnauba wax powder (MicroKlear 418).

NEW BIOBASED 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. Four different materials were considered and evaluated for use as an industrial wax additive:

- Hydrogenated castor oil (HCO) powder
- Rice bran wax (RBW) powder
- PHBV powder
- Rice bran wax (RBW) emulsion

1. Hydrogenated Castor Oil Powder

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 that can be micronized into a fine or coarse powder (*Figure 2*).

TABLE 2—Test Sample Comparison

PROPERTY	HCO POWDER	SYNTHETIC WAX	POLYETHYLENE
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

Hydrogenated castor oil is a 100% naturally derived, biodegradable, renewable, and sustainable material. In powder form, it was evaluated as a functional alternative to synthetic wax and polyethylene waxes (*Table 2*).

Tests were conducted to compare the level of lubricity (coefficient of friction) and Sutherland Rub resistance in printed materials between hydrogenated castor oil, synthetic wax, and polyethylene.

- For the COF test, dosed hard water-based PUD coatings (*Formula 2*) 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, water-based black flexo 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 (*Chart 2*).

Ink transfer (printed surface to unprinted surface) was assessed by Sutherland Rub (*Figure 3*).

FORMULA 2—Hard Urethane (PUD) Coating

Anionic Aliphatic Urethane (38% Solids)	97.5
Surfactant	2.0
Polyether Modified Siloxane	0.2
Defoamer	0.3

CHART 2—Coefficient of Friction (COF) Results - Hydrogenated Castor Oil Powder

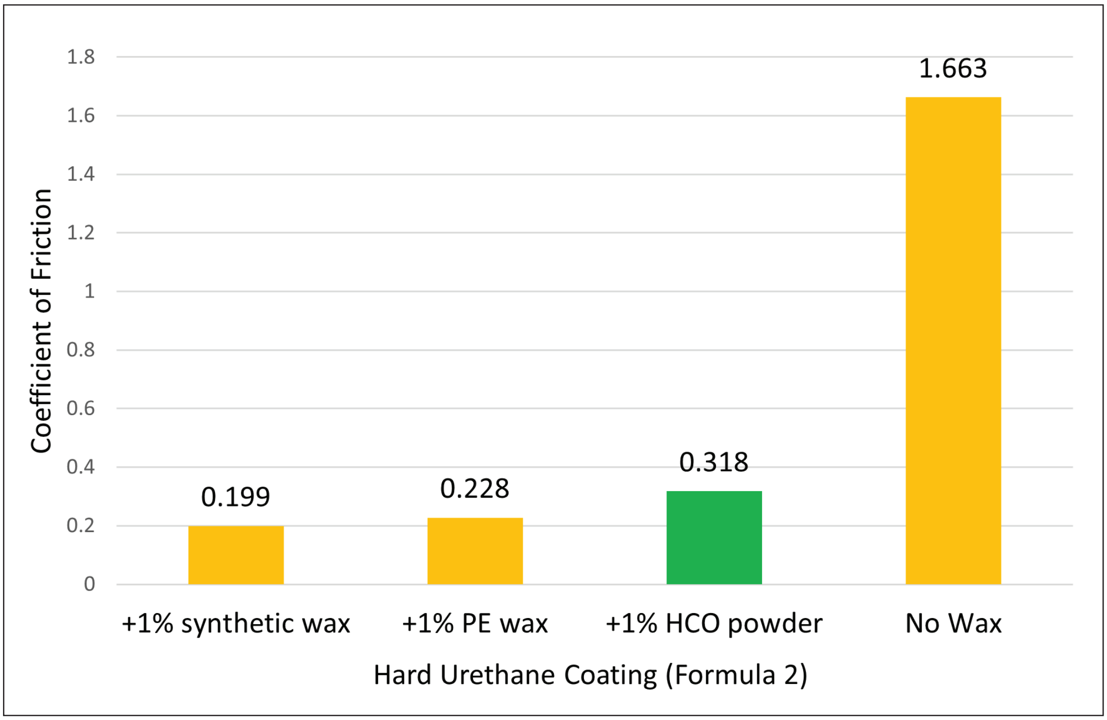
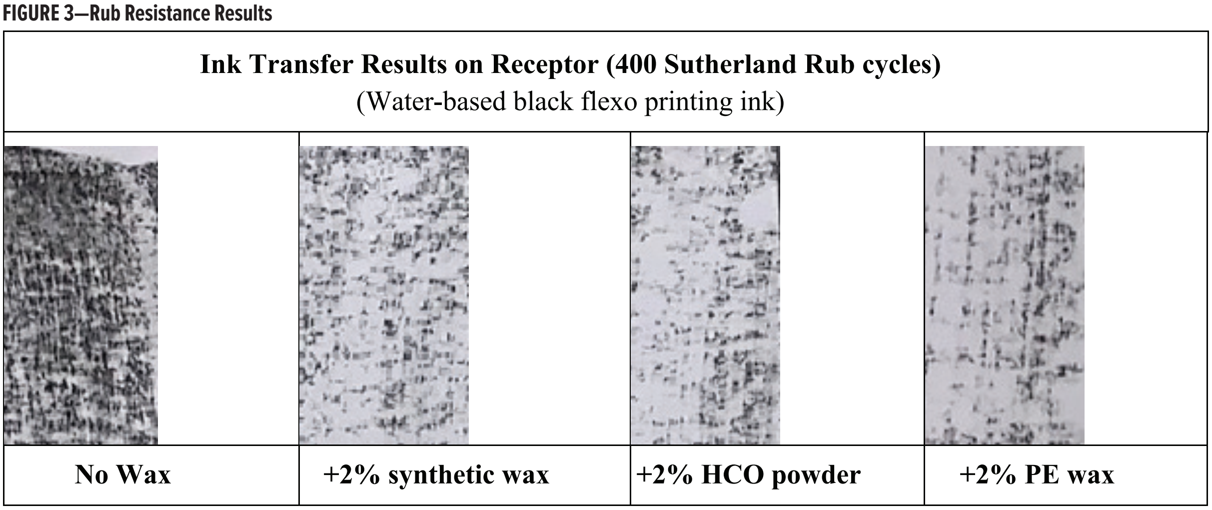


FIGURE 3—Rub Resistance Results



The rub resistance of the hydrogenated castor oil powder was found to be superior to synthetic wax but not as good as 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 CO_2 within 28 days. The mean results show that hydrogenated castor oil achieved a biodegradation of over 60% within 28 days. As a result, hydrogenated castor oil can be categorized as inherently biodegradable in freshwater.

2. Rice Bran Wax Powder

Rice bran wax powder is 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 upcycled as a natural wax powder that

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FIGURE 4—Derivation of Rice Bran Wax

TABLE 3—Test Sample Comparison

PROPERTY	RBW POWDER	POLYPROPYLENE	HDPE/PTFE	LDPE/PTFE
Chemistry	Rice Bran Wax	Polypropylene	HDPE/PTFE	LDPE/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

CHART 3—Coefficient of Friction (COF) Results: Rice Bran Wax Powder

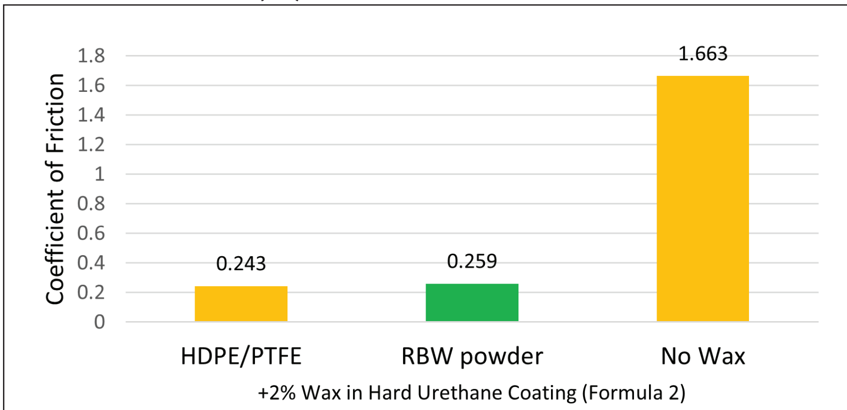
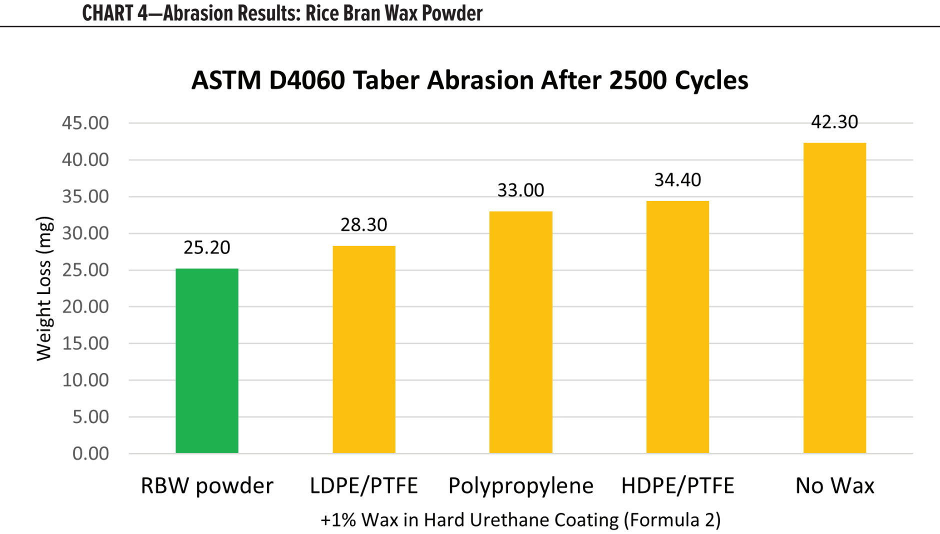


CHART 4—Abrasion Results: Rice Bran Wax Powder



can add functionality and natural content to inks and coatings (*Figure 4*).

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 (*Table 3*).

Rice bran wax has broad FDA compliance (21CFR 175.300, 176.170, 176.180). In addition, rice bran wax conforms to 21 CFR 172.890 as a direct food additive.

Micronized rice bran wax provides similar slip and lubrication properties when compared to a polyethylene/PTFE wax powder (*Chart 3*).

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 (*Chart 4*).

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 CO_2 within 28 days. The mean results show that rice bran wax achieved a biodegradation averaging 70% within 28 days. As a result, rice bran wax can be categorized as inherently biodegradable in freshwater.

3. PHBV

This micronized ultrafine powder is based on poly-(hydroxybutyrate-*co*-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 biodegradable in both seawater and freshwater. PHBV is one of the most common types of polyhydroxyalkanoates, having the generic structure shown in *Figure 5*.

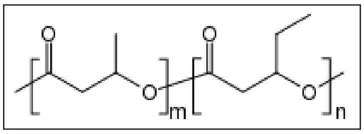
PHBV is a 100% natural, biodegradable, renewable, and sustainable material. It can be evaluated as a functional alternative to polypropylene powder (*Table 4*).

Micronized PHBV shows improved durability and resistance to burnishing, or "gloss-up" after a mattified surface is abraded (*Chart 5*) in an acrylic paint (*Formula 3*).

Micronized PHBV shows a similar matting efficiency profile when compared to a synthetic-based wax (*Charts 6* and *7*).

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 CO_2 within 28 days. The results show a biodegradation of 68%. As a result, PHBV can be categorized as inherently biodegradable in freshwater.

FIGURE 5—PHA Generic Structure



FORMULA 3—Acrylic Paint

Water	24.09
Modified HEC	0.20
Wetting Agent	0.20
Propylene Glycol	1.03
Silicone Defoamer	0.11
Carbon Black	4.80
Nepheline Syenite	30.00
Xantham Gum	0.10
Biocide	0.16
Surfactant	0.16
Wax	2.00
100% Acrylic Binder	35.00
HEUR Rheology Modifier	2.15

TABLE 4—Test Sample Comparison

PROPERTY	PHBV POWDER	POLYPROPYLENE
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

CHART 5—Burnish Results: PHBV Powder

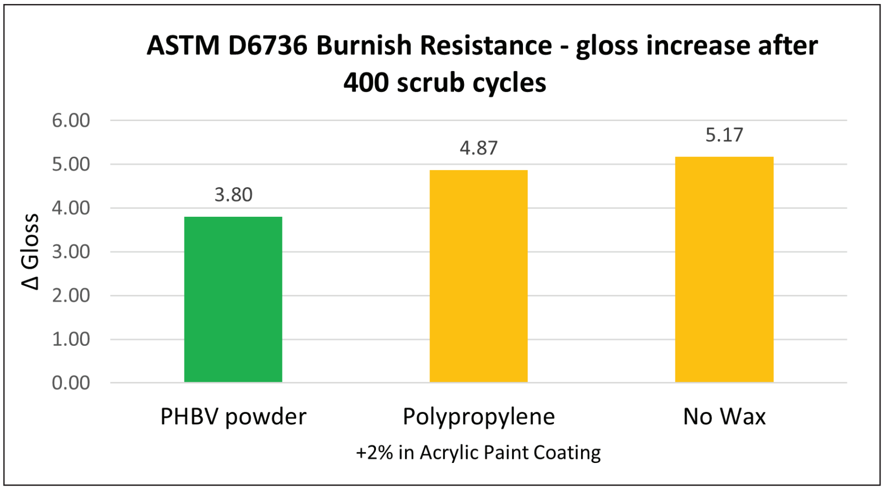


CHART 6—Gloss Results: PHBV Powder

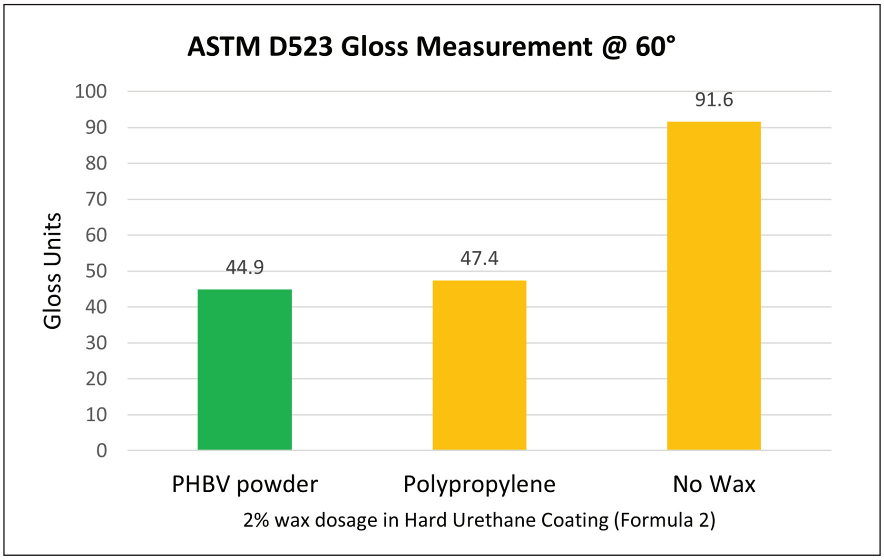


CHART 7—Matting Efficiency: PHBV Powder

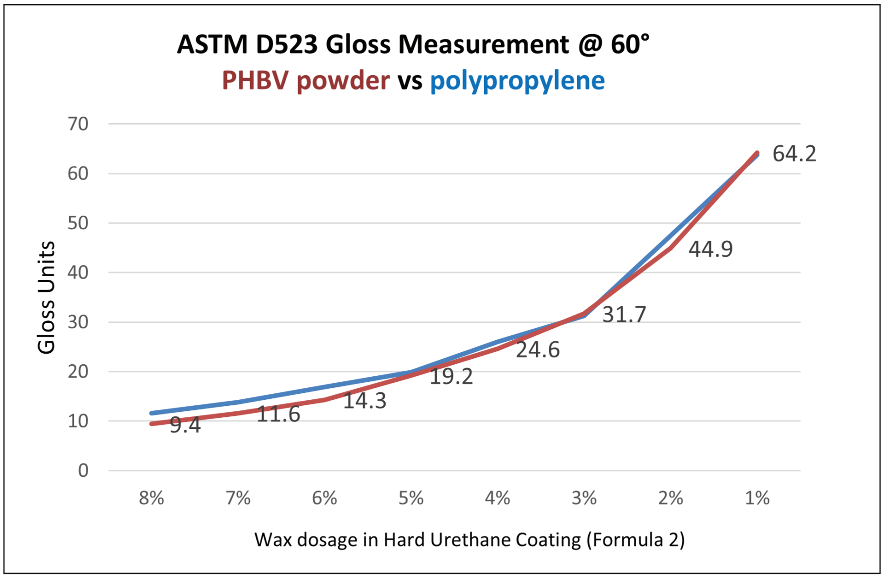


TABLE 5—Rice Bran Wax Emulsion Properties

PROPERTY	
Chemistry	Rice Bran Wax
Emulsifier Type	Nonionic
Wax Solids	50%
Viscosity @ 25 °C (cP)	500–2,000
Melting Point (°C)	78–82

TABLE 6—Test Sample Comparison

EMULSION	CARNAUBA	PARAFFIN	POLYETHYLENE (PE)	PE/PARAFFIN
Emulsifier Type	Anionic	Anionic	Anionic	Nonionic
Wax Solids	35%	63%	25%	40%
Viscosity @ 25 °C (cP)	<500	<500	<500	<500
Melting Point (°C)	85	54	140	100

FIGURE 6—Contact Angle Results

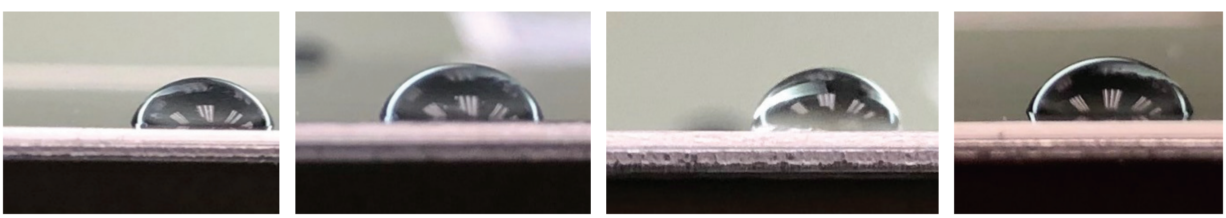


CHART 8—Coefficient of Friction (COF): Rice Bran Wax Emulsion

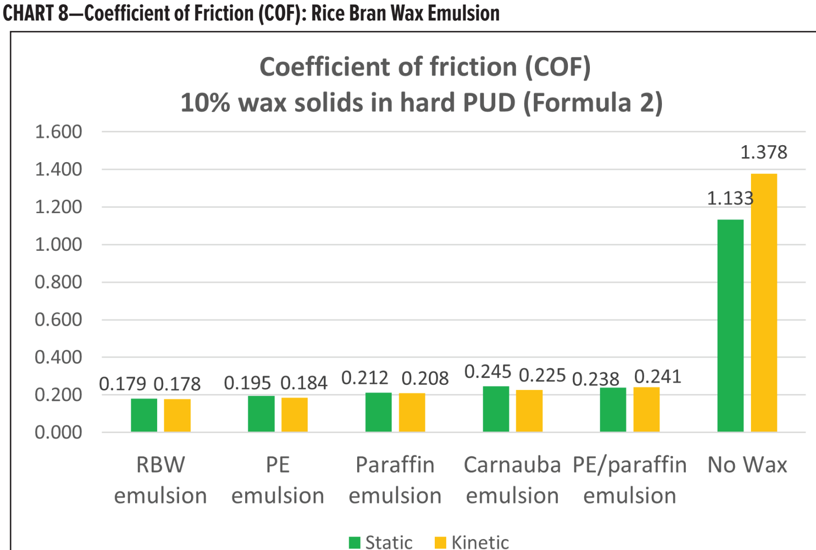
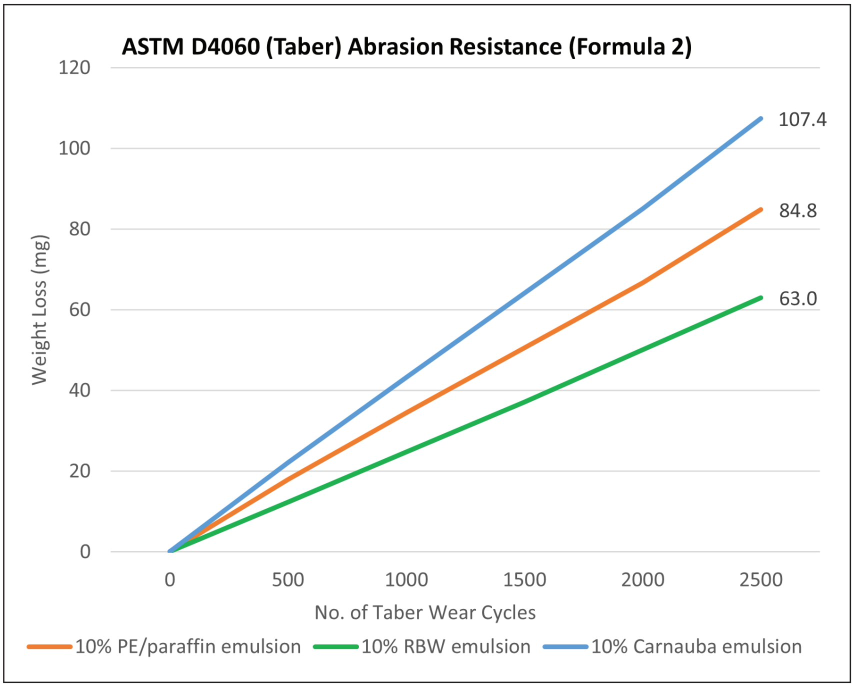


CHART 9—Abrasion Results: Rice Bran Wax Emulsion



Under OECD 306, a material is considered biodegradable in seawater if 60% or more of the organic carbon in the material is converted to CO_2 within 28 days. The results show that the test sample achieved a biodegradation of 70–80%. As a result, PHBV can be categorized as biodegradable in seawater.

4. Rice bran wax emulsion

Rice bran wax can be emulsified using the same processing methods used to manufacture synthetic-based wax emulsions including paraffin and polyethylene emulsions *(Table 5)*. Since wax emulsions are composed of particles in the submicron range, they are especially suited for surface modification of high gloss surfaces. This compares to the previously described rice bran wax powder, which will lower gloss to some extent depending on dosage.

Several commercially available wax emulsions based on both synthetic and natural waxes were used to compare performance against the rice bran wax emulsion (*Table 6*).

This water-based rice bran wax emulsion has broad FDA compliance (21CFR 175.300, 176.170, 176.180). In addition, rice bran wax conforms to 21 CFR 172.890 as a direct food additive, and has the same biodegradability as previously described for the powder.

The rice bran wax emulsion was compared to other typical wax emulsion chemistries as follows:

- *Formula 2* was dosed with 10% wax emulsions (based on wax solids)
- Coatings were applied with a #60 wire wound rod to produce approximately 2 mil DFT coatings
- All coatings were allowed to cure for 7 days at room temperature at ~50% humidity

Contact angle measurements were taken to compare surface hydrophobicity (*Figure 6*).

The rice bran wax emulsion showed the highest contact angle against the comparative emulsions.

Static and kinetic coefficient of friction (COF) were measured (*Chart 8*).

The rice bran wax emulsion showed the lowest static and kinetic coefficient of friction against the comparative emulsions.

Finally, the rice bran wax emulsion was compared to other emulsions for abrasion resistance (*Chart 9*).

In summary, the rice bran wax emulsion showed superior performance when compared against the other wax emulsions:

- Highest contact angle
- Highest static and kinetic COF
  - Note that the kinetic COF of 0.178 is similar to that of PTFE
- Best abrasion resistance (lowest weight loss in Taber testing)

CONCLUSION

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

- High natural content
- Biodegradability
- Superior functional performance when compared to many synthetic-based waxes
- Scratch and abrasion resistance
- Burnish resistance
- Water repellency ❊

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