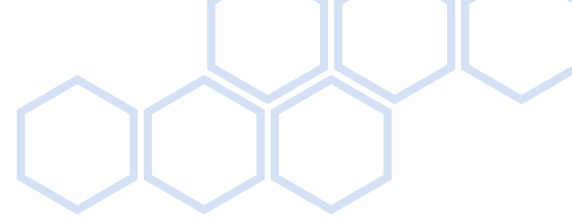


SURFACE MODIFIERS TECHNOLOGY AND BENEFITS



TECHNOLOGY INTRODUCTION

Lubrizol Surface Modifiers

Lubrizol surface modifiers are additives used to achieve specific surface effects in paints, coatings and inks. The technology enables formulators to enhance and protect appearance, feel, slip, abrasion resistance and overall durability of paints, coatings and inks. Products are available in powder and liquid form including micronized powder, aqueous and solvent-based dispersions and emulsified forms. In addition to wax based surface modifiers, Lubrizol also offers wax treated silica, along with other specialty products. A broad range of polymer chemistries and particle sizes are available to control performance properties. Lubrizol's world class manufacturing and quality control procedures ensure consistent batch-to-batch performance.

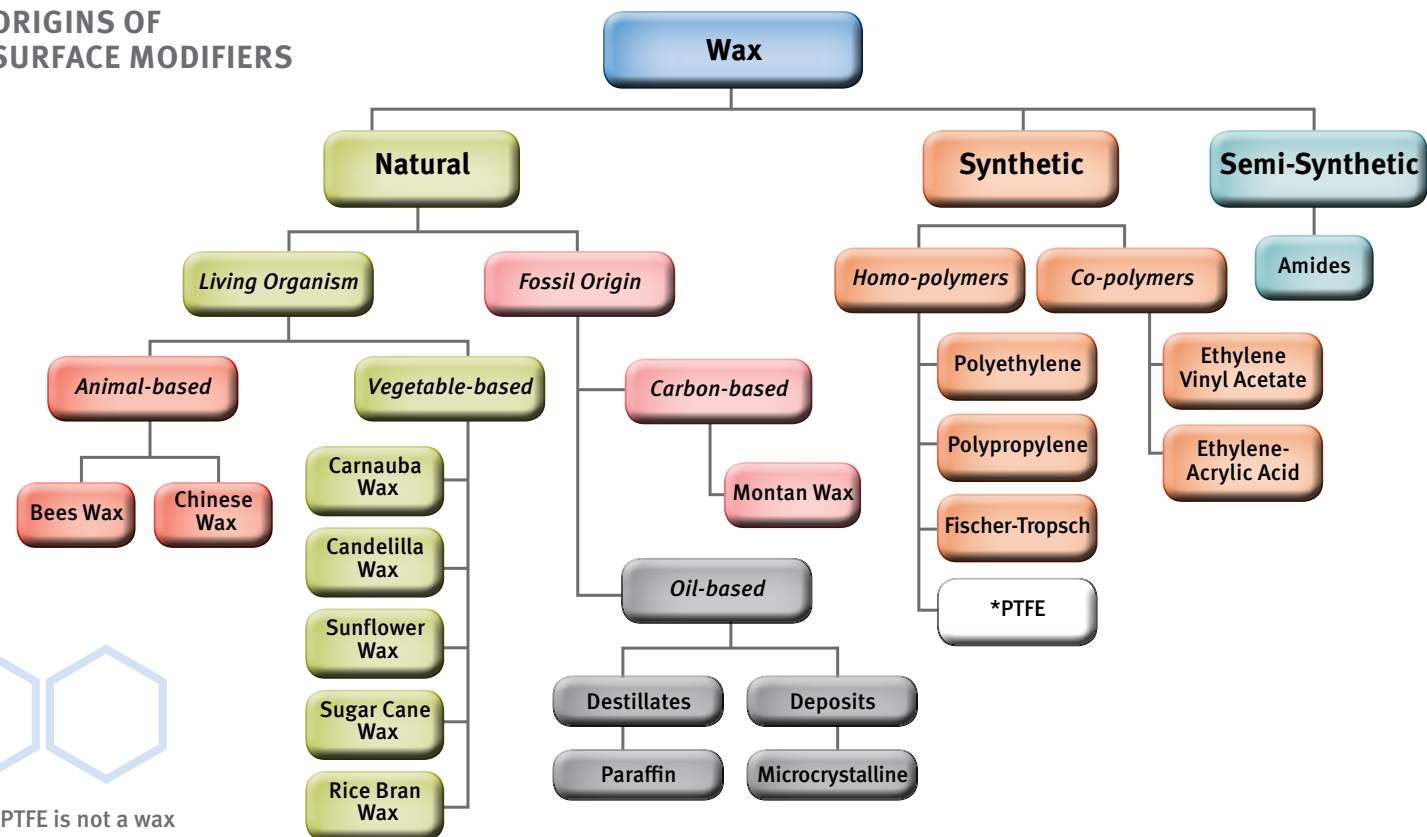
SURFACE MODIFIER CHARACTERISTICS

Definition of a Surface Modifier

Many surface modifiers are formulated using combinations of waxy polymers. The main properties of wax are described below:

- A wax is a low melting organic material or compound which is solid at 40°C.
- Chemically, waxes may be hydrocarbons, alcohols, amides or esters of fatty acids.
- Waxy polymers are insoluble in water.
- Waxy polymers may be soluble in organic solvents. Solubility is dependent on polymer chemistry, solvent choice and may require elevated temperatures (~50-100°C).
- Waxy polymers have a sharp melting point and reach the minimum melt viscosity a few degrees above the melt temperature.

ORIGINS OF SURFACE MODIFIERS



APPLICATIONS

Choosing the right surface modifier for a formulation is dependent on the performance requirements of the coating or ink application. Typical applications and the properties surface modifiers can impact are outlined below.



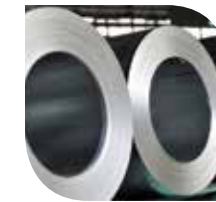
Wood Coatings

Surface modifiers provide improvements in scratch and abrasion resistance, anti-blocking properties, matting and soft feel. Additionally, they can reduce the sedimentation of silica matting agents and improve sandability.



Powder Coatings

Surface modifiers improve the fluidization, antistatic properties, and degassing during powder coating application and cure. They can also affect mechanical properties such as slip and impact resistance and aesthetic effects including matting and texturing.



Coil Coatings

Properties achieved with surface modifiers include slip, anti-blocking, scratch and abrasion resistance. Addition of surface modifiers influences durability and matte appearance. During the metal forming process, surface modifiers aid in preventing damage to the coating surface.



Can Coatings

Surface modifiers aid in protecting metal containers from abrasion damage in conditions such as high-speed production or during transportation. They can improve overprintability, promote heat-sealing stability and provide release properties without influencing porosity.



Industrial Coatings

There are many types of industrial applications such as plastics, metal, film and foil with various performance requirements. The choice of surface modifier will depend on the properties desired during processing and use.



Architectural Coatings

The main properties needed in architectural coatings are metal marking resistance and anti-blocking, especially for doors and windows. Surface modifiers can also provide smooth surface feel and matting.

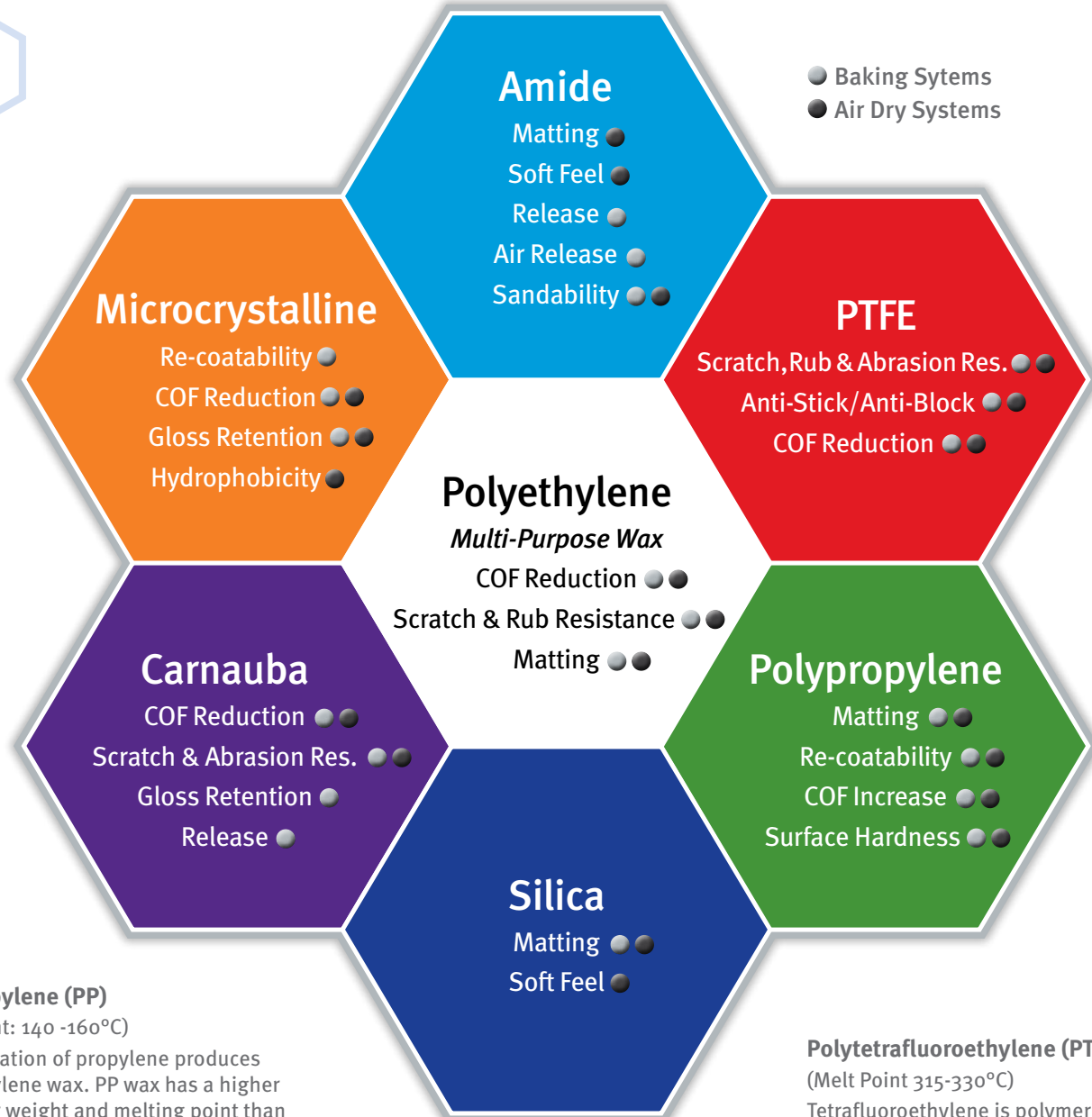


Inks and Overprint Varnishes

Surface modifiers are used to improve rub resistance and anti-blocking properties with minimal influence on gloss at low film weights. They are also used to control slip and mobility during production and handling.



SURFACE MODIFIER BUILDING BLOCKS



Polypropylene (PP) (Melt Point: 140-160°C)

Polymerization of propylene produces polypropylene wax. PP wax has a higher molecular weight and melting point than most other waxes. Plastic-like properties of polypropylene, such as high elasticity and toughness, are used in combination with PE waxes to optimize properties.

Carnauba (Melt Point: 82-86°C)

Carnauba wax is extracted from the leaves of the carnauba palm tree and is available in refined and virgin grades. Carnauba wax is a hard, brittle wax with the color ranging from light to straw yellow.

Fischer-Tropsch (F-T) (Melt Point: 93-110°C)

The reaction of carbon monoxide and hydrogen produces Fischer-Tropsch wax, also known as hard paraffin. FT is chemically similar to polyethylene and is typically less branched and more crystalline than PE. The types used in coatings melt around 100°C.

Microcrystalline (MC) (Melt Point: 60-90°C)

Microcrystalline is refined from petroleum. Microcrystalline wax is high molecular weight, highly branched hydrocarbon with low crystallinity. The melting point varies based on the structure.

Amide waxes (Melt Point: 73-140°C)

Mono- and bis-amides are semi-synthetic waxes. The reaction of fatty acids with amines and diamines produce mono- and bis-amides respectively. Mono-amides have a lower melt point and bis-amides have a higher melting range. Both types have low penetration and are brittle.

Polytetrafluoroethylene (PTFE) (Melt Point 315-330°C)

Tetrafluoroethylene is polymerized to produce PTFE. PTFE is not a wax, it does not dissolve or melt, but functions like one. PTFE is chemically inert and produces a very low coefficient of friction in coatings and inks. It is commonly formulated with PE.

Polyethylene (PE) (Melt Point: 100-130 °C)

Polymerization of ethylene produces polyethylene wax. The reaction conditions determine the crystallinity and molecular weight. PE wax is hard, brittle and the most commonly used polymer type for surface modification.

Silica

Silica is available from several different manufacturing grades including precipitated silica, fumed silica and silica gel. Unlike all other surface modifiers discussed in this document, silica is a crystalline material and does not melt.

Functions of a Surface Modifier

Many factors must be considered when selecting the best surface modifier:

1. Surface modifier chemistry and particle size
2. Coating properties such as film thickness and resin chemistry
3. Application and cure methods

Additive performance is evaluated using a variety of quantitative and qualitative test methods.



SURFACE PROPERTY	IS DEFINED AS...	DEPENDS ON...	TEST METHOD
Slip/COF Reduction	Low friction resistance on a surface	The surface energy and surface topography of the coating	Slip can be expressed as the static or dynamic coefficient of friction (COF) and measured using instruments such as the Altek Mobility Tester.
Abrasion/Rub Resistance	Resistance to damage by hard or rough objects	The hardness and elasticity of the coating	Abrasion can be evaluated by weight loss using the Taber Abraser or visually with the Sutherland Rub Tester.
Scratch/Mar Resistance	Resistance to damage by sharp or hard objects	The hardness, COF and film thickness of the coating	There are qualitative methods available such as coins, fingernails and rings and quantitative mechanical methods such as the multi-finger scratch tester.
Metal Marking Resistance	Resistance to marking by metal, especially on light-colored pigmented coatings	The hardness, the pigmentation and the COF of the coating together with its surface topography	Coins, rings and similar metal objects are used for testing.
Anti-Blocking	The property which prevents coated surfaces from adhering together	The surface energy, hardness, topography and the Tg of the resin/binder	Two surfaces are pressed together at a specified pressure and temperature. After a specified time, the two surfaces are separated and inspected for damage.
Soft Surface Feel	The haptic effect or silky feel of a surface	The COF, the topography and the chemistry of the surface	Subjective evaluation vs control coating.
Sandability	The ease with which a coating can be sanded	The Tg, lubricity and brittleness of the coating and additive	Subjective evaluation on test coating includes ease of sanding and resistance to gumming or binding of sanding media.
Matting	The gloss reduction of a coating surface	The additive particle size, curing conditions and the pigmentation of the coating	The ratio of reflected light to incident light is measured with a gloss meter.



Small Particle Surface Modifier Production

Why is particle size distribution so important?

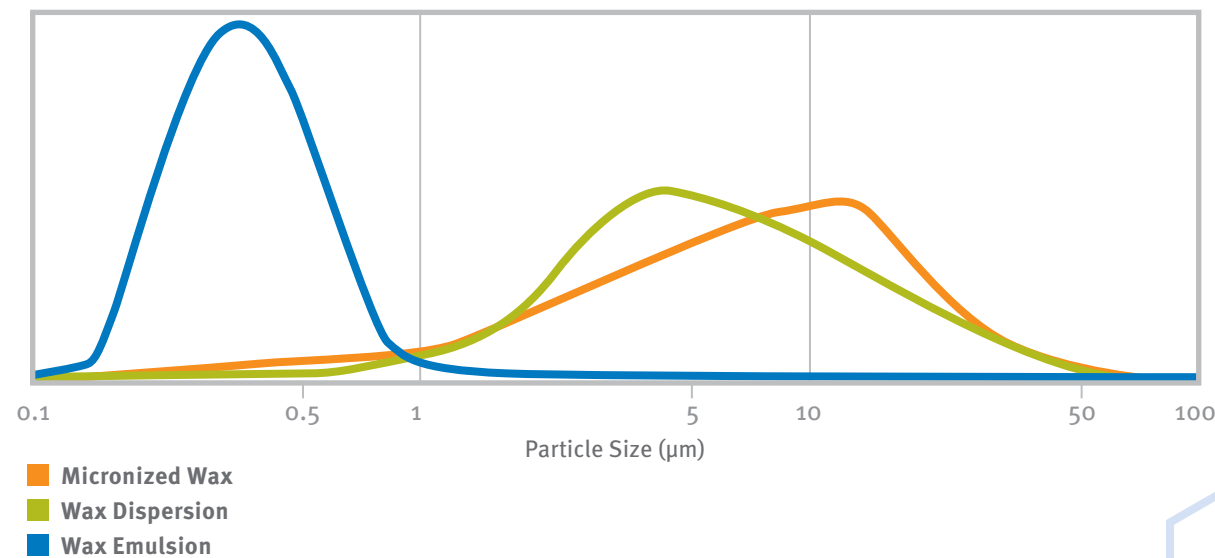
Choosing the right particle size surface modifier is essential to develop the targeted performance in the coating or ink. Particle size distribution is typically reported at the Dv50, Dv90 and Dv98 levels. The Dv {value} is defined as the percentage by volume or population of particles less than the reported value. For example, Dv50 ≤ 6.0 μm means that 50% of the particles in the sample are less than or equal to 6.0 μm. Various instruments are available to measure the particle size using volume of particles or population of particle algorithms to calculate particle size.

Typically, surface modifiers with a Dv50 particle size less than 6 microns are required to protect thin film applications such as rigid metal can coatings, coil coatings, inks and other thin films used in printing and packaging without impacting appearance properties. Selection of products with Dv50 > 6 microns for these same applications can negatively impact aesthetics. Conversely, larger particle size surface modifiers are required for thicker film applications such as industrial clear wood coatings or powder coatings so that the polymer particles are at the air-coating interface to affect target properties, e.g. abrasion resistance or gloss reduction.

Waxy polymers used for surface modification are typically supplied in prilled or flaked forms. The particle size for surface modification is optimized to balance ease of incorporation, compatibility and performance without compromising secondary properties. The particle size can be controlled using micronization, dispersion and emulsification techniques. The chart below illustrates the average particle size range using these techniques.

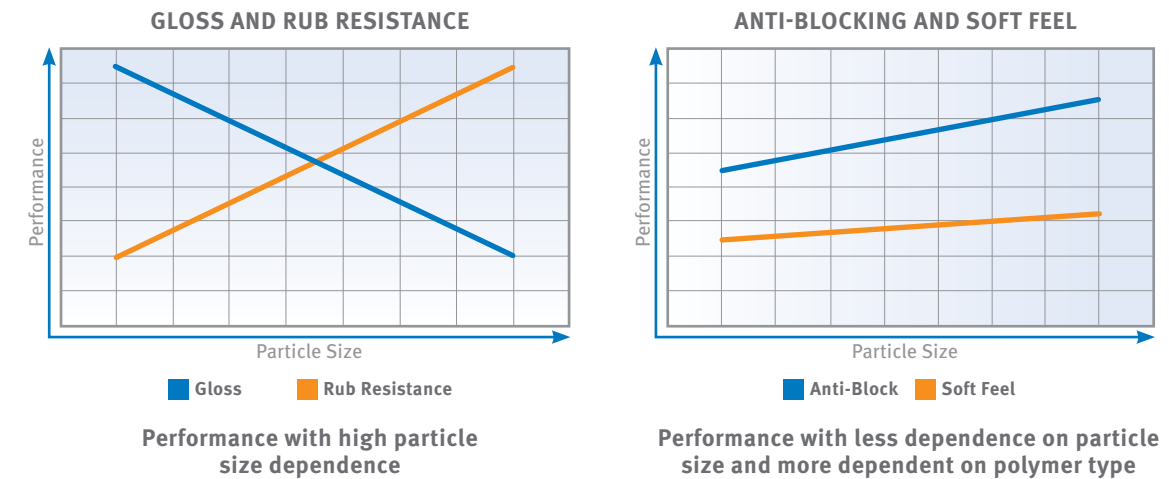


PARTICLE SIZE DISTRIBUTION
Typical particle size distributions of different preparations



The graphs below demonstrate performance trends based on a surface modifier at varying particle sizes. The performance trends below are based on an industrial coating containing an equivalent amount of a specific surface modifier applied to a common substrate at the same dry film thickness (dft).

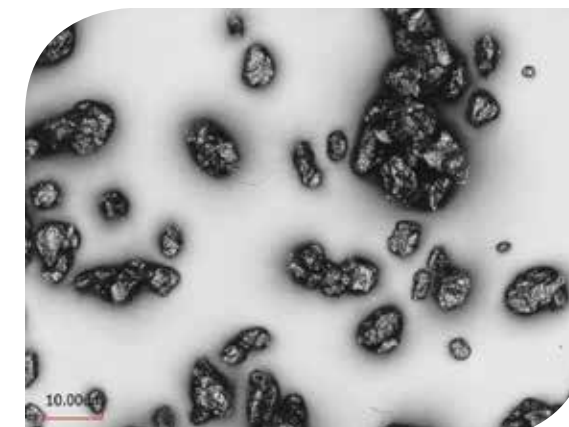
PARTICLE SIZE EFFECTS



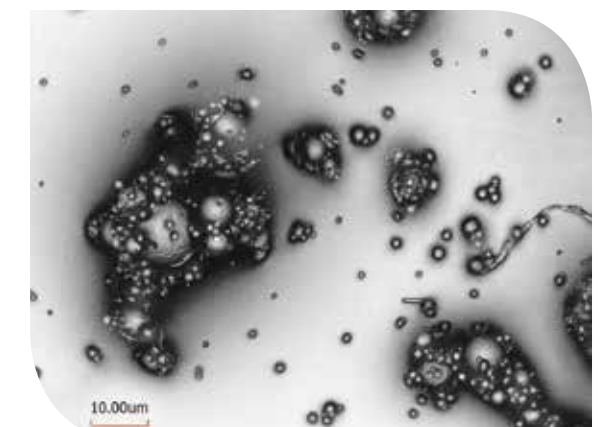
Micronization

Fluidized bed jet mills and melt spraying are the two most commonly used methods to produce micronized powder. Particle-to-particle collisions occur when polymers pass through opposing jets of high pressure air in fluidized bed jet mills producing fine powdered wax polymers. Controlling the flow rate through the milling chamber and the pressure of the opposing jets enables micronization of a wide range of waxy polymers. In-line classifiers are used to adjust and control the resultant particle size distribution into the targeted range. Melt spraying techniques generate fine, spherical wax particles when molten waxy polymers are sprayed into a cooling chamber. Particles are separated from the gas stream in a cyclone chamber or filter bag house. Polymers and polymer blends with broad melting range typically process more efficiently, yielding a narrower particle size distribution when micronized with a fluidized bed jet mill compared to melt spray methods.

Air jet micronized wax
150x magnified



Spray micronized wax
150x magnified

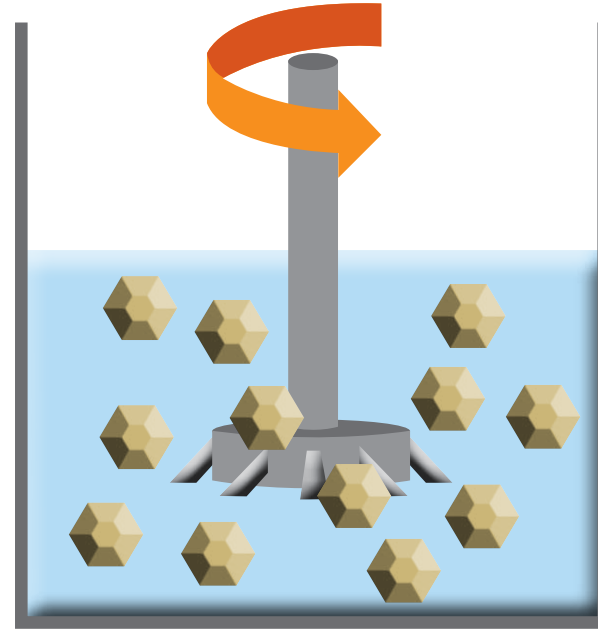


Dispersions and Emulsions

Wax dispersions are a combination of natural and/or synthetic polymers that are mechanically dispersed in organic solvents, water or other liquid carriers using a variety of media mills or high-speed Cowles dispersion techniques. Dispersion of polymers into water typically requires the use of wetting agents to stabilize the organic polymers into water.

Wax emulsions are a stable mixture of one or more natural or synthetic waxes in water. Emulsions always contain a wetting agent package adjusted to the appropriate HLB value depending on the wax being emulsified. Processing is performed at temperatures above the melt point of the wax. If the wax melt point is above the boiling point of water, the emulsion must be processed under pressure to prevent the water from boiling.

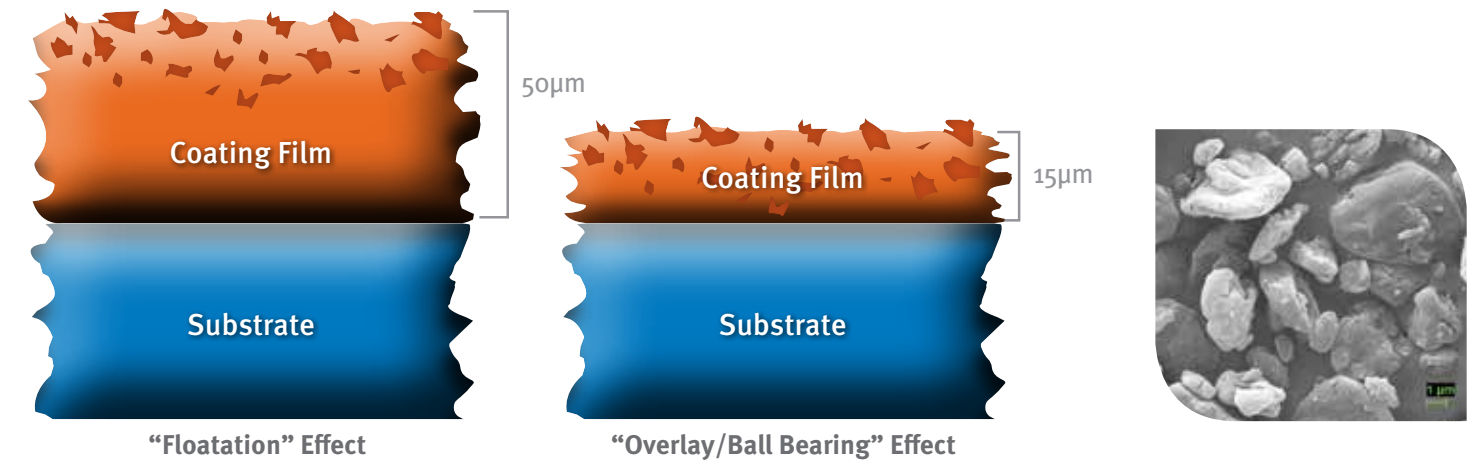
Ease of incorporation, efficiency, cost, stability, bulk coating chemistry and compatibility must all be considered when selecting the surface modifier form.



Surface Modifier Curing Mechanisms

The performance of a surface modifier is dependent on the ability of the particle to be present at the coating-to-air interface. The two mechanisms to accomplish this are described below:

1. Surface modifiers float to the surface due to density differences or incompatibility between the additive and the bulk coating. This is referred to as the **floatation effect**.
2. The average particle size of the additive is larger than the dry film thickness of the coating/ink or the concentration of particles is high enough to facilitate stacking near the coating-to-air interface. This is referred to as the **ball bearing or overlay effect** respectively.

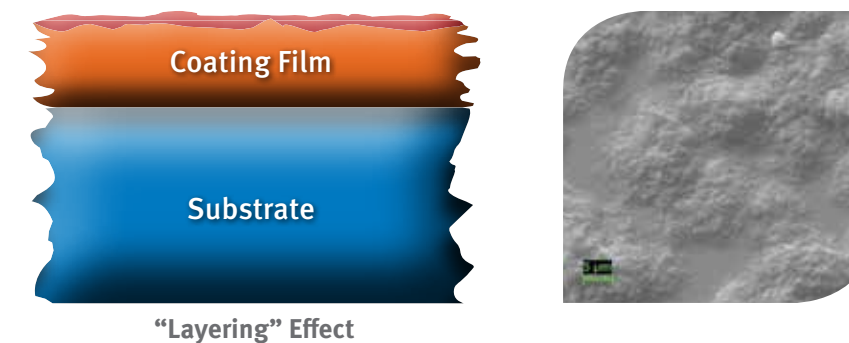


The curing mechanism affects the migration of the additive to the surface of the film and can also influence the performance of the finish itself.

Density differences between the wax and liquid enable the wax to migrate to the surface of air dried, solvent based or water based coatings or inks. Convection currents are generated during solvent evaporation, causing the additive to float to the coating-to-air interface. As solvent evaporates, the volume of coating or film decreases, causing film shrinkage which allows the formulator to take advantage of the ball bearing or the overlay effect.

In UV cured, high-solids or solvent-free systems, viscosity and degree of film shrinkage impact surface modifier performance. As a result, the mobility of the surface modifier and the ability to float to the coating-to-air interface is limited. Rapid cure cycles constrain the mobility of a surface modifier to migrate to the surface in UV cured systems. Due to these constraints, the floatation effect is limited in these systems, and the overlay/ball bearing effect has a greater influence on performance. Therefore, selecting the correct particle size surface modifier is critical to achieving the targeted performance characteristics.

The curing temperature is important because it influences the viscosity and the mobility of the additive particles. If it is above the melting point of the additive, it can lead to significantly different performance because a microscopic wax layer can be formed at the coating-to-air interface. This is known as the **layering effect**.



Micronized

- Typically Dv_{50} ranges from 5-9 microns
- High efficiency (100% active)
- Most effective matting option
- Broadest compatibility
- Most cost effective solution



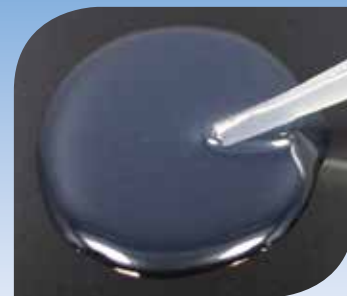
Dispersion

- Small particle size Dv_{50} ranges from 2-6 microns
- Wide range of liquid carriers
- Ease of incorporation/handling
- Limited effect on gloss
- Good in-can/formulated stability



Emulsion

- Generally particle size $Dv_{50} \leq 1$ micron
- Water-based applications only
- Ease of incorporation and handling
- Great gloss retention/highest clarity
- Good in-can/formulated stability



HANDLING GUIDELINES

Incorporation

Dispersed and emulsified surface modifiers can be easily incorporated into inks and coatings using low speed mixers. Occasionally, high-speed mixing is required. Caution should be taken if using high-speed mixing to avoid foam generation and overgrinding.

Micronized waxes can be easily dispersed using mixers or dissolvers. Formulation variables such as viscosity, solvent package, resin type, selection of dispersant and pigment surface treatment can influence the ease of incorporation. Processing temperatures should be maintained below 40°C to prevent particle swelling in solvent based systems.

A pre-dispersion of micronized wax can be prepared to simplify incorporation into coatings or inks. As a guide, 15-30% micronized wax could be pre-dispersed in a blend of resin and solvent consistent with the ratios in the coating. Pre-dispersion of micronized wax into an aqueous system will require the use of wetting agents. Temperature control is important in solvent based systems to prevent particle swelling and viscosity drift.

Addition Rate

Typically, surface modifiers are used between 1-5% to achieve targeted performance properties.

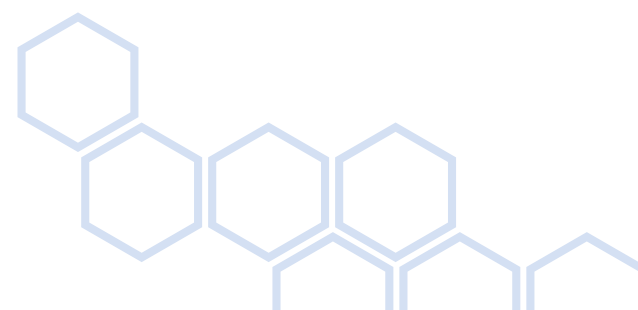
Storage

Surface modifiers are stable under standard conditions (5-40°C). Product data sheets should always be referenced for specific storage recommendations. It is important to protect wax preparations from extreme temperature conditions such as frost and high heat. Solvent based dispersions should not be stored above 40°C to prevent swelling and viscosity drift. Aqueous dispersions should be protected from freezing.



Food Grade Applications

Many surface modifiers comply with FDA regulation 21 CFR § 175.300, 175.105, 176.170 and 176.180 in addition to other food content regulations. Additional regulatory compliance information on Swiss Annex, Nestle, EU 10/2011 and other regional food compliance requirements can be obtained from the product manufacturer.



PRODUCT LINES FOR PAINTS, COATINGS AND INKS

Depending on the application, Lubrizol offers a variety of micronized and liquid wax preparations.

Dry Powders

Lanco™ and Pinnacle™ micronized waxes suitable for water-based, solvent-based and UV systems.

Lanco™ Matt micronized wax treated silica matting agents suitable for water-based, solvent-based and UV systems.

PowderAdd™ micronized waxes designed especially for use in powder coatings.

Liquid Preparations

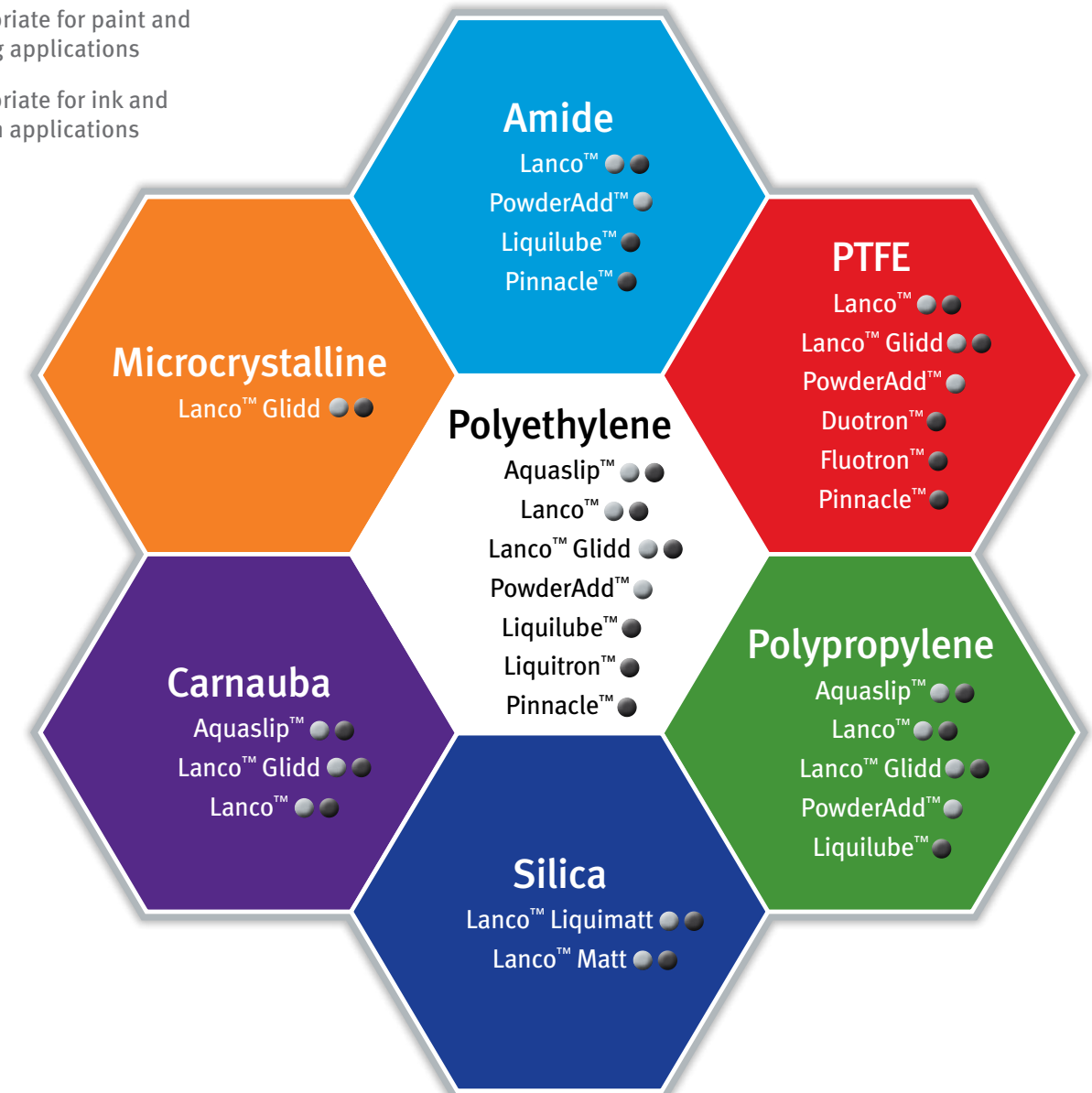
Lanco™ Glidd, Liquitron™ wax dispersions available for water-based, solvent-based and UV systems.

Lanco™ LiquiMatt matting dispersions offered for solvent and water-based systems.

Fluotron™ and Duotron™ wax dispersions based on pure PTFE or PE/PTFE suitable for water-based systems.

Aquaslip™ and Liquilube™ wax emulsions for water-based systems.

- Appropriate for paint and coating applications
- Appropriate for ink and varnish applications





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