Decision tree “design of biobased coatings”

Brought to you by the COOCK+ project AddBIO

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Inhoudstabel

1. Introduction

1.1 Prupose of the decision tree

In the current transition towards more sustainable and eco-friendly industrial practices, the coatings industry is increasingly seeking solutions that align with environmental regulations and consumer demands. One of the primary shifts is towards bio-based materials that can replace traditional petrochemical-based components in coatings, offering benefits such as biodegradability, reduced environmental impact, and improved safety profiles. **However, the selection of the appropriate bio-based ingredients for a coating formulation can be a complex process**, given the diversity of performance requirements and the range of available bio-based materials. To address this complexity, we have developed a decision tree approach that helps guide coating manufacturers through the process of selecting bio-based materials that meet their specific technical and performance needs.

The decision tree is structured around three fundamental questions that form the basis of the selection process:

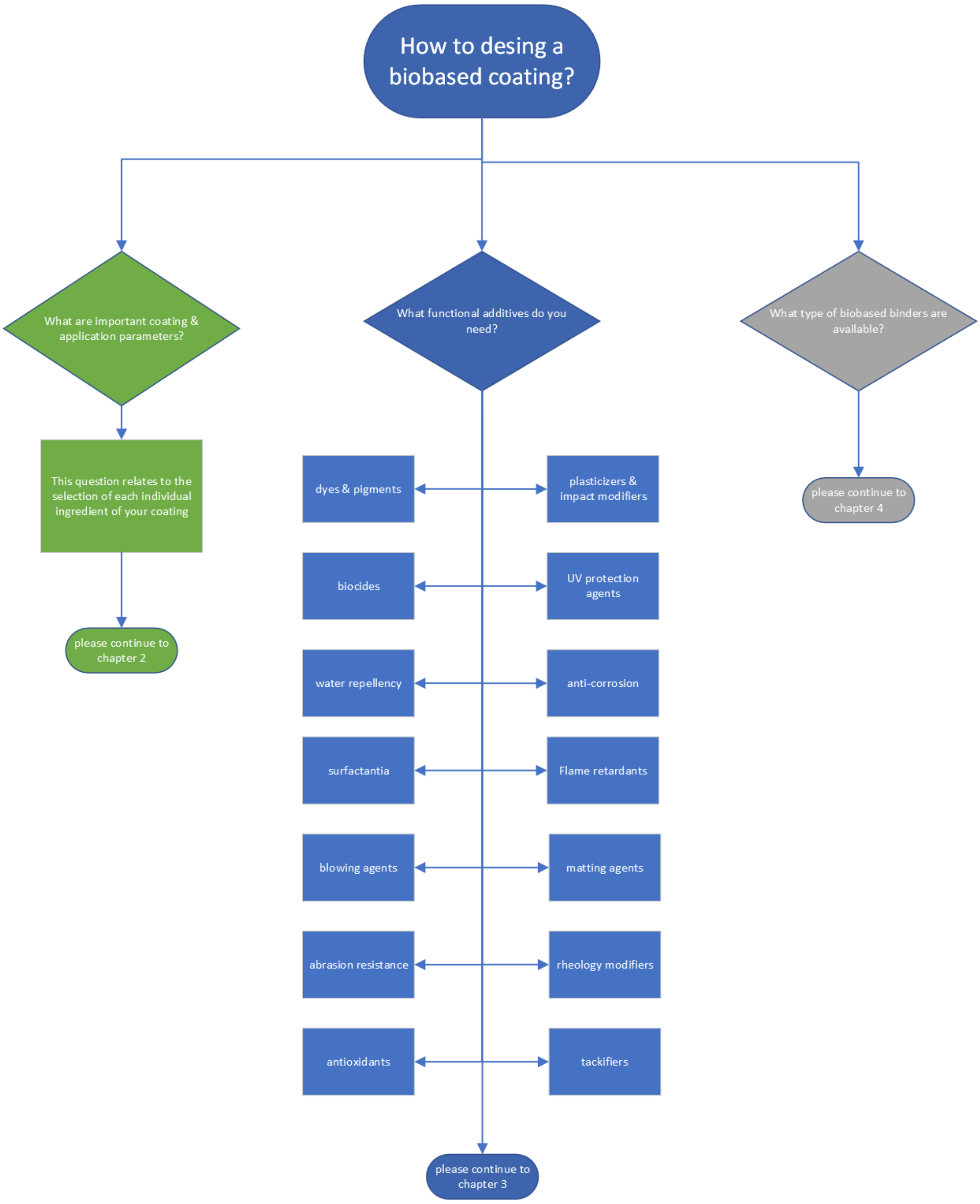
1. **Coating and Application Parameters:** The first step in the decision-making process is to define the key parameters that are critical to the performance of the coating. These parameters might include barrier properties (such as resistance to water, oxygen, or chemicals), mechanical durability (e.g., hardness, flexibility, and wear resistance), biodegradability, or compatibility with application processes (such as heat curing, UV curing, or ambient drying). This step ensures that the bio-based materials chosen meet the fundamental requirements for the coating's intended use. By prioritizing these parameters, manufacturers can filter potential materials and focus on options that align with both performance goals and environmental objectives.

2. **Additive Selection:** Coating formulations often require the addition of specific additives to achieve desired functional properties. These additives may include plasticizers for flexibility, flame retardants for fire safety, water repellents for moisture resistance, or biocides for antimicrobial properties. In this step, manufacturers identify the necessary additives that their formulation requires and determine whether bio-based alternatives are available. The growing market for bio-based additives provides opportunities to integrate sustainable options without compromising on performance. This stage of the decision tree ensures that every component of the coating formulation is aligned with the sustainability goals of the project.

3. **Bio-based Binder Selection:** The binder is the backbone of any coating formulation, providing film formation and adhesion to the substrate. Selecting an appropriate bio-based binder is crucial as it directly affects the coating's overall performance, such as its elasticity, hardness, and environmental resistance. In this step, we guide manufacturers through the process of choosing a bio-based binder based on the functional requirements established in the first step. Options include biodegradable polymers like polyvinyl alcohol (PVOH), polyhydroxyalkanoates (PHA), polylactic acid (PLA), and polycaprolactone (PCL) for biodegradable systems, or more durable bio-based alternatives such as bio-based polyurethanes (PU), bio-epoxies, and bio-acrylates for applications requiring durability and resistance to environmental factors.

This decision tree approach allows for a structured, methodical evaluation of bio-based options tailored to specific needs, rather than a one-size-fits-all solution. By breaking down the selection process into key parameters, additive requirements, and binder types, manufacturers can make informed decisions that strike a balance between performance and sustainability. Furthermore, the flexible nature of the decision tree enables it to accommodate a wide range of coating types and applications, from industrial to consumer products.

In subsequent sections, we will dive deeper into each of these three areas, exploring the specific criteria and considerations for each step. This will include detailed guidance on bio-based material options, their performance characteristics, and how they can be integrated into various coating systems. By following this structured approach, manufacturers can ensure they are making well-informed choices that not only meet technical requirements but also contribute to a more sustainable future for the coatings industry.



1.2 About the authors & acknowledgements

This study was conducted by Centexbel and Sirris as part of the COOCK+ project AddBIO. Centexbel-VKC is a collective research center for the textile and plastics sector. It operates three facilities across Belgium, focusing on material science research with several specialized laboratories (accredited laboratories for physical, chemical, fire, and microbial testing, as well as pilot lines for plastics processing, coatings & inks, and textile processing). Within its R&D activities, there is a strong focus and expertise in biobased polymers, recycling and circular economy, smart textiles, and composites. This study was coordinated by Brecht Demedts, with contributions from multiple experts in materials science research (see author list). AI tools were utilized in a supportive manner in accordance with European Commission guidelines, with ChatGPT-4 being employed to ensure the completeness of content.

Centexbel and Sirris wish to thank VLAIO for supporting this project. VLAIO is the Flemish the innovation and funding agency of the Flemish government for all entrepreneurs in Flanders. Flanders could be more ambitious when it comes to entrepreneurship. We need more startups, more growth, and more innovation. Therefore, VLAIO aims to initiate projects that encourage, support, or guide entrepreneurs in their ventures. Together with our partners, we pool our strengths and resources. AddBIO is part of a network of initiatives you can benefit from. Discover them all at www.vlaio.be/expertisedatabank. #sterkondernemen.

2. Decision making for biobased coatings

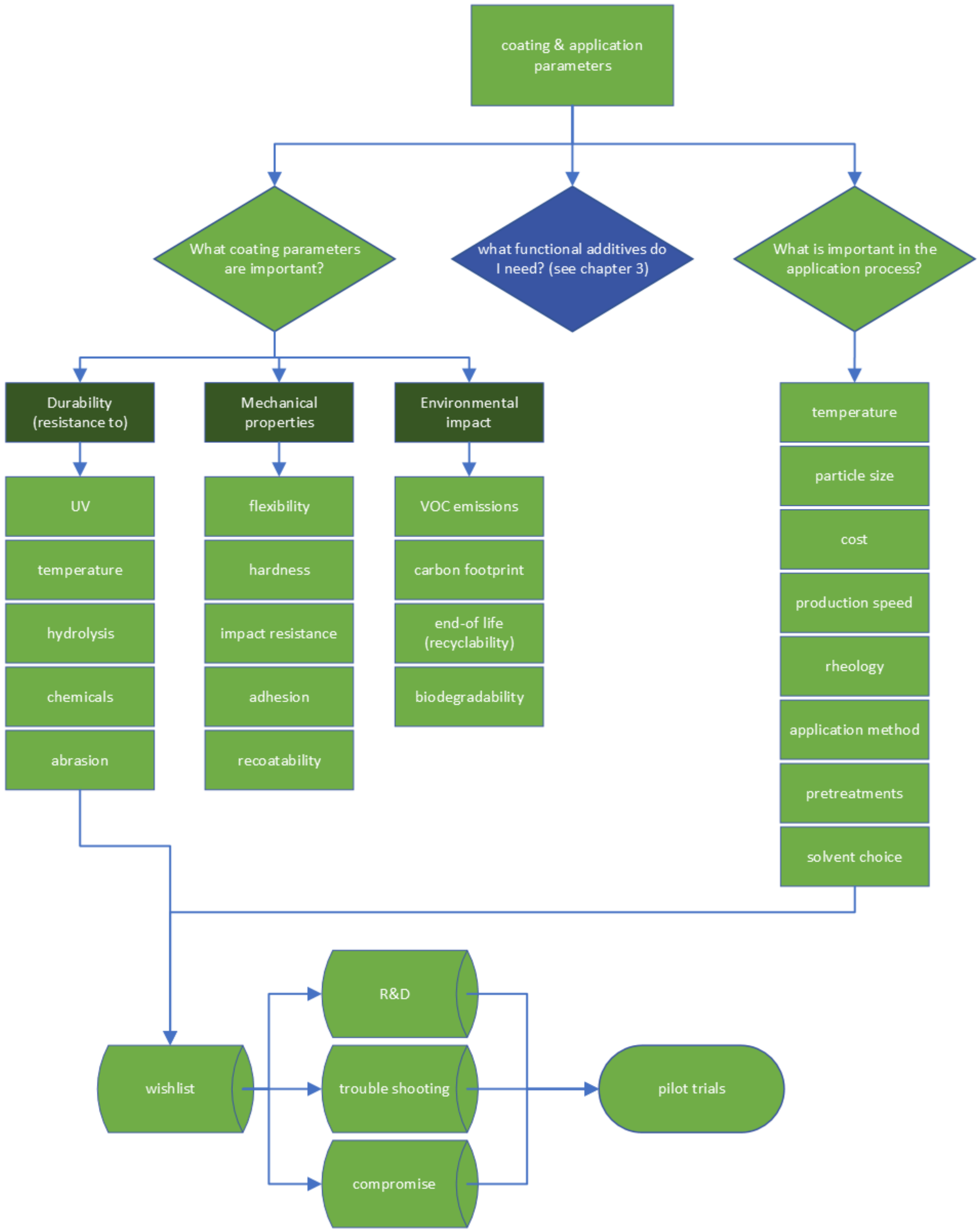
We all want performant, durable, ecological, beautiful and cost-efficient coatings. The challenge, however, lies in balancing sustainability with performance, cost, and process efficiency. Developing a biobased coating isn't just about choosing environmentally friendly materials—it's about ensuring these materials perform as well as or better than their traditional counterparts and fit seamlessly into existing production processes.

When approaching the development of a biobased coating, two key areas of consideration emerge: **the desired properties of the coating itself** and **the requirements of the application process**. These areas together form the backbone of the decision-making framework for selecting and formulating biobased materials.

On the one hand, the **performance characteristics** of the coating are crucial. Depending on the specific application, coatings may need to withstand extreme conditions, protect surfaces over time, or even degrade safely in the environment once their lifecycle is complete. **Durability**, for instance, encompasses resistance to UV radiation, water, chemicals, and mechanical wear. Coatings applied to outdoor surfaces must retain their integrity despite constant exposure to the elements, while those used in industrial or harsh environments need protection against chemicals and high temperatures. **Mechanical properties**, such as flexibility, impact resistance, and scratch fastness, also play a critical role, particularly in coatings that must endure physical stresses without cracking, flaking, or becoming brittle.

At the same time, sustainability factors have come to the forefront, with an increasing emphasis on **environmental impact**. Coatings that minimize the release of volatile organic compounds (VOCs), avoid harmful heavy metals, and reduce the risk of microplastic pollution are increasingly in demand. Biodegradability and recyclability are key considerations, especially for products designed for short-term use or those expected to contribute to a circular economy. For example, coatings used in packaging must balance the need for protection and appearance with the ability to degrade or be recycled after use. These properties form a complex matrix of needs that must be addressed through careful selection of biobased raw materials and additives.

On the other hand, **the practicalities of applying the coating play a crucial role in determining whether a formulation is feasible** for large-scale production. The application process involves numerous technical and economic factors. Temperature requirements, for example, influence the choice of curing methods—whether heat, UV, or air drying. Solvent choice impacts not only how well the coating flows and adheres during application but also its environmental footprint and worker safety. A formulation may need to be adjusted to accommodate the specific equipment used in a facility, from spray systems to dip-coating machines. Similarly, the viscosity and particle size of the coating influence how well it spreads and forms a uniform layer, directly affecting the final finish quality. These parameters also determine whether the coating can be applied at the speed required to keep production lines efficient and cost-effective. Cost is another critical factor; biobased materials often come at a premium, so any added expenses need to be weighed against the performance benefits and the company's sustainability goals.



Once all these considerations are taken into account, a "wishlist" is created—a list of essential properties that the biobased coating must possess. This wishlist serves as the foundation for guiding the formulation process, helping to identify where innovations are needed or where compromises may be required. From here, the development path typically diverges into three potential directions: research and development (R&D), troubleshooting, and making compromises.

In some cases, the wishlist may reveal gaps in current material offerings, prompting further R&D. This could involve searching for new biopolymers or creating custom additives to improve specific performance traits, such as UV resistance, biodegradability, or elasticity. On other occasions, pilot testing might expose issues that require troubleshooting—perhaps the coating isn't curing properly, or the mechanical properties aren't up to standard. In these cases, iterative adjustments to the binder system, curing process, or choice of additives are essential to refine the formulation. Finally, there are instances where compromises need to be made. Some performance traits may be inherently in conflict with others, or budget constraints might limit the use of certain biobased materials. Here, careful decision-making is necessary to find a balance that aligns with both the performance expectations and sustainability targets of the project.

The ultimate goal of this process is to reach the pilot trial stage, where the biobased coating can be tested under real-world conditions. It's here that the true performance of the formulation is assessed—how well it adheres, how durable it is, and how efficiently it can be applied in an industrial setting. These trials provide invaluable feedback, offering insights that guide final tweaks to the formulation before it is ready for market entry.

This approach, while methodical, is essential for navigating the complexities of biobased coatings development. By considering the full spectrum of both performance and process-related parameters from the outset, companies can ensure they are not only reducing their environmental footprint but also delivering coatings that meet the rigorous demands of their customers and end-users. Biobased materials have several specific aspects that characterize them. In the next sections, we highlight some of these aspects, like biological variation, mass balance, smell & color, chemical stability, impurities, greenwashing, certification and the importance of LCA.

2.1 Is there **biological variation** to take into account?

A challenging aspect of using biobased raw materials is the significant variability that can occur in biological organisms and crops. Plants are highly adaptable to diverse conditions and can quickly adjust to factors like drought, UV exposure, and temperature changes. These adaptations result in changes in their composition and structure. As a result, biomass can be difficult to process, or its properties may vary from year to year. Additionally, certain biobased products are very heterogeneous. This is particularly true for materials like lignin, suberin (cork), and secondary metabolites, which are only produced under specific conditions.

In the context of utilizing agricultural (by)products in the chemical and coatings industry, this biological variation is a crucial consideration. Certain industrial precautions can be taken to mitigate these challenges. For example, in producing "high-grade" lignin fractions, only paper mills that primarily process one specific type of wood (such as birch) may be suitable. Similarly, in oleochemistry, it is common practice to blend different batches of, for example, rapeseed oil from various regions to achieve a more consistent fatty acid composition.

In coatings production, these variations in biobased materials can have a direct impact on the final product. Coating formulations rely heavily on the consistency of raw materials to ensure uniform properties like durability, viscosity, and drying time. Variability in biobased feedstocks could lead to inconsistencies in these key performance areas. For instance, lignin from different sources may have differing molecular structures that can affect its role in providing UV protection or mechanical strength in coatings. Similarly, natural oils used in binders or additives might vary in composition, potentially altering the flexibility or curing behavior of the coating.

Understanding and controlling for this variability is critical when transitioning to biobased ingredients in coatings. Steps like sourcing from regions with similar environmental conditions or blending batches of materials can help manufacturers maintain the necessary consistency in their formulations, ensuring that biobased coatings meet industrial performance standards.

2.2 **Mass balance,** identical to fossil-based ingredients or not?

Mass balance means that the raw ingredients, that before were fossil based, can be replaced by biobased sources, e.g. vegetable oil in stead of mineral oil. Some processes will lead to exactly the same end-product, but can be biobased in stead of fossil based. However, in mass balance, it can be that during a the production of a full year, only during 2 months vegetable oil is fed to the synthesis, the other ten months fossil based oil. Nonetheless, products can be labeled as 2/12 or 16% biobased on mass balance. However, this is not the reality. At one time of the year, the product can be 100% biobased, on other times, it will be 0% biobased. Therefore "mass balance" is a bit a confusing term that relies on auditing systems that ensures that indeed biobased raw materials are used in the correct ratio.

This approach requires careful monitoring and certification to ensure that claims about biobased content remain accurate and credible. The industry must invest in technologies and processes that can manage the variability of biobased raw materials while maintaining the integrity of the mass balance. This also impacts product certification, as certain standards use carbon dating to determine "biobased content," and these are verified through random sampling. With the mass balance concept, however, one batch may have a very high percentage of biobased carbon content (as measured by the C14 method), while another batch may have almost no biobased carbon content at all.

2.3 Take into account undesired colors and smells

Many biobased components have a **certain color or odor, which is often undesirable**, even if the color is attractive or the scent is pleasant. When additives and biobased materials are colorless and odorless, they can be marketed more widely across various applications. However, deeply colored additives (e.g., surfactants derived from lignin that are dark brown to black) can often only be used in technical applications where color is not a critical factor.

Odor can not only be bothersome and unpleasant, but it can also conflict with legal limits. Odorous compounds are volatile, and many markets have legal limits on volatile compounds, known as VOCs (volatile organic compounds). VOCs are often measured as "total VOCs" without distinguishing between harmful and non-harmful VOCs. Natural components that contribute to VOC emissions are therefore a sensitive issue, particularly in applications where this parameter is critical, such as interior furnishings, automotive applications, and toys.

2.4 Biobased ingredients and their chemical stability

Chemical stability is a crucial factor in the production and application of biobased ingredients and raw materials. This stability determines how well a material retains its properties under various conditions such as temperature, humidity, light, and oxygen. Biobased ingredients, often derived from natural sources like vegetable oils, proteins, and natural dyes, can be susceptible to different forms of chemical degradation that negatively impact their functionality and aesthetic qualities. Here, we outline some common unwanted effects.

Proteins, which are often used in biobased products such as coatings, food packaging, and cosmetics, can denature when exposed to extreme temperatures, pH levels, or mechanical forces. Denaturation leads to the loss of the native structure of the protein, which can result in reduced functionality, such as a loss of water-binding capacity or decreased film formation. Natural colorants are vulnerable to degradation by UV light and sunlight. This often leads to fading or discoloration of products over time, posing a challenge for the aesthetic quality of biobased cosmetics, textiles, and packaging. Chemical reactions, such as the oxidation of dyes, can accelerate color loss.

In the processing of biobased ingredients, particularly at elevated temperatures, the Maillard reaction and caramelization can occur. These reactions, which take place when sugars, fats, and/or proteins are heated, can result in unwanted color changes and degradation or the formation of undesirable chemical compounds. In general, biobased polymers and other organic materials are often more susceptible to thermal degradation than their petrochemical counterparts. At high temperatures, these materials may decompose, leading to charring or the formation of carbon residues, which negatively affect the structural integrity and appearance of the final product.

Many biobased materials, particularly the common biobased polyesters, are also prone to hydrolysis. This chemical reaction, where a molecule breaks down in the presence of water, can lead to diminished mechanical properties such as brittleness or a loss of elasticity in products like coatings and packaging. Oxidation is another frequent issue with biobased ingredients, especially oils and fats. When exposed to oxygen, these materials can become rancid, which not only affects the taste and smell but also the chemical stability of the product.

Additionally, there is always a risk of biological and enzymatic degradation, especially with natural raw materials. This is particularly challenging during the storage and use of biobased materials, especially in humid environments where enzymatic activity increases.

To address these challenges, various strategies are employed in the chemical industry. These include the use of stabilizers and antioxidants, adjusting processing temperatures and times, and developing barrier coatings that provide protection against moisture, oxygen, and UV light. Research is also being conducted into modifying biobased materials to improve their intrinsic stability, for example through chemical cross-linking or the addition of synthetic components that extend the product's lifespan.

2.5 (im)purities of biobased ingredients

In biobased ingredients, which are often derived from natural sources such as plants, animals, or microorganisms, impurities can present a significant challenge, especially in the context of coatings. These impurities can range from organic and inorganic compounds to microbes and enzymes, all of which can negatively affect the final product's performance and quality. Controlling impurities is crucial to ensure the consistency, safety, and reliability of biobased coatings.

The variability in the raw materials themselves can lead to inconsistent purity levels. Factors such as seasonal changes, environmental conditions, and geographic differences impact the purity of the harvested materials, making it harder to maintain predictable production processes and consistent product quality. For example, natural oils, waxes, sugars, and lignin found in biobased feedstocks may not always be fully removed during extraction, potentially affecting the final coating's appearance, reactivity, and overall performance. Organic impurities like these can cause processing issues, discoloration, or even interfere with chemical reactions in coatings.

In addition to organic impurities, inorganic contaminants like soil, sand, or residual minerals and salts may be introduced during harvesting or processing. These inorganic substances can also affect the stability and durability of coatings, especially in high-performance applications where purity is critical.

Microbial contamination is another concern for biobased coatings. Since many biobased ingredients are organic, they can be prone to bacterial, fungal, or yeast growth. This not only affects the shelf life of the coating but especially also the pot-life of consumer products like paint.

To address these issues, the chemical industry employs various purification techniques, including filtration, distillation, chromatography, and fermentation processes, to reduce the levels of impurities. There is also growing research focused on improving extraction methods and developing new technologies to increase the purity of biobased ingredients. Despite these efforts, managing impurities remains an ongoing challenge due to the inherent variability of natural sources.

For coatings, this means constant attention to the sourcing, purification, and quality control of biobased materials is necessary to ensure that the coatings perform consistently in terms of appearance, durability, and protective properties.

2.6 Importance of LCA studies

Life Cycle Assessment (LCA) is an analytical method used to evaluate the environmental impacts of a product, process, or service throughout its entire life cycle. This method, based on ISO 14040 and 14044 standards, is essential for understanding the sustainability of materials, including biobased coatings. An LCA can be conducted as a cradle-to-grave analysis, covering all stages from raw material extraction, production, and transportation, to usage and disposal or recycling. Alternatively, a cradle-to-gate approach focuses only on the initial stages of extraction and production, providing insights into the manufacturing phase without accounting for the product's entire lifecycle.

For biobased coatings, an LCA offers a critical tool for assessing their ecological footprint, highlighting areas of significant environmental impact, and aiding in making informed decisions for more sustainable production and consumption practices. Factors such as the use of agricultural land, water, fertilizers, pesticides, energy consumption, and transportation all influence the LCA outcomes of biobased materials. While biobased coatings are often seen as more environmentally friendly than their fossil-based counterparts, this is not always the case. The production of biobased materials can still have significant environmental effects depending on how they are sourced and processed.

An LCA involves several important steps, starting with defining the scope and objectives. A comprehensive inventory is then created to track all inputs and outputs—such as raw materials, energy, emissions, and waste—associated with the product's lifecycle. These inputs and outputs are then linked to environmental impact categories, such as climate change, ozone depletion, water use, and land degradation.

In coatings, a key impact often considered is the emission of volatile organic compounds (VOCs), which contributes to air pollution and smog formation. Additionally, the type of biobased raw materials used, such as plant oils or cellulose derivatives, can result in varying LCA outcomes due to differences in land use and agricultural practices. For example, using tall oil—a byproduct of the paper industry—may result in a lower carbon footprint if it’s considered a waste product rather than a co-product.

While LCA helps identify potential hotspots in the lifecycle of biobased coatings, interpreting the results requires context. Standards like the Environmental Product Declaration (EPD) and the Product Environmental Footprint (PEF) aim to make LCA results more comparable. However, differences in methodology mean that results are only comparable within the same framework.

Ultimately, LCA studies for biobased coatings are critical for making informed, scientifically grounded decisions regarding their environmental impact. Although biobased does not necessarily equate to environmentally friendly, a detailed LCA provides the necessary insights to ensure that coatings contribute positively to sustainability goals.

2.7 Greenwashing

Greenwashing refers to a deceptive marketing practice where companies make their products or services appear more environmentally friendly than they actually are. By using vague or misleading information, businesses can create a false impression of sustainability to appeal to environmentally conscious consumers. This tactic can range from overstating a product's eco-benefits to hiding its environmental costs.

There are common strategies of greenwashing, sometimes used unintentionally:

1. **Vague Claims**: Terms like "natural," "eco-friendly," or "sustainable" are often used without proper explanation or certification, misleading consumers into thinking the product is greener than it is.

2. **Incomplete Information**: Companies might highlight an environmentally friendly feature while downplaying the negative impacts. For instance, a product may be made from bio-based materials but produced through highly polluting processes.

3. **Irrelevant Claims**: These are technically true but meaningless in context. For example, advertising that a product is "CFC-free" (chlorofluorocarbons, which have been banned for years) to give an impression of environmental responsibility.

4. **Concealing Harmful Practices**: Some companies spotlight small green initiatives to obscure the fact that their core activities are environmentally damaging. For example, an oil company promoting its renewable energy projects while downplaying its significant fossil fuel operations.

Greenwashing is harmful because it undermines consumer trust and makes it harder for genuinely sustainable products to stand out. It can also perpetuate environmental damage, as consumers may unknowingly purchase products that are not as eco-friendly as they appear.

To avoid greenwashing, consumers should critically assess environmental claims and seek third-party certifications. Companies, on the other hand, should be transparent, backing their claims with verifiable data to ensure that they contribute to real environmental progress, rather than just appearing to do so.

In the context of bio-based coatings, greenwashing can easily occur, especially when manufacturers overemphasize the use of renewable resources while ignoring the environmental cost of production processes, energy use, or waste management. Transparency and clear certification are key to avoiding these misleading practices.

2.8 Certification and testing

The testing and certification of materials has become a critical industry. Both commercial and non-commercial entities play an essential role in testing these materials. A certificate, often a voluntary label, provides consumers with specific information about a product, such as its bio-based content. Besides certifications, there are numerous accredited tests developed by organizations like the European Committee for Standardization (CEN). These standardized tests can only be conducted by accredited laboratories, which in Belgium receive their accreditation from Belac. Accredited labs must meet rigorous requirements, including participation in interlaboratory tests.

Certification bodies accept test results from all accredited labs, and if a product meets the necessary criteria, it can receive certification. Certification providers usually conduct random checks to ensure that certified products on the market continue to meet the required standards. While there are costs associated with certification, it is crucial for certification providers to make their labels widely recognized by the public, as well-known certifications can generate revenue for the providers.

In the context of bio-based coatings, certifications validate a product’s bio-content or biodegradability claims, providing transparency and building consumer trust in the product's environmental credentials. Note that biodegradability and biobased content are very different. An coating can be biodegradable, but not biobased (e.g. polycaprolactone), while other coatings may be biobased but highly durable and not biodegradable at all (e.g. polyurethanes). Therefore, a proper knowledge of common terms used may also be important to highlight to customers.

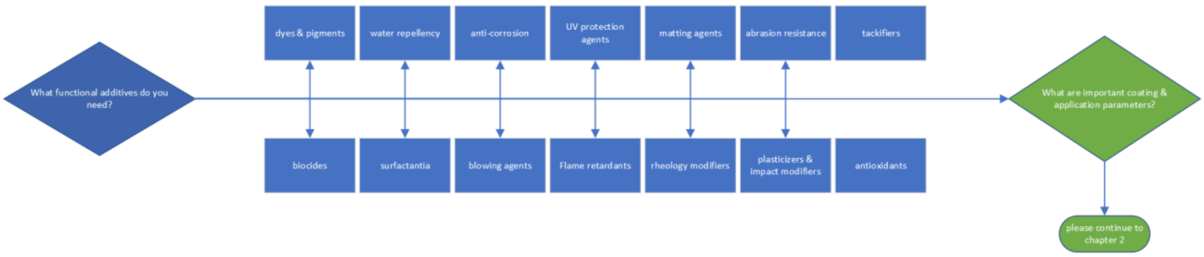
Label	Indication of biobased content	Standards	Owned by/Granted by
OK biobased	**stars:** *: 20-40% **: 40-60% ***: 60-80% ****: >80%	**Organic carbon content** TÜV AUSTRIA document TS-OK20 **Biobased content** ASTM D 6866 DIN SPEC 91236	*TÜV AUSTRIA*
DIN-Geprüft Biobased	**number on label:** 20-50% 50-85% >85%	**Organic carbon content** EN 13039 DIN 18128 **Biobased content** ISO 16620 ASTM D 6866 DIN SPEC 91236	*DIN CERTCO*
Bio-based content	**number on label**	**Organic carbon content / Biobased content** EN 16785-1	Managed by *NEN*, granted by *TÜV AUSTRIA* or *DIN CERTCO*

Figuur: example of commonly used certificates

3. Additive selection

In the formulation of coatings, additives play a crucial role in tailoring the final product to meet specific performance and aesthetic requirements. While the binder provides the structural framework for the coating, additives fine-tune properties such as flexibility, color, durability, and resistance to external factors like moisture, UV radiation, or microbial growth. In recent years, the shift towards bio-based materials has spurred the development of sustainable additives that can replace their synthetic counterparts without compromising on performance.

Additives are essential for optimizing coating formulations across a wide range of applications, from decorative finishes to protective industrial coatings. They can influence the application process, the curing behavior, and the long-term performance of the coating. In bio-based coatings, selecting appropriate additives is a delicate balancing act between maintaining high-performance standards and achieving environmental sustainability. Bio-based additives are derived from renewable sources, offering reduced environmental impact, lower toxicity, and improved biodegradability compared to traditional petrochemical-based additives.



In this chapter, we will explore the key types of additives used in bio-based coatings, explaining their function, the challenges they address, and providing examples from each category. The goal is to help formulators identify suitable bio-based alternatives for traditional additives, ensuring that the overall formulation meets both technical and sustainability objectives. It is important though to realise that all the aspects of chapter 2 apply for each and every single additive you select, and that is where the difficulty of biobased ingredients lay. They often have “side-effects” that don’t comply with your coating application process or final properties, such as durability, odor or color, even if the performance of the biobased additive may be excellent.

3.1 Plasticizers and impact modifiers

Plasticizers are additives used primarily in plastics, especially thermoplastics, to make the material softer and more flexible. These molecules are usually liquid at room temperature and have low volatility. When added to polymers, plasticizers interact through non-covalent bonds, lowering the glass transition temperature (Tg) and increasing the material’s ductility and elongation. They are also used as inexpensive fillers in products like sealants and coatings, and in paints to improve coalescence during drying, where they are often called "coalescing agents."

Plasticizers come in many forms and cover a wide range of molecules. Historically, they have had a negative reputation due to the widespread use of ortho-phthalates like bis(2-ethylhexyl) phthalate (DEHP) since the 1930s, which were later found to be teratogenic and endocrine-disrupting. As a result, numerous alternative plasticizers have been developed. While synthetic plasticizers (such as phthalates, benzoates, adipates) still dominate the market, several partially bio-based options exist (such as succinate esters, citric acid esters, fatty acid esters, and isosorbides). Contrary to popular belief, not all plasticizers are harmful to the environment or human health.

The largest volume of plasticizers in the coatings sector is used for PVC plastisol coatings. These are used for tarpaulins, tents, vinyl flooring, artificial leather, blood bags, and electrical wiring. Beyond PVC, plasticizers are used in polyurethane (PU), paints, sealants, and inks. While phthalates are still widely used due to their cost-effectiveness and high performance, low-molecular-weight ortho-phthalates are associated with health risks, especially in food-contact applications. Bio-based polymer plasticizers are increasingly used in these cases, offering food contact safety but at a higher cost.

Bio-based plasticizers come in several key types. One major category includes esterified oils, fatty acids, sugars, or citric acid. These esters, often partially bio-based, are cost-efficient and food contact approved but can degrade in moisture over time, releasing odors as a result of hydrolysis. Epoxidized oils, such as epoxidized linseed or soybean oil, are another type. While they are not highly effective plasticizers, they serve as radical scavengers in PVC, improving its stability during processing.

Polymeric plasticizers are particularly effective, produced by polymerizing small diols (often glycerol-derived) with dicarboxylic acids, such as sebacates or succinates. These can be sourced from fermented sugars or high-quality oils like castor oil. They are typically used in toys and food-contact applications, such as the sealing layers in jar lids or pharmaceutical blister packs, where they provide excellent barrier properties to slow down oxidation.

Plasticizers can be especially handy in the formulation of coatings because sometimes it allows to add more of other compounds. For example, higher amounts of natural fillers can be added when using plasticizers because the viscosity of the coating pastes will be typically lower. Of course there are drawbacks, excessive use of plasticizer can lead to migration or weaker coatings.

3.2 UV-additives

UV protectants are substances that absorb, reflect, or scatter UV radiation to prevent damage to the skin and other materials. UV radiation can create oxidative radicals that degrade polymers, fade dyes, cause sunburn, and increase the risk of skin cancer. Various types of polymers are susceptible to UV damage, which can make them brittle and lead to crumbling or powdering. As a result, numerous UV protectants are added not only to cosmetics and sunscreens but also to polymers, coatings, paints, and adhesives. There are three main types of UV protectants:

1. **Antioxidants:** These substances neutralize oxidative radicals formed by UV radiation, preventing damage to the polymer. Highly effective antioxidants include HALS (hindered amine light stabilizers), which can regenerate themselves, providing continuous antioxidant protection. In plants, vitamins C (water-soluble) and E (fat-soluble) are effective antioxidants.

2. **UV Blockers:** These are typically pigments that fully absorb, reflect, or scatter specific wavelengths of UV light, preventing harmful UV radiation from reaching underlying layers. Common examples include titanium dioxide and zinc oxide, which have high refractive indices. In plants, the waxy cuticle layer also reflects sunlight.

3. **UV Fluorescent Agents:** These molecules absorb UV light and then fluoresce at lower energy levels (usually as blue light), losing a small amount of energy as heat.

Sometimes, all three classes of additives are used in combination to achieve a synergistic effect. In coatings, UV protectants are often applied in topcoats, where light exposure is greatest. It is essential for these protectants to maintain their efficacy throughout the lifespan of the coating, which can be a challenge for bio-based molecules that often have a shorter duration of action.

A notable example of an agricultural by-product being used as a UV protectant is grape skins, which are rich in resveratrol—a colorless compound that fluoresces across a broad spectrum of UV wavelengths. This suggests that exploring agricultural waste from sun-exposed plant materials for UV-protective additives could be a promising avenue for future research in bio-based coatings.

3.3 Flame retardants

Flame retardants are essential in preventing or slowing down fires by disrupting the ongoing fire. Flame retardants operate by inhibiting the supply of heat, oxygen, and/or fuel.

Fire Cycle and Flame Retardants

The fire cycle begins with an ignition source (e.g., flame or heat), which triggers a pyrolysis reaction in the polymer, breaking it down into smaller hydrocarbon molecules that generate combustible gases and free radicals. These gases mix with oxygen, leading to exothermic chemical reactions that produce water and carbon dioxide, note that incomplete combustion can release toxic gases, which is especially relevant for bio-based materials containing nitrogen or sulfur.

Flame retardants can act chemically and/or physically in both the condensed and gas phases. They interfere with combustion processes by reacting with the polymer during heating, decomposition, or ignition, thereby slowing down flame spread.

Mechanisms of Action

Flame retardants mainly utilize physical and chemical mechanisms:

- Physical Mechanisms: These include cooling through endothermic reactions (e.g., aluminum trihydrate releasing water) and forming protective layers that shield the polymer from the ignition source and oxygen. Phosphorus-based flame retardants create such barriers by converting into phosphoric acid during thermal decomposition, forming a protective char layer.
- Chemical Mechanisms: Halogenated flame retardants work by trapping free radicals produced during pyrolysis, thus suppressing exothermic reactions in the gas phase. However, they are often criticized for their environmental persistence.

Bio-based Flame Retardants

Flame retardants often make negative headlines as pollutants, particularly brominated (halogenated) compounds. These products tend to be persistent, leading to their accumulation in the environment. Therefore, there is a strong rationale for transitioning to alternative flame retardants. Bio-based materials rich in nitrogen (e.g., proteins) and phosphates show potential as flame retardants. These substances can facilitate char formation and may also cause an intumescent layer.

Flame retardancy requirements vary by product type, with numerous standards dictating parameters such as flame spread, smoke density, smoke toxicity, and smoldering for different product classes. A flame retardant must primarily extend evacuation times, and the applicable fire classes will be stricter in transportation and public spaces than in home use.

In Belgium, several companies are active in formulating flame-retardant compounds, such as CTF2000, Devan, and EOC. In recent years, there has been a growing market for bio-based flame retardants, such as those developed by Devan in Ronse. Maes Mattress Ticking, in collaboration with Centexbel, has also developed the bio-based flame retardant M-Pure, specifically for the mattress market.

3.4 Dyes and pigments

Color is ubiquitous and plays a vital role in the perception, design, and marketing of every product. Color can be imparted to materials using dyes or pigments. **The key difference is that dyes are soluble (in water or solvents) and can bond with the material, while pigments are largely insoluble** and provide color without forming bonds, instead embedding in the matrix. Dyes are typically organic and yield transparent colors, while pigments are often inorganic and provide opaque colors.

Pigments are usually minerals obtained from nature, such as iron oxide (ochre), lapis lazuli (blue), and carbon black (soot). Nowadays even inorganic pigments are mostly synthesised. Some companies offer also natural or bio-based pigments in masterbatches for the plastics processing industry.

Dyes interact with the materials to achieve a semi-permanent binding, with different types suitable for specific materials: (i) Acid dyes for cationic materials like polyamide, wool, and silk. (ii) Basic dyes for anionic materials, mainly used on acrylic fibers. (iii) Direct dyes for paper, cotton, leather, wool, silk, and polyamide. (iv) Vat dyes temporarily convert to a water-soluble form during dyeing (e.g., Indigo for denim). (v) Reactive dyes form covalent bonds with the matrix, primarily for cotton and other cellulose fibers. (vi) Disperse dyes dissolve in the matrix of the material, mainly used for dyeing polyester and (vii) azo dyes are formed from two components during dyeing; however, their toxic nature has limited their use.

There are also various bio-based dyes extracted from plants, insects, or bacteria, which can be classified similarly to synthetic dyes. For instance, Archroma produces bio-based reactive dyes called "Earthcolors" from agricultural waste, such as almond shells and cotton residues. Despite chemical modifications, these dyes remain compostable.

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Figuur – dyes from natural waste streams, note that the colors are often dull and not vivid, as the vivid natural colorants are often short lived and not suitable for use in high performance durable coatings. (source Archroma EarthColors TM)

Examples of bio-based vat dyes include Indigo, derived from plants like Indigofera, and Alizarin from madder root. Synthetic Indigo is preferred for cost and efficiency, though LCA studies suggest varying ecological impacts between synthetic and natural indigo due to the complex purification process of the latter. Mordant dyes require additives (mordants) for fixation, with many natural dyes being mordant dyes. Examples include chamomile, madder, and onion skins. However, many mordants are based on heavy metals and should be avoided.

Many natural dyes lack lightfastness for industrial applications, limiting their use primarily to the food sector. Natural pigments like chlorophyll, carotenoids, and curcumin may fade quickly when exposed to light, making them suitable mainly for products shielded from direct sunlight.

3.5 Biocides

Biobased biocides are antimicrobial agents derived from natural sources such as plants, microorganisms, or animal products. They are utilized to inhibit or kill harmful organisms, including bacteria, fungi, viruses, and insects. Although biobased biocides are often perceived as more environmentally friendly and safer, this is not always the case (e.g., nicotine, neurotoxins). Generally, they tend to be less persistent, as they are more readily biodegradable. It is essential to recognize that this class of products is very diverse, with fungicides, algicides, bactericides, insecticides, etc., each having entirely different modes of action. Many industrial applications require prolonged efficacy, which contradicts the faster biodegradation of biobased biocides. Nonetheless, various biobased biocides are used across a range of applications, including coatings.

Essential oils, such as tea tree oil, eucalyptus oil, and thymol, possess natural antimicrobial and insect-repelling properties. Plant extracts like neem and permethrin are commonly used as natural pesticides and fungicides, demonstrating a broad spectrum of activity against various pests and pathogens. **Quaternary ammonium compounds (QACs)** form a significant category of biocides, often produced from biobased fatty acids and lecithins. When positively charged, they can interact with cell membranes and biological processes, leading to inhibition of numerous biological activities, making them broad-spectrum biocides. However, many QACs can be harmful to the environment, necessitating in-depth research to synthesize or isolate non-toxic compounds. A similar mechanism is observed with chitosan, a biopolymer derived from chitin (found in crustacean exoskeletons), which has antimicrobial properties and is used in agricultural protection, food packaging, and even medical applications.

Organic acids, such as acetic acid and citric acid, or specific fatty acids like monolaurin, naturally occurring in plants, can function as biocides by inhibiting the growth of bacteria and fungi. They are widely used in food products and cleaning agents. Their primary action may be attributed to a low pH, which limits bacterial growth, or there may be specific interactions between the organic acid and vital cellular components (e.g., monolaurin).

Many biocides exhibit only partial biocidal action, often effective solely against gram-positive or gram-negative organisms, necessitating their combination. Many combinations yield synergistic effects, which is why they are utilized as "biocidal boosters," often avoiding more stringent regulations.

Preservatives are added to a variety of liquid, water-containing products, ranging from paints to emulsions, coatings, and adhesives, as well as for wood treatment to prevent rot. In water-based products, fungi and yeasts can rapidly spoil the products. Synthetic isothiazolines (CMIT, BIT, MIT, etc.) are widely employed, but regulatory pressures often lead to the end products containing these substances being labeled with risk and safety phrases. Given that B2C companies prefer to avoid safety symbols on consumer products, there is currently significant demand for alternative preservatives. New formulations are being explored, such as benzoates or parabens, which attract fewer safety labels.

Anti-biofilm formation is another specialized sector within biocides, technically referred to as anti-fouling. "Soft-fouling" includes typical microbial (including biofilm) and algal (green) deposits, which are prevalent in coatings for facades, pool liners, pipes, and porous surfaces. Hard fouling primarily pertains to marine applications involving mussel growth, barnacles, or snails. Biofilms cause considerable damage, such as clogging pipes or impeding flow. They also have a significant impact on shipping, as biological growth on ship hulls leads to poorer streamlining and increased fuel consumption. A major ecological issue is the substantial amounts of anti-fouling paint on ship hulls, contributing to bioaccumulation in port areas. Many anti-fouling paints must exhibit broad-spectrum efficacy against both mollusks and algae, leading to the historical use of heavy metals (tin compounds). These have gradually been replaced by copper-based compounds (the typical color of paint or ship hulls), which can also cause ecological problems. Certain biobased products, such as menthol, show good efficacy against mollusks, but their lifespan in these applications is short.

Europe plays a leading role in regulating harmful substances. This role is crucial, not only for public health but also for reducing environmental impact, and has a global effect since European regulations often serve as a model for improved legislation elsewhere. Biobased antimicrobial additives are considered biocides and are included in the list of substances of very high concern (SVHC list) due to potential allergic reactions, teratogenic effects, carcinogenic properties, neurotoxicity, hormonal disruption, or other harmful effects. Consequently, the Biocidal Products Regulation (528/2012) (BPR) has been established to control the use of these products, replacing Directive 98/8/EC on biocides. This also means that products containing biocides are considered biocidal themselves. The BPR distinguishes 22 product types (PT), classified into four families (disinfectants, preservatives, pest control, and others).

Legislation and permitted biocides will vary within PT1 (biocides for human hygiene) and PT2 (surface disinfection), making biocide legislation very complex. To use chemicals as biocides in coatings, products must undergo an approval process through the Biocides Committee of ECHA. This lengthy and costly procedure has led to many new biocides not reaching the market, including numerous biobased products (e.g., tannic acid, carvacrol, thymol, cinnamaldehyde) that have never been approved. However, in response to the COVID-19 outbreak, the European Commission has decided to allow exceptions to normal licensing requirements for biocides, enabling faster approval for new biocides. Nonetheless, legislation remains a significant issue, and various "evasion mechanisms" are employed by the industry.

As discussed, introducing new biocides is not straightforward from a legal standpoint, and chemical companies rarely register new biocides. However, numerous new products are entering the market under different names. Often, this is under the label of "anti-odor," where a product claims to counteract the smell of sweat in clothing. However, the odor is invariably not a result of sweat but of bacterial growth, and the additive works through antibacterial action, which is not explicitly claimed. Instead, an anti-odor effect is presented, avoiding compliance with biocide legislation.

A similar phenomenon is observed with cosmetic ingredients, where many "dispersing agents" are actually quaternary ammonium compounds that do not serve as dispersants but possess strong antimicrobial properties.

Many "antimicrobial boosters" are also marketed. These products are not claimed to be "antimicrobial" themselves but are combined with an existing registered biocide to work synergistically. Often, the booster functions adequately even without the registered biocide, allowing the registered biocide to remain below the threshold for safety labeling.

Lastly, numerous "fragrances" also exhibit antibacterial properties. Deodorants frequently contain mixtures of limonene, carvacrol, and thymol, officially presented as fragrance components but, in reality, are products with biocidal action. In this way, these products do not need to be registered as biocides.

Resistance is a common problem with all biocides, and promoting "smart use" of biocides, with correct dosages and application where necessary, should be a focus not just for antibiotics but for all biocides. Natural variation can provide examples, as plants within the same family can produce molecules that differ slightly, resulting in a broader spectrum of active ingredients.

Biobased biocides are increasingly significant in the biobased chemical industry as environmentally friendly alternatives to synthetic antimicrobial agents. They find application across various sectors, including agriculture, cosmetics, food, construction, and water treatment. Despite challenges like cost, regulation, and stability, biobased biocides can offer valuable benefits. Moreover, they are products with substantial economic value, allowing secondary metabolites or extracts found in small concentrations in plants to still hold significant economic worth.

3.6 Water repellency and water resistance

Water-repellent agents play a crucial role in various industries where protection against moisture is essential. They ensure that materials become water-repellent, significantly improving the lifespan and performance of products. In the textile, construction, paper, and coating industries, water-repellent agents are widely used to protect materials from water absorption, which can lead to damage, wear, and degradation.

Water-repellent agents work by forming a layer on the surface of the material that exhibits hydrophobic properties. This means that treated surfaces repel water rather than absorbing it. These agents can coat surfaces of materials such as textiles, paper, wood, and concrete, making them resistant to water penetration.

The hydrophobic effect is often achieved by applying substances containing fluorinated or silicone compounds. These compounds reduce the surface tension of the material, causing water droplets to form spherical shapes that roll off the surface rather than penetrate. Both fluorinated compounds (16 mN/m for PFAS) and silicone compounds (20-25 mN/m) have exceptionally low surface tension, while natural chemicals do not achieve such low levels. The best performance can be obtained with fatty acids and waxes (typically starting from 30 mN/m), which are sufficient for water repellency but inadequate for oil repellency.

Many fats and waxes can be directly used for hydrophobization. For example, wax emulsions are applied to gypsum boards to make them water-resistant. Waxes are also used in paper coatings; however, they complicate recycling processes, as a wax layer does not form a strong film that easily detaches during repulping. Additionally, fats and waxes can be easily removed through wear and abrasion and often attract dirt. Therefore, for more durable applications, water repellency is achieved through coatings. Particularly, polyurethanes are well-suited for this purpose, and a considerable number of highly performant biobased polyurethanes are already available. For effective hydrophobicity, a polyol with large hydrophobic side chains is necessary. The producers of these polyols synthesize them, utilizing biobased fatty acids as handy and versatile building blocks. Such water-resistant coatings can provide a degree of water repellency, but primarily they serve as excellent water barriers.

Alternatives for achieving low surface tension can be realized through nanostructuring. Nature is very efficient in this, as seen in the surfaces of lotus leaves, butterfly wings, and shark skin. These surfaces exhibit water repellency due to their nanostructuring. However, the challenge with nanostructuring is its tendency to wear off easily, requiring it to be highly abrasion-resistant in materials research contexts, which is difficult to achieve. Moreover, the nanostructuring must be fine and consistent (<40 nm) to achieve water repellency, making it a technically challenging task to mimic nature in this regard.

3.7 Anti-corrosion

Additives are essential components in coatings and lubricants that protect metals from rust and corrosion. Traditionally, various synthetic chemicals have been used to prevent corrosion, with zinc remaining one of the most effective options due to its galvanic protection. Zinc, applied in the form of zinc-rich primers or galvanized coatings, offers an excellent level of protection by acting as a sacrificial material that prevents the underlying metal from rusting. This method continues to be one of the most effective strategies in the fight against corrosion.

However, in the pursuit of more sustainable solutions, there is increasing research into biobased alternatives for anticorrosive additives. Protective oils, such as vegetable oils, represent one of the simplest and most accessible options. These oils create a physical barrier on the metal surface that prevents moisture and oxygen from reaching the metal, thereby slowing down rust formation.

Lanolin, a waxy substance derived from sheep wool, is another promising biobased alternative for anticorrosive additives in lubricants. Lanolin and its derivatives possess excellent water-repellent properties and can effectively serve as a protective layer to shield metal surfaces from corrosion. They provide an environmentally friendly alternative to more traditional petrochemical anticorrosive lubricants.

In the realm of anticorrosive coatings, it is crucial to select a chemistry that creates a highly impermeable barrier to moisture and oxygen. Polymers with good moisture, water vapor, and oxygen barriers are necessary, along with coatings that exhibit high scratch resistance, as scratches often initiate corrosion. Epoxy coatings frequently emerge as primers in this context, many of which are already biobased. The topcoat is often a polyurethane (PU) coating, which contains a limited but increasing biobased component, as polyurethanes typically offer better UV protection than epoxy coatings.

Other biobased solutions include extracts from plants, such as tannins, which possess corrosion-inhibiting properties due to their ability to form a protective layer on metal surfaces. Additionally, proteins like casein are being investigated for their potential application in biobased anticorrosive coatings. Although these biobased alternatives are still in development and often do not match the performance of zinc and other traditional methods, they hold significant potential for future use in sustainable corrosion protection.

3.8 Antioxidants

Antioxidants are molecules that counteract oxidation processes in cells or materials by neutralizing free radicals. Free radicals are reactive oxygen species that can cause damage to polymers, often originating from light (UV damage), ozone, or chemicals. In coatings, antioxidants are employed to extend the lifespan and performance of these materials. For instance, antioxidants can be used as protection against radicals formed at elevated temperatures (e.g., during high temperature curing), oxidative degradation, color stabilization, UV protection, ozone protection, or even to counteract advanced crosslinking.

A crucial point regarding antioxidants for materials applications is that they typically need to function over extended periods. Natural antioxidants often present challenges in this regard. While they may work excellently (e.g. vitamin C or vitamin E), or even outperform synthetic options, their effectiveness is often very limited in duration. Living organisms have a continuous biosynthesis system that can regenerate used antioxidants, but this is not the case for plastics. One particular type of antioxidant, Hindered Amine Light Stabilizers (HALS), regenerates itself through a complex cascade of reactions, making it a long-lasting antioxidant. However, biobased alternatives for these commonly used antioxidants are currently lacking.

Nonetheless, there are some antioxidants for materials applications that can indeed be biobased. One example is epoxidized soybean and linseed oil, which act as antioxidants when processing PVC. PVC is a chlorinated polymer that is not stable at its melting point; a significant amount of HCl is released when it is heated above 180°C. Epoxidized oils are very effective in reacting with the formed HCl to remove it. In addition to epoxidized oils, other thermal stabilizers are still necessary for PVC applications.

3.9 Surfactants, emulgating agents, detergents, foaming agents and defoamers

A very important class of molecules for the coatings industry includes surfactants, emulsifiers, detergents, foaming agents, and defoamers, which play a crucial role in the production and operation of numerous processes. These substances enhance the performance and functionality of coatings during both application and end use due to their unique properties related to surface tension, miscibility, and stabilization. Although this class of chemicals is highly diverse, they are grouped here because they are characterized by the combination of a hydrophilic and a hydrophobic part within the same molecule. This allows them to engage in interesting physicochemical interactions with both water-based and fat-based components. They make fats miscible in water, some can foam, stabilize foams, create emulsions, lower surface tension, and more.

Under the collective term "soap," this class of molecules has been known since ancient times. Many of these products are very inexpensive, and to create added value, the dispersing agent must offer exceptional performance in a specific application. **There are countless (biobased) surfactants, and most are classified based on their ionic nature and their so-called HLB (Hydrophilic-Lipophilic Balance) value**. The HLB system quantifies a surfactant's affinity for water (hydrophilic) or oil (lipophilic). This system aids in predicting the function and behavior of surfactants in various applications, such as emulsion formation and stabilization. The HLB value is a number that indicates the balance between the hydrophilic and lipophilic parts of a surfactant, ranging from 0 to 20. Surfactants with low HLB values are more lipophilic (oil-soluble) and are often used as water-in-oil (W/O) emulsifiers. Conversely, surfactants with high HLB values are more hydrophilic (water-soluble) and are commonly used as oil-in-water (O/W) emulsifiers.

Another important parameter of surfactants is their ionic nature. Ions can usually be found in the part of the molecule that has an affinity for water. Most often, these are anions (e.g., carboxyl groups or sulfonates), but cationic surfactants (e.g., ammonium groups) are also available. Cationic dispersants often have a negative environmental impact (e.g., on aquatic organisms), leading to less frequent use of these cationic agents. They are sometimes specifically utilized for certain antimicrobial properties (e.g., quaternary ammonium compounds). There are also many non-ionic dispersants, which have the advantage of being highly compatible with other substances. Non-ionic dispersants are typically only partially biobased, as the most commonly used non-ionic hydrophilic part is polyethylene glycol. However, biobased examples do exist, such as sugar groups (e.g., polyglycosides or alkyl glycosides), although they are more expensive to synthesize. Biobased dispersants also include zwitterionic (or amphoteric) examples (containing both anionic and cationic groups), such as lecithins, which are often highly efficient emulsifiers.

When it comes to **emulsions**, the type of emulsion is initially considered. The majority are oil-in-water emulsions, for which surfactants with HLB values between 8 and 18 are used. Water-in-oil emulsions (often oily creams in cosmetics) exist to a lesser extent, and surfactants with HLB values between 3 and 8 are suitable for these. The stability of the emulsion is also crucial. When droplet particles have affinity for each other, they can "fuse," leading to easy separation of the emulsion. This is typically counteracted by using ionic dispersants, which repel each other. Specific "block" copolymers are also utilized, which have large side chains that can sterically hinder each other.

Foam is a unique case. Foam is essentially a collection of micelles, where the hydrophobic tails of many molecules come together to form a bubble. These can be singular or double. There is an entire scientific expertise surrounding foams. A requirement for surfactants that can foam is their ability to organize well. Most fat-based dispersants meet this requirement. The HLB value of foaming agents typically lies in the middle (around 10), with both additives that stabilize foam and those that destabilize foam available. Foam can be a desired property, for example, in shampoos or in the production of foamed industrial products (e.g., foam coatings). However, foam is often unwanted, as it leads to the undesired mixing of air bubbles, poor pumpability, defects in coatings, increased volume, and is often difficult to wash away.

Therefore, there are numerous defoamers on the market for various applications. These products typically have very low HLB values.

Quillaja saponaria (soap bark) is a natural foaming agent derived from the Soap Bark tree, native to central Chile. Decyl glucoside is a mild and pure natural surfactant derived from 100% renewable plant sources, produced by reacting glucose from corn starch with decanol from coconut. Cocamidopropyl betaine (CocoBetaine), obtained from coconut oil, provides a smooth, silky texture and good foam formation and is frequently used in the cosmetics sector. Coco glucoside, an ultra-mild surfactant made from coconut and fruit sugars, can be used as a foaming agent, conditioner, or emulsifier, and is gentle on the skin while providing a smooth feel to products. Sodium cocoamphoacetate, an organic compound from coconut oil, acts as a surfactant, foam booster, and conditioner, ensuring a soft and smooth application. Honeyquat, derived from honey, serves as a natural foaming agent with moisturizing and conditioning benefits, improving the texture and smoothness of products.

In addition to foams, there are also **degassers**. These products are also surfactants and primarily facilitate the escape of air added by mixing powders from a formulation. A well-known phenomenon is that when powder is added to water, it tends to clump together as aggregates, trapping a significant amount of air in the formulation. Degassers are products that facilitate the wetting of clusters of dry powder. Such products are crucial in processes where powders are mixed with water, such as in the paint industry.

Wetting agents are crucial in the coatings & paint industry, where forming a uniform layer on a substrate is important. However, an important parameter can cause the applied liquid to create so called wetting defects. If the surface tension of the coating formulation is higher than that of the substrate, this occurs. Since the surface tension of water is relatively high (72 mN/m), water is actually a difficult liquid to apply to various substrates. The performance of a wetting agent depends on how effectively it can reduce this surface tension. The most effective wetting agents are silicone-based and can reduce the surface tension to 20 mN/m, sufficient to wet even challenging substrates.

There is also a large class of **antistatics** that is based on biobased surfactants. These are surfactants that migrate to the surface when incorporated into plastics or coatings. Their hydrophobic tails are embedded in the hydrophobic polymer, while the hydrophilic heads face the plastic surface. If these heads are hygroscopic, they can attract water and moisture from the air, which can provide sufficient electrical conductivity to discharge the polymer from its static charges. This class of antistatics is only applicable when there is enough humidity in the air. There are also permanently electrically conductive additives, such as carbon black, but these are rarely biobased for this application.

Many of the above additives are sold by specialized companies and we see that the biobased content is increasingly more important in this product range. A careful selection should allow to make selections of each of the above additives as this class of molecules is very often derived from fatty acids that are sourced from nature.

3.10 Solvents

Biobased solvents are a growing category of solvents derived from natural, renewable sources. The rise of these solvents is primarily driven by the increasing demand for environmentally friendly alternatives to traditional, petroleum-based solvents. This shift is partly due to stricter environmental regulations and growing awareness of the impact of chemical substances on both the environment and human health.

The transition to biobased solvents is an important step toward a more sustainable chemical industry. Less desirable solvents such as THF, NMP, and DMF, despite their excellent functionality, can potentially be replaced with more sustainable alternatives. With the ongoing development of new products and technologies, biobased solvents are expected to play an increasingly significant role across various sectors, from agriculture to cleaning and coatings.

A common class of biobased solvents is the so-called 'dibasic esters.' Solvent blends of such esters are typically produced from adipic acid, glutaric acid, and succinic acid (butanedioic acid). These solvents are often non-flammable, biodegradable, non-corrosive, and typically have a mild, fruity scent. Known producers of such solvents/solvent blends include Syensqo (Rhodiasolv solvents), Eco-Point, iBiotec (Fast Clean solvents, Neutralene solvents), and Solvay (Augeo).

The most well-known example of a green solvent is probably Cyrene, designed as a sustainable alternative to NMP and DMF by the Circa Group. Lambiotte also produces green solvents based on acetals, which can be used as alternatives for a wide range of more harmful solvents. We also see that solvents often need to meet very specific requirements, such as those for dissolving agrochemicals that must be biodegradable. This has led to new biobased developments in the market (e.g., PuraSolv green solvent from Corbion).

3.11 Tackifiers

Tackifiers are chemical products added to various adhesives to adjust their stickiness. They are a typical additive for adhesives, especially pressure-sensitive adhesives (PSAs)—these are adhesives that stick when pressed—and hot melt glues. Tackifiers are crucial for adhesives because they not only improve adhesive strength but also expand the temperature range in which an adhesive can be used. An adhesive is primarily characterized by two parameters: (i) tack/stickiness, which indicates how strong the adhesive bonds when pressed, and (ii) shear resistance, which shows how well the adhesive resists sliding. Adhesives typically have a narrow temperature range for use; below their glass transition temperature, they are too brittle to stick, while at too high a temperature, they become too soft to provide sufficient shear resistance. Tackifiers are widely used in adhesives and hot melts, making them key ingredients in a large class of coated products.

Tackifiers are of significant economic importance because they are often the most expensive ingredient in an adhesive formulation and are used in large concentrations (10-40%). Today, they are largely biobased and are mainly known from pine resin (colophony), the typical amber-colored resin obtained from injured pine trees. It mainly consists of abietic acid.

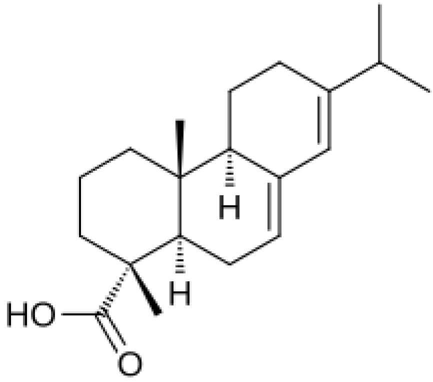

Figure: Pine resin (left) is the typical amber-colored sap that can be isolated from injured pine trees. It consists primarily of abietic acid (right).

Usually, pine resin is dehydrogenated (removal of double bonds) because this process makes the resin colorless. Furthermore, they are often combined with glycerol or pentaerythritol, which can result in slightly different properties or better compatibility in formulations. The pure product is usually solid with a melting point between 40 and 80°C and is either dispersed or dissolved in plasticizer or solvent before being added to adhesive formulations.

One of the problems with pine resin is its allergenicity. Besides abietic acid, a small fraction of protein is also extracted, and about 1-4% of the population is allergic to it. This is one of the reasons why many high-end applications (e.g., medical adhesives) are looking for alternatives to pine resin. These can be synthetic, but a biobased success story involves polyterpenes, which can be polymerized from limonene, for example. Limonene is so important that in the US and Europe, orange peels are no longer considered waste. Whether such ingredients can also be harvested in Flanders requires further research, as terpenes form a broad class of chemical compounds often present in an oil mixture, typically recognized as essential oil (e.g., from oranges, thyme, lavender, hops, rosemary). There are also more experimental crops (e.g., dandelions) that contain significant terpene fractions. Moreover, for each of these terpenes, chemical processing will almost certainly be required to create a tackifier.

3.12 Polyoles

Polyoles, also known as polyalcohols, polyols are a versatile class of compounds with multiple hydroxyl groups (-OH) that are widely used in the chemical industry. Their unique properties make them suitable for a broad range of applications, particularly in coatings, inks, and paints.

Theoretically, many molecules can be considered polyols. However, a technically useful polyol must meet certain conditions. These are molecules with a very controlled stoichiometric number of OH groups (usually 2, the diols). Moreover, the most valuable diols are large, complex molecules (prepolymers) that can be very diverse. They can be used for further polymerization into polyurethanes (PU) or alkyd resins. Polyurethanes, in particular, are known as highly durable polymers used for a wide variety of applications (paints, coatings, boots, shoe soles, foams, poured floors, etc.). The diversity of polyurethanes is much greater than that of many other polymers and is highly dependent on the polyol used. Biobased polyols are almost exclusively 'polyester polyols,' indicating that they are relatively large oligomeric molecules that have been esterified from smaller molecules. In the case of diols, thermoplastic polyurethanes are obtained. If the polyol has more than two OH groups, more crosslinking occurs, and the resulting polyurethane will be thermoset.

The most important biobased building blocks for polyols come from oleochemistry. Specifically, fatty acids that naturally contain hydroxyl groups (such as ricinoleic acid and castor oil) are particularly relevant in the production of polyols. Additionally, dicarboxylic acids (often sebacate derived from castor oil) are frequently used to polymerize into a polyester polyol together with a small diol (often from glycerol, ethylene glycol, or propanediol). These reactions are often performed by oleochemical companies (e.g., the Belgian company Oleon, as well as other oleochemical companies like Croda, Vertellus, and Alberdingk Boley).

Biobased polyols do not solely originate from oleochemistry. There are several examples of polyols made from fermentation products of sugar. Examples include polyols based on lactic acid or succinic acid, both fermentation products of glucose. Additionally, some companies specialize in producing polyols from sorbitol (Roquette’s isosorbides).

Both polyurethanes and alkyd resins are reaction products between a polyol and a “curing agent.” In the case of polyurethanes, this is an isocyanate (for which there are almost no biobased alternatives), and in the case of alkyd resins, it is a dicarboxylic acid, which is rarely biobased at present. Alkyd paints are self-drying paints still commonly used as wood paints and varnishes. There is a visible trend toward "biobased paints," but often these paints are only partially biobased, with the polyol typically contributing to the biobased content.

In addition to high-molecular-weight diols, there are many small molecules sold as polyols for applications in food or pharmaceuticals. These are polyols based on, for example, maltitol, mannitol, xylitol, etc., and thus are often 'specialty carbohydrates.' These can also potentially be modified into flame retardants by incorporating phosphate and ammonium groups.

3.13 Rheological additives

Rheological additives play a crucial role in the processing of many liquid chemicals and are indispensable in the coatings industry. These additives are designed to optimize the flow properties and mechanical performance of materials, resulting in improved workability, consistency, and final product quality.

Rheological additives are chemical substances added to a formulation to control and improve viscosity, flow, and stability of the product. These additives influence how a material responds to forces and how it flows under different conditions. Rheological additives work exclusively for certain classes of chemistries (e.g., water-based, solvent-based, high solid). They are often synthetic polymers with an affinity for their matrix. A very large and important class for water-based chemistries are polysaccharides (see earlier). Commonly used in the chemical industry are cellulose derivatives (e.g., carboxymethylcellulose), but certain polysaccharide thickeners have very specific properties for which a higher value is paid.

Examples include thickeners that work specifically when the solution is heated, thickeners that have a high or low viscosity at certain temperatures (e.g., gellan gum), thickeners that provide thixotropy (e.g., for crepe), thickeners that form films (e.g., acacia gum), thickeners that stabilize emulsions (e.g., negatively charged alginates), thickeners with antimicrobial properties (e.g., chitosan), thickeners that form very uniform films (for use in paints), and finally, products that do not thicken liquids but prevent particles from settling (e.g., microfibrillar suspensions for spray applications). Rheology additives are typically used in very small quantities. Thickeners like carboxymethylcellulose can be very inexpensive, but when a thickener has specific properties, it can become a fairly expensive additive (e.g., acacia gum or alginates).

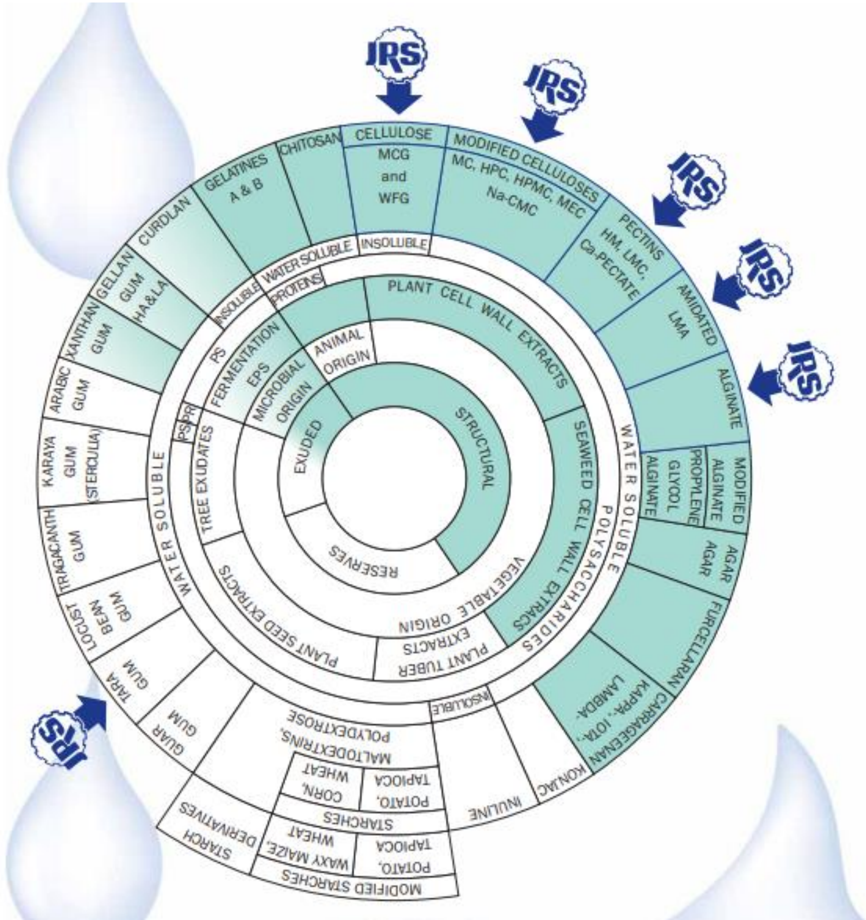

Figure – overview of many biobased thickeners for water-based systems. They range from bacterial polysaccharides, seed extracts, celluloses to animal derived protein thickeners. (reference JRS Rettenmaier)

Thinners are also frequently used. These additives reduce viscosity, which can be important when very low viscosities are required for processing (e.g., in sprays). It is often important to apply thinners to allow for the addition of more inexpensive fillers (e.g., lime). Viscosity-reducing additives are more commonly used in high-solid formulations where solvents cannot be added for some reason. Therefore, they are often hydrophobic formulations, such as epoxy poured floors, 2-component systems, PVC plastisols, sealants, and adhesives. A plasticizer is often used, but sometimes a combination of a dispersant with an inert, slow-evaporating, exuding solvent is chosen. Typical examples include gasoline-like components, which are inert enough not to react with the components, and after the chemistry has cured, they migrate to the surface and slowly evaporate. These synthetic products are often very toxic, and we are seeing environmentally friendly biobased alternatives appearing on the market, which are usually a mixture of a partially biobased dispersant and a type of biodiesel.

3.14 Blowing agents

Blowing agents are typically substances that decompose into gaseous components under the influence of temperature. They are still used extensively in foam coatings in the artificial leather and wall paper industry. Typical blowing agents include powders like ADCA (azodicarbonamide), which decompose into N2, CO, and CO2 at high temperatures, generating large volumes of air. Due to regulatory actions, ADCA has been placed on the SVHC (Substances of Very High Concern) list, which has led to increased research into (biobased) alternatives. The biobased products are only partially biobased and are a combination of bicarbonates (baking soda) and organic acids. Depending on particle sizes, compositions, and stabilizers, they can now be used in a broad range of applications. In the range of these carbonates, Solvay has launched its product line "Alve-one", that can help in the replacement of ADCA and OBSH.

Microcapsules that expand are also emerging as an alternative to blowing agents (e.g., Expancel by Nouryon (formerly AkzoNobel), which also announced new variants based on biopolymers are under development). Natural foams exist as well, cork being an example that can easily be used for the production of, for instance, floating structures where a closed-cell structure is desired.

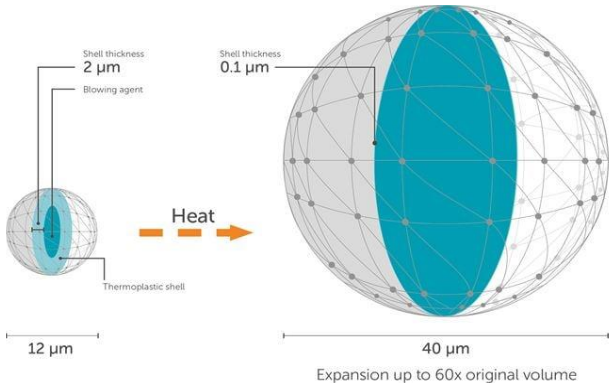

Figure - Microcapsules as an alternative to blowing agents, where the capsule can be made of biobased polymers (figure by Nouryon). An alternative to blowing agents are the use of mechanical foams, for which many biobased alternatives exist. These are discussed under surfactants in this study.

3.15 Matting agents

Matting agents are additives added to coatings, paints, plastics, and other materials to achieve a matte or non-glossy finish. They are widely used in the paint and coating industry, as well as in printing inks, cosmetics, and plastics, to adjust the appearance and surface properties of a product. The use of matting agents is essential in situations where high gloss is undesirable, such as to reduce glare or for aesthetic reasons.

Matting agents work by altering the structure of the surface of a coating or plastic. They create microscopic irregularities on the surface, which scatter incoming light instead of reflecting it, resulting in a matte appearance. This effect can be achieved by adding different types of particles, such as silica, wax, polymer beads, or organic and inorganic substances. There are several biobased particles that are suitable, such as natural waxes, particles from biopolymers (PLA, PHA), and various biobased particles. However, there are several important parameters that matting agents must meet: they should preferably be colorless, resistant to the processing temperatures used, protrude from the surface, and disperse easily.

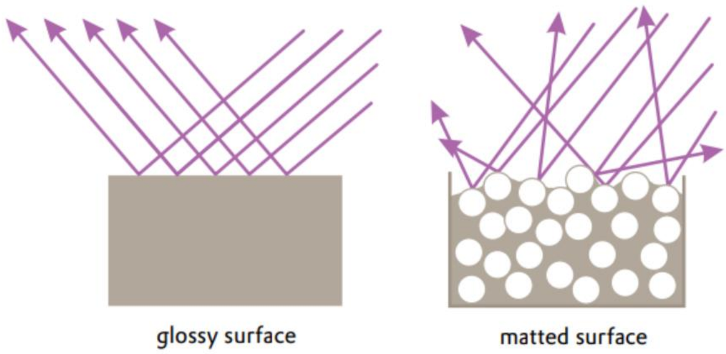

Figure 16: Light refraction on a surface will be very different when matting agents are used (figure: Evonik)

The type of matting agent, particle size, and concentration determine the degree of matting and the smoothness of the surface. Larger particles can produce a strong matting effect but may also make the surface texture rough. Smaller particles provide a subtler matte finish and a smoother surface. Matting agents are widely used in decorative and industrial paints and coatings. They help to prevent glare and give surfaces a luxurious, non-reflective appearance. This is particularly important for applications such as interior walls, furniture, and metal surfaces, where a glossy finish is undesirable. In the printing industry, matting agents are used to control the gloss of inks on various substrates. This can help improve the readability of printed materials or achieve a specific aesthetic appearance.

With the rise of sustainable chemistry, there is also increasing interest in biobased matting agents. These can be made from renewable sources such as plant-based waxes or biopolymers, helping to reduce the environmental impact of coatings and other products. This can also be important in combating microplastics, as protruding particles like matting agents are the first to wear off a surface. Amongst the biobased matting additives on the market we will find PHA, PLA, bioPA and biobased waxes.

Similar particles are also used as "anti-blocking" additives. These are additives that prevent films from sticking together on a roll, for example, because they are too smooth. Irregularities caused by anti-blocking additives prevent this from happening.

3.16 Abrasion resistance

Just like matting agents, particles are sometimes added to coatings and overprint varnishes to improve wear resistance. This can be achieved in two ways: either by adding a particle that is very strong and wear-resistant, preventing the surface from wearing down, or by using a type of lubricant, making the surface slippery so that friction causes less damage.

In the first category, mainly wear-resistant products are used (e.g., ceramic beads). There are only a few biobased examples, but PA11 is one of them. PA11 is a very sturdy polyamide with excellent wear resistance. This biobased polyamide is available in a very fine, easily dispersible powder that adheres well to other plastics and coatings.

In the second category, there are several biobased waxes (mainly from soy or sugarcane) that are used to make the surface smoother.

3.17 Humectants

Humectants are substances that attract and retain moisture from the environment, helping to maintain the moisture balance of products. They are widely used in the cosmetics, food, pharmaceutical, and graphic (ink) industries due to their ability to keep products hydrated and prevent drying out. Their action is especially important in products that are prone to drying, such as creams, lotions, food, print heads, and medicines.

Humectants work by attracting water molecules from the air and holding them within the product in which they are incorporated. This process, known as hygroscopy, helps to regulate and stabilize the moisture content of a product. In skincare products, for instance, humectants draw water into the outer layers of the skin, keeping it hydrated and supple.

The effectiveness of humectants is based on their chemical structure, which often contains hydroxyl groups that can easily form hydrogen bonds with water molecules. This allows them to effectively absorb and retain moisture. Humectants are often biobased, with glycerin being one of the most commonly used humectants, both in cosmetics and food products. Glycerin is a colorless, odorless liquid that helps hydrate the skin and keep food products moist. As a byproduct of biodiesel production, it is also extremely inexpensive.

However, there may be reasons to use more expensive (also biobased) humectants, which is often the case in skincare products (e.g., hyaluronic acid, which can hold up to a thousand times its weight in water) or in technical applications where the humectant must not migrate. In such cases, polymeric forms (e.g., polyglycerol) are also used. Other biobased components with excellent hygroscopic properties include sugars.

4. Bio-based binder selection

There are many biopolymers available. We will discuss some of the more significant examples here. An important aspect of biopolymers is that some are thermoplastic and remain so (they have a melting point), while others are no longer remeltable after processing (e.g., epoxy). Naturally, they will have completely different processing methods. Thermoplastic polymers are most often applied in the coating field as extrusion coating or hotmelt coating, whereas thermoset chemistries are applied as precursors in the wet stage, that harden or cure upon drying.

Many biopolymers are the reaction products of monomers, where the raw material usually doesn't cost much. Often, this raw material is sugar (e.g., PLA, bioPE, bioPET, bioPVC) or a specific oil (e.g., bioPA, bioPU, PHA, epoxy) that forms the basis of the polymer. In the case of polymers made from sugars, fermentation technology drives the process, such as fermentation to lactic acid (PLA) or ethanol (bioPE, bioPET, bioPVC). There are often not many suppliers in this area because the chain to produce polymers from sugars can be complex. For PLA, there are only three major suppliers (NatureWorks, TotalCorbion, and the Belgian Futerro). For ethanol-based polymers, Braskem produces in Brazil, where sugarcane serves as the basis for cheap ethanol production. Ethanol can be easily dehydrated into ethylene, the building block used for producing polyethylene or polyethylene glycol.

In the case of oil based materials, castor oil is often used. The production of this oil rarely occurs in Europe and is primarily found in India. Notably, this oil can be split into 11-aminoundecanoic acid and sebacic acid, the building blocks for PA10 and PA11, respectively. These polymers are extremely durable, with exceptional strength and resistance to alkali. This demonstrates that biopolymers do not always have to be of low quality. Polyamides are typically pricier, and may not solely be used as a coating matrix, but also as an additive, such as matting and abrasion additives.

In coatings, cast floors, 2K mastics, and injection molding resins, biobased polymers can also be of very high quality. This is true for biobased epoxy and PU systems. In particular, in epoxy 2K systems, one component has long been a biobased component. This involves epoxidized oils (mainly derived from linseed oil and soybean oil) and particularly polyunsaturated fatty acids that can be employed. PU resins are also very durable and versatile and are described in more detail in this study under the section on polyols, which are the main building blocks of PU.

The examples above indicate that biobased polymers certainly do not have to be natural polymers. All the examples mentioned are synthetic but utilize only biobased raw materials. Most of them are also not biodegradable; it is a common misconception that biobased polymers are also biodegradable.

Another well-known example of a biopolymer is that of drying oils. These have been used for treating wood and as paint since ancient times, such as in the works of the old Flemish masters. The double bonds found in unsaturated oils can oxidize, forming covalent bonds with each other. For this to happen, the oil must be sufficiently polyunsaturated. This is the case with linseed oil, as well as some other oils like tung oil and calendula oil, which are classified as drying oils. It is important to note that catalysts, often heavy metals (e.g., manganese ions), are typically used to speed up this process, which can be a point of concern with drying oils.

Natural polymers also exist. A well-known example and one of the first polymers widely used is natural rubber, which comes from a plant sap consisting of terpenes that can quickly polymerize into a film that seals the plant's wound. Such saps can be found in multiple plants, but they are primarily known from the rubber tree (*Hevea sp.*), which grow in tropical conditions.

Another interesting type of naturally occurring biopolymer is polyhydroxyalkanoate (PHA). It is a bacterial polymer produced by certain classes of bacteria when they have sufficient nutrients but not the conditions to divide. Under such circumstances, the bacteria absorb the available nutrients and convert them into granules (called carbonosomes), which essentially form small particles of PHA polymers. PHA is a collective term for polymers, as bacteria produce various variants of the same polymer. This results in many different grades of PHA (PHB, PHBV, PHBH, PH3HB4HB, etc.) being available for various plastic applications. PHA can also be used in coating applications, as Centexbel demonstrated for applications in artificial leather, pressure sensitive adhesives and paper coatings.

Currently, PHA is primarily produced from palm oil. Numerous initiatives (also through Horizon Europe projects) are focusing on producing PHA from waste streams such as sewage sludge, green waste, milk waste, brewer’s spent grain, and more. The conversion rate of sugar-containing waste streams is traditionally lower than that of fat-containing waste products. Some producers also report successful trials using waste oil, including the Belgian division of the Japanese producer Kaneka.

Because PHA is a natural product, it will break down rapidly in nature. The biodegradability of PHA is assured in almost all conditions (from compost to saltwater), emphasizing the role of organisms in the biodegradability of plastics. PHA is the class of biopolymers showing one of the strongest growth trends in the projections of European bioplastics, a federation of bioplastics. Therefore, it could be beneficial for the plastics industry in Flanders and Europe to become acquainted with these relatively new types of plastics in a timely manner.

5. Conclusion

In conclusion, the development of biobased coatings presents a significant opportunity for the coatings industry to align with the growing demand for sustainable and eco-friendly solutions. The decision tree approach outlined in this document provides a structured methodology for selecting appropriate biobased materials that meet specific technical and performance requirements. By focusing on key parameters, additive selection, and binder types, manufacturers can make informed decisions that balance performance and sustainability.

The transition to biobased coatings involves addressing challenges such as biological variability, chemical stability, and the potential for greenwashing. However, with careful consideration and the use of life cycle assessments (LCA), the environmental impact of biobased coatings can be minimized. The integration of biobased additives, such as plasticizers, UV protectants, flame retardants, and biocides, further enhances the functionality and sustainability of these coatings.

As the industry continues to innovate and develop new biobased materials, it is essential to maintain transparency and adhere to certification standards to build consumer trust. The collaborative efforts of researchers, manufacturers, and regulatory bodies will be crucial in advancing the adoption of biobased coatings and contributing to a more sustainable future for the coatings industry.