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From A for Automobile to Z for Zest Coating

Waxes – Properties Profile and Application

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Abstract: As the primary component or as an additive with a content of less than three percent, waxes determine or modify the properties of the respective material system. The areas of application are numerous. The following article presents fundamental data on substance and structure as well as on the manufacture of important waxes. Functions and properties of various wax additives are explained in detail using the examples of powder coating, UV coatings, the processing of technical thermoplastics, cleaning products, and plant protection products.

Keywords: Wax-additive cosmetics · Wax-additive paints/coatings · Wax-additive plant protection products · Wax-additive plastics · Waxes

1. Introduction

Beeswax candles during the Advent or Christmas season, freshly polished furniture or the freshly polished floor in Grandma's hallway – each of us associates these (waxy) smells with particular memories and yet this is still merely a tiny selection of what waxes and their derivatives are suited to.

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2. History

Even as far back as the highly developed Egyptian culture, beeswax was used for mummification. Indeed the word 'mumuya' which came into the Arabic language from Persian actually means wax. Later it came to mean bitumen or asphalt and was used as the term for preserved Egyptian corpses [1].

Similarly, wax was a fundamental component of the oldest casting techniques for bronze or gold, a technique which became familiar under the term waste-wax casting and was used in Italy as early as the 7th century BC by the Etruscans [2]. The art of bronze casting experienced a unique upsurge in the 'golden age' of the city of Augsburg, under Kaiser Maximilian I (1459–1529). Nowhere else in Germany is the face of a city so strongly marked by bronze artworks. They are closely associated with the names of such artists as Adriaen de Vries, Hubert Gerhard or Hans Reichle [3]. And even today, the waste-wax method is still in use in the manufacture of gold jewelry. Wax was also used as a sealant as well as a component in ointments and dressings. With the advent of classical chemistry, waxes advanced to industrial products in the second half of the 19th century. Further developments in chemistry in the 20th century led to new knowledge in this field of substances. For example, crude montan waxes were chemically refined for the first time. In 1935 success was achieved in the manufacture of synthetic waxes by the Fischer-Tropsch method which is still in use today.

Due to the variety of chemical compositions, on the one hand, and the many applications on the other, waxes today have a wide range of possible uses. The spectrum ranges from A for automobile polish to Z for zest coating (Table 1). The waxes are available as powder, flakes, fine powder, granules, and micronized ultrafine powder. The applications are also numerous, as particles or molten baths, as a pure substance in solution, in aqueous dispersions or solvent dispersions as well as pastes or gels.

3. Definition and Classification

The term 'wax' describes a series of naturally or synthetically occurring substances with common physical and technical application properties [4][5]. It has become accepted practice to group them into natural and synthetic waxes. Natural waxes can be further sub-divided into fossil waxes – such as montan waxes –

CHIMIA 2002, 56, No. 5

Table 1. Areas of application for wax – Examples

Cleaning agents for floors	Printing ink
Coatings and paints	Separators
Paper and sheet coating	Corrosion protection
Coating of citrus fruits	Metalwork
Textiles	Leather
Cosmetics	Road surfaces
Shoe care	Automobile polish
Candles	Buildings
Pharmaceuticals	Electronics industry
Plastics	Pigment concentrate

and non-fossil waxes such as beeswax and carnauba wax. In the case of synthetic waxes, we differentiate between wholly synthetic and semi-synthetic manufactured types. Polyolefin waxes, for example, are manufactured wholly synthetically, montan esters or montan soaps, by contrast, are produced semi-synthetically. Fig. 1 offers a comprehensive overview of the classification of the most important wax types.

A characteristic feature is the fact that these are never chemically homogenous substances but always consist of a substance mix. Should one wish to distinguish between the material class 'waxes' and other material classes, fats and oils would appear on the low-molecular side with plastics on the high-molecular side. In their chemical functionality, waxes are long-chain hydrocarbons with varying terminal groups. However, waxes are always crystalline compounds, characterized by narrow melting ranges and comparatively low viscosity in their molten form.

4. Structure, Manufacture and Application of the Most Important Wax Types [4–8]

In terms of their chemical structure, paraffins, Fischer-Tropsch (FT) paraffins and polyolefin waxes belong to the *aliphatic hydrocarbons* and are extracted from petroleum/synthesis gas. They occur in linear or branched form without functional groups.

Polyolefin waxes are synthesized through a catalytic process from C_2 or C_3 olefins at low pressure with Ziegler catalysts or radically initiated at high pressure. However, the thermal degradation of plastics is also possible. The properties of the products are determined by the process and the monomers and monomer combinations used. Ziegler ethylene-homopolymers are characterized by minimal branching of the C-chains and high thermal stability, have a greater density and a higher melting point than 'high pressure waxes' with a larger number of side chains. Crystallinity and, consequently, melting point, density and hardness can be varied within a wide range by adding comonomers.

These products are frequently used as separators, rheology agents, lubricants, binding agents in the manufacture of pigment or additive masterbatches, as dispersing agents incorporating pigments, in the manufacture of ultrafine powders or wax dispersions as well as educts for the synthesis of polar functionalized products.

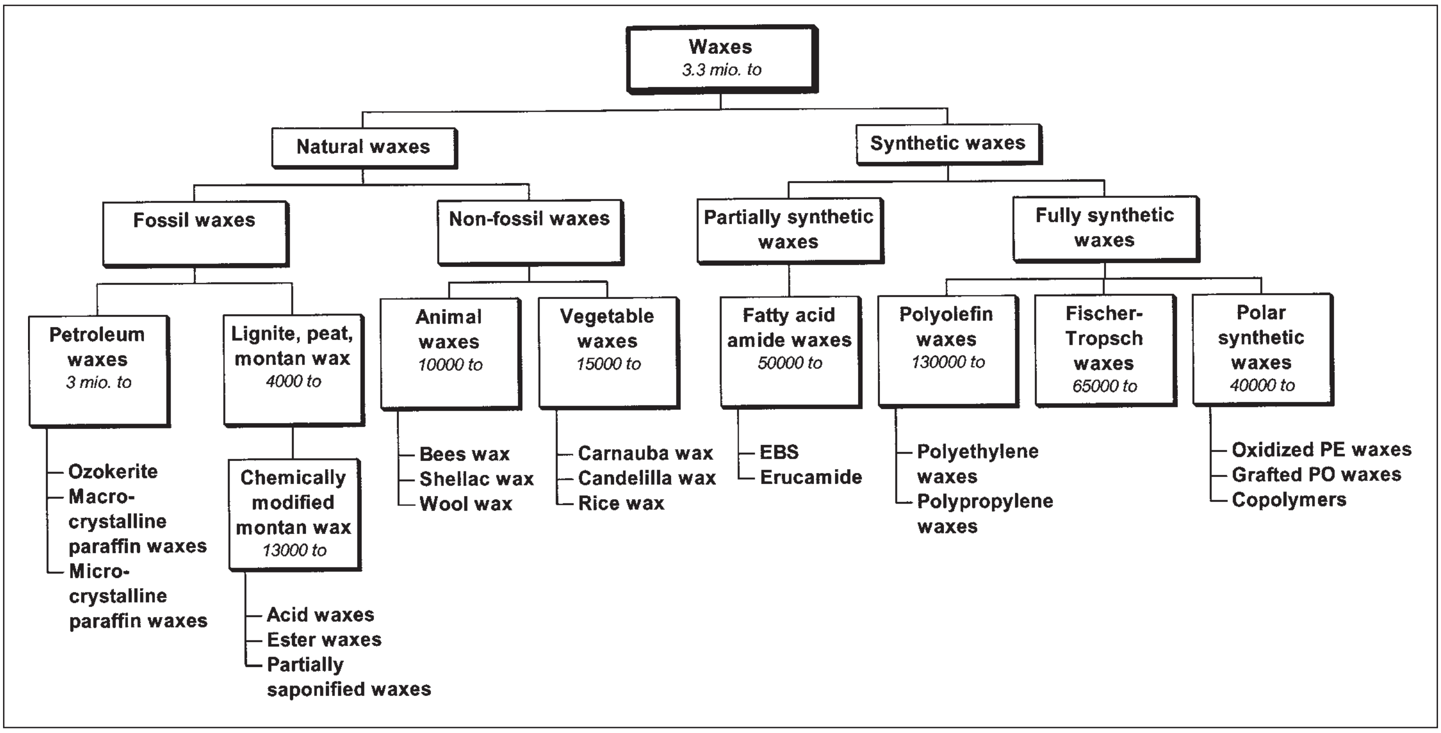


Fig. 1. Classification of waxes

CHIMIA **2002**, *56*, No. 5

A completely new process for the manufacture of copolymers is currently in its pilot phase: 'Single site' metallocene catalysts expand the product range to include innovative waxes not previously accessible, which are characterized, for example, by homogenous molecular structure and close molar-mass distribution. Recently, the first pilot batches of the metallocene waxes from Clariant have become available under the trade name Licocene®. These products, which are supplied for evaluation purposes, originate in a continuously operating pilot plant in Frankfurt-Höchst. There, the new technology is currently being transferred to a production plant. The target for production commencement is the year 2005.

Oxygen-containing waxes are obtained by oxidation of polyethylene plastics, polyethylene waxes, paraffins or by copolymerization of ethylene with oxygen-containing comonomers such as acrylic acid or vinyl acetate. They are characterized in particular by their interface-active effect. As a result, this wax class is particularly suitable for the manufacture of aqueous dispersions and for use as a lubricant in the processing of polar plastics. Polar modification of polypropylene waxes can be achieved by grafting, *e.g.* with maleic anhydrides. These products, in turn, can be aqueously dispersed or are used as adhesion promoters in polyolefin/fiber composites.

The group of *semi-synthetic waxes* includes products based on fatty acids and amines or polyols: bisstearoyl/palmitoylethylenediamine, erucic amide, behenic acid amide, steramide as well as fatty acid complex esters. They are used primarily as lubricants in the processing of various plastics, as a lubricant in the pressing of powder metal and as lubricants in metal processing or as ultrafine powder for use in coatings and printing ink.

Montan wax, beeswax, carnauba and candellila all belong to the group of *natural waxes*. Montan waxes are of fossil origin and are extracted from lignite. They still contain resins and bituminous substances as impurities and are therefore limited in their range of applications. Crude montan waxes, by their nature, exhibit differences in quality caused by climatic changes during the growth period of the plants. The basic raw material must therefore be refined to make it suitable for a broad range of applications.

During the chemical refinement, the resins and bituminous substances are oxidized using chromic acid. The C-chains of the wax components remain unchanged. Only hydrolysis of the wax esters and oxidation of the wax alcohols to acids take place. The chain length distribution of the carboxylic acids lies between C_{22} and C_{34}. This acid mix is further processed in manifold forms.

A typical example is the esterification of fatty alcohols and polyhydric alcohols such as ethane diol, glycerol or pentaerithritol, as well as the salt formation of the –COOH carboxyl groups. These products can then be combined with one another as well as formulated with hydrocarbons, resins or emulsifying agents.

The application possibilities are manifold and range from fruit coating, release agents for plastics or auxiliary agents in textiles to use in improving the scratch resistance in printing ink and coatings or in the production of cleaning agents. Here the properties familiar from the waxy surfaces of plants are exploited such as evaporation retardation, hydrophobing and surface protection.

Carnauba, candellila, and beeswax, on the other hand, are examples of recent natural waxes with similar possible applications. However, the possibility of further adaptation is severely curtailed as recent natural waxes are generally used without chemical refining.

5. Waxes as Additives

Whether as aqueous formulations, finely ground or applied in molten form – waxes protect the substrate below, ensure clean surfaces or, as in the case of pigment dispersion, permit low dust or even dust-free formulations [9]. In cosmetic products, for example, waxes influence consistency and gloss [10]. Added to asphalt mixtures for road construction, certain modified products improve processing characteristics. Furthermore, they also increase the heat resistance of asphalt thus helping to prevent the formation of 'trades' [11]. As mentioned above, waxes can be used as coatings for citrus fruit, as components in furniture polish or cleaning agents. In general, waxes modify the properties of the respective materials systems – whether as the main components or as an additive with a content lower than three percent.

Innovative applications and functions of wax additives in paints, plastics, cleaning agents and cosmetics as well as plant protection are presented in the following text.

5.1. *Montan Waxes in Powder Coatings*

Electrostatic Powder Spray Coating (EPS) [12]

The 'EPS method' is the most significant powder coating method. Here, the earthed work piece is coated in a cabin using an electrostatic powder spray gun. Electrostatic charging of the paint particles causes them to be drawn towards the work piece. The little overspray which does occur is consequently reclaimed. Particularly suited to small parts is a variant which works in a fluidized bath. The characteristics of the spray cloud have a decisive influence on the coating result. Suitable nozzle systems are available for adaptation. The main areas of application for powder coatings are facade coatings, automobile paints, equipment and industrial coatings and corrosion protection. In addition to metal, powder coating systems are also excellently suited to such surfaces as wood or plastic. The most significant growth markets are the automobile industry and the can and coil coating industry.

Powder coatings suitable for electrostatic coatings make it possible to apply plastic-like coatings – as a solvent-free paint – almost without losses by overspray. This method offers advantages such as environmental compatibility, high functionality, excellent surface quality as well as variable substrates and materials.

1 to 2% waxes which are necessary in this process improve the process, the manufacture and the application of powder coating, as well as the coated surface itself, in a number of ways. For example, they optimize the flow properties of the powder in pipelines and spray equipment. Here they act as lubricants thus reducing wear. As a result, the life of the equipment is extended and the maintenance intervals increased. In stove enameling, the wax promotes the flow therefore creating a uniformly hard-wearing surface with a high degree of scratch resistance, excellent slip and good antiblocking.

Recent studies prove that the surface of the coating can be specifically structured using a combination of suitable micronized waxes. Montan waxes demonstrate their special abilities as additives in coating powder extrusion. With suitable recipes energy consumption can be reduced by up to 30% with considerably

CHIMIA 2002, 56, No. 5

increased throughput (Fig. 2). At the same time, the pigment dispersion can be increased in pigmented systems, which manifests itself in improved color strength. Fig. 3 shows the relationship between the addition of a micronized montan wax (Ceridust 5551; Manufacturer: Clariant) and the resulting color strength.)

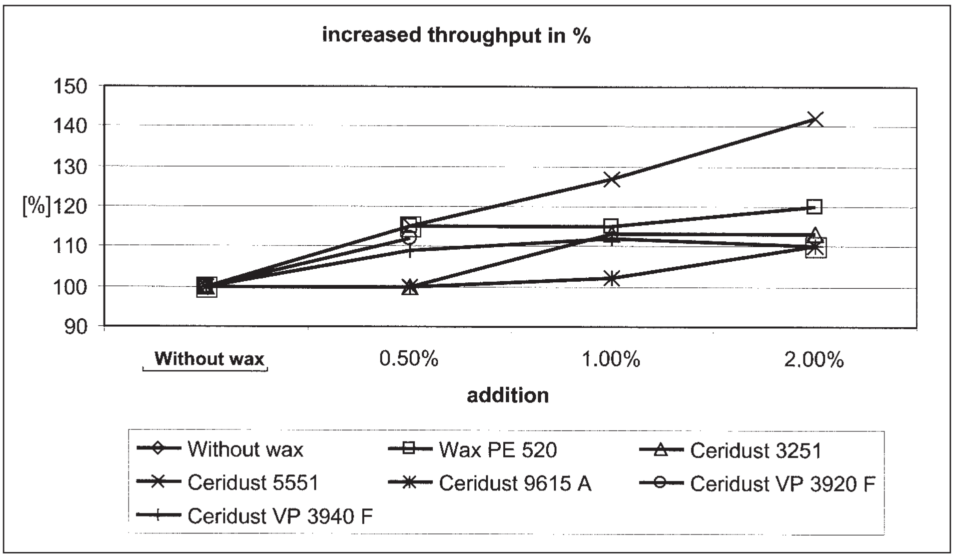


Fig. 2. Increased throughput

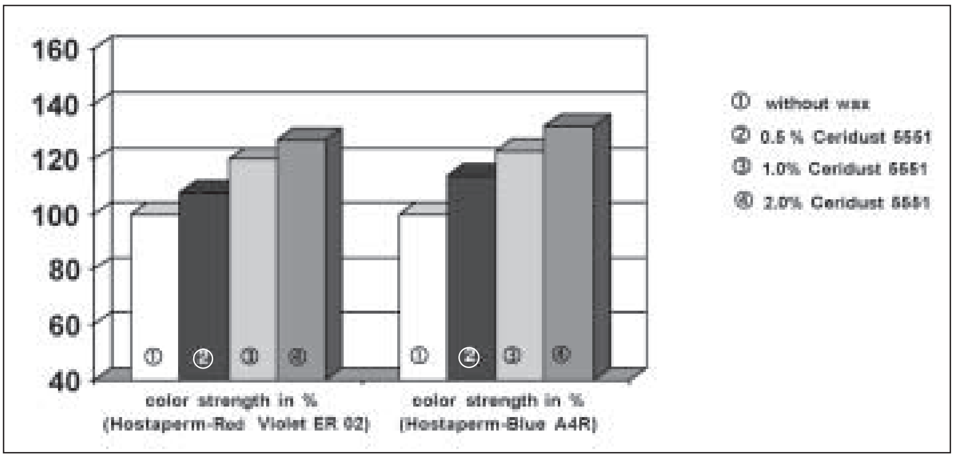


Fig. 3. Increasing color strength in pigments

5.2. *Migration-resistant UV-active Waxes*

Light curing of coatings has become firmly established in all those areas in which the advantages of this technology – such as high production speed and low heat – can most quickly be realized and in which the disadvantages of adhesion have a less serious effect due to the roughness of the substrate. These conditions most readily apply to the materials wood and paper. Light-curable paints for these two substrates now account for around 80% of this paint technology [13].

Principle of Light-curing [14]

Using UV light, a photo-initiator is split into two radicals. These highly reactive particles are able to react with an acrylate double bond. The resulting radical can, in turn, react with monomers thus continuing the reaction chain. The use of multi-function monomers leads to three-dimensional networks. Light-cured paints can be processed in the same way as other liquid coatings. They differ from other paint systems only in that they harden within seconds. In addition to the aggregates for paint application, the UV-curing plant constitutes the heart of the system. Instead of drying ovens, a number of UV lamps connected in series of compact installation can be used as hardening equipment. By increasing the number of lamps, the curing speed of the paints and, consequently, the throughput, can be increased. Immediately after curing, the coated parts can be stacked or further processed, *e.g.* sanded or painted again.

The use of waxes in coating systems leads to a number of significant improvements with regard to matting, scratch resistance, blocking and much more. Up to now, however, all known waxes behaved chemically inertly in UV coatings and, as a result of undesired migration, gradually lost their effect. A new UV-active wax, in contrast, is firmly anchored in the coating film [15].

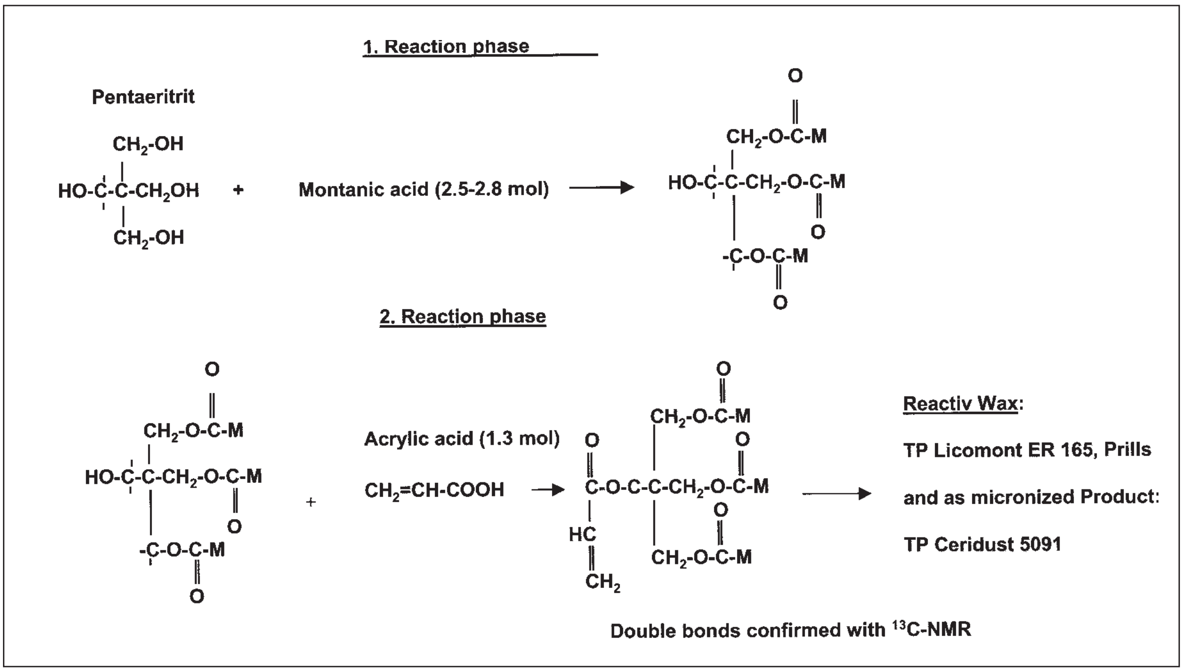
Starting point for the synthesis of the (UV-active) reactive waxes are carboxyl groups, which are formed in the course of the refining process of crude montan waxes. Following partial esterification with pentaerithritol, the reaction with acrylic acid leads to the desired UV-active wax (Scheme). With the aid of IR studies, it could be shown that the double bond reacts and the valences thus released form new bonds with other reaction partners in the paint system. As a result of the stable anchoring of the wax in the paint, dulling, scratch resistance, resistance to chemicals, resistance to polishing and temperature stability, as well as glideability and anti-blocking, have been extremely positively influenced – and with a particularly long-lasting effect.

The new product is marketed under the brand names Licomont® ER 165 and Ceridust® 5091 (manufacturer: Clariant). The two types are chemically identical and differ only in grain size and form. The Licomont waxes are available as pastilles or powder. The term Ceridust is used exclusively for micronized waxes which – due to a special grinding process – are in ultrafine powder form. Ceridust waxes can be manufactured with a fineness of under 5 μm (d_{50}-value).

5.3. *Additives for Technical Thermoplastics*

The use of waxes facilitates not only the processing of technical thermoplastics – such as polycarbonate, polyester or polyamide – but also leads to improved use properties in the finished article. In addition to nuclearization and flowability, properties such as removal from the mould, gloss, yield and dispersion of pigments, additives or fillers are also significantly improved. The decisive factor in their function is the polarity of the waxes chosen. Various waxes are used, depending on the type of plastics involved (Table 2) [16].

CHIMIA 2002, 56, No. 5



Scheme. Synthesis of a UV-reactive wax

Table 2. Summary – Waxes for plastics [12]

Wax type	PVC	PO	PC	PS	PET	PA	TPU
PO-wax	X	X	X	X			
Wax oxide	X				X		
Polymer oxidate	X						
Montan wax	X	X	X	X	X	X	X
Ceridust		X	X		X		
EBS			X	X	X	X	X

Waxes which are incompatible with the polymer matrix have an external effect as a lubricating film between the molten mass and the metal surface of the processing machinery. They therefore prevent sticking and reduce, for example, the mold-release power in injection molding.

Waxes compatible with the matrix mix act as an internal lubricant and improve the flow of the molten mass through reduction of the internal friction. Compatible waxes can also be used for working in fillers or pigments. Their use often leads to improved mechanical and optical properties.

The function of the nucleation agent is based on the fact that crystallization of the polymer in the added particles begins at different points at the same time. The speed of crystallization is increased as a result and the degree of crystallization standardized. In contrast to inorganic nucleation agents such as talcum, waxes act simultaneously as lubricants, separators and dispersion agents.

5.4. *Waxes for Daily Beauty Care*

Synthetic acid waxes and wax esters are of such interest to the cosmetics industry in particular because the branched varieties are capable of forming vapor-permeable films [17][18] which do not prevent the skin from breathing. In addition, acid waxes and ester waxes are excellently compatible with the other lipids, vegetable oils, paraffin hydrocarbons, solvents, *etc.* used in the cosmetics industry, and are therefore preferred [19].

Waxes in cosmetic products serve as lubricants. When applied to the skin, they can penetrate the rifts in the epidermis thus smoothing the skin and reducing roughness. As the waxes are very readily absorbed, they also serve here as emollients. They lend the skin excellent flexibility and softness.

Furthermore, waxes regulate the moisture balance of the skin. Their penetration behavior permits the skin to absorb moisture. The film formed by the waxes also has an occlusive effect, *i.e.* moisture loss is significantly reduced so that a moisturizing effect can take place in the deeper layers of the skin.

Undoubtedly the semi-synthetic waxy acids and wax esters will become increasingly firmly established in the cosmetics industry. A major benefit, in addition to assured production, is the consistent quality ensured at Clariant by the ISO 9001 quality assurance system. As a result of this control, impurities or contamination can be ruled out, which is not always the case with natural products. By setting precise values such as acid number, dropping point or saponification value, the resulting finished product can be manufactured to a consistent quality. Finally, continuous availability and price stability should also be mentioned in this context.

5.5. *Auxiliary Substances in Pesticides*

The manifold properties of wax formulations can be used in the application of pesticides. Dispersions with non-ionic, anionic and cationic emulsification agents, adapted to the active ingredients of the pesticide, have been developed and are used in tank mix application. Through the addition of wax, the effect of the pesticide can be made safer for the user. For example, lower levels of evaporation, less washing out, improved absorption, lower level of weather sensitivity, and lower phytotoxicity can be achieved. Where the wax is incorporated directly into the pesticide formulation, the proportion of highly volatile solvents can be reduced. As a result, a considerably more environment-friendly form of crop protection is possible. Fig. 4 shows the effect of wax on the evaporation behavior of Cyhalotrin, an insecticide with pyrethroid ingredients. Without added wax, the availability of the active ingredient drops to less than 20% within five days. With the addition of wax, the release of the active ingredient can be significantly decelerated and, with this reduction in initial activity, the duration of the effect increased.

In the case of fertilizers, the use of waxes also produces a slow-release effect and can consequently reduce the pyroxic effect, *e.g.* of nitrolime. They reduce the level of dust formation and caking as well as the attraction of moisture and thus considerably simplify the use, particularly for fertilizers for the home and garden area. (Here too aqueous formulation wax dispersions can be used.)

Furthermore, waxes are also used in seed dressers where they improve the distribution and fixing of the active ingredient. By forming a thin film on the dressed seed, they prevent dust formation and abrasion and the associated loss of active ingredients. At the same time, the film serves as a lubricant and ensures an easier throughput of the seed in the sowing machinery.

6. Protecting, Separating, Creasing ...

The areas of application for waxes and the variety of wax formulations are so manifold and varied that it is almost impossible to list them. Due to the variety of chemical compositions, on the one hand, and the range of delivery forms on the other, waxes can be combined with the most common materials. As the main component or an additive with a proportion under three percent, waxes determine or modify the properties of the respective material system. Protecting and improving appearance, binding and separating, bonding and lubricating – these are just a few of the diverse tasks that waxes can perform in materials systems.

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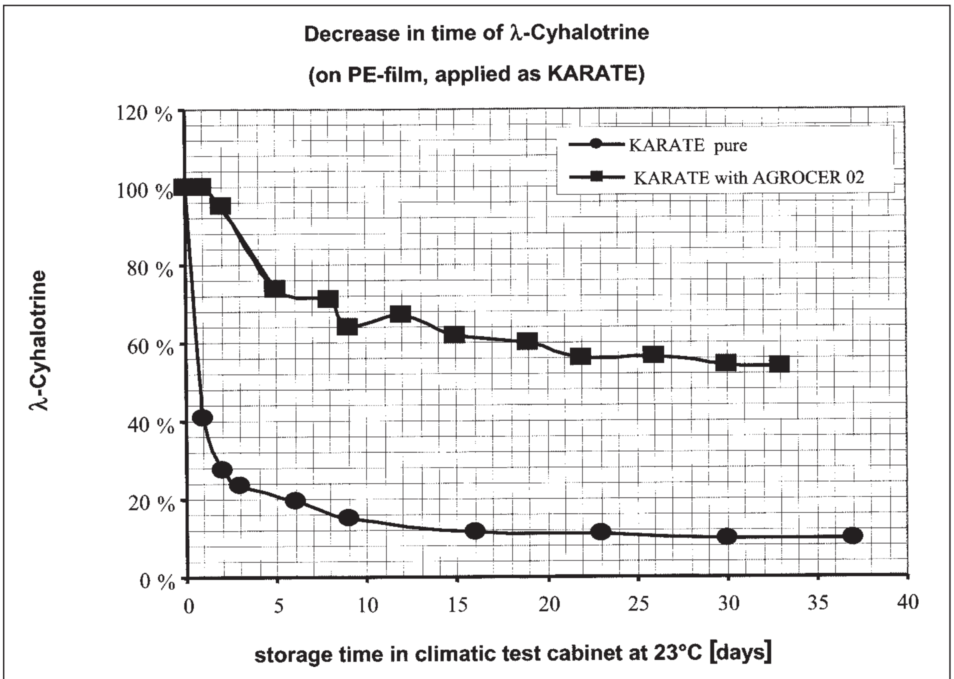

Fig. 4. Evaporation tests of λ-Cyhalotrin with and without wax

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