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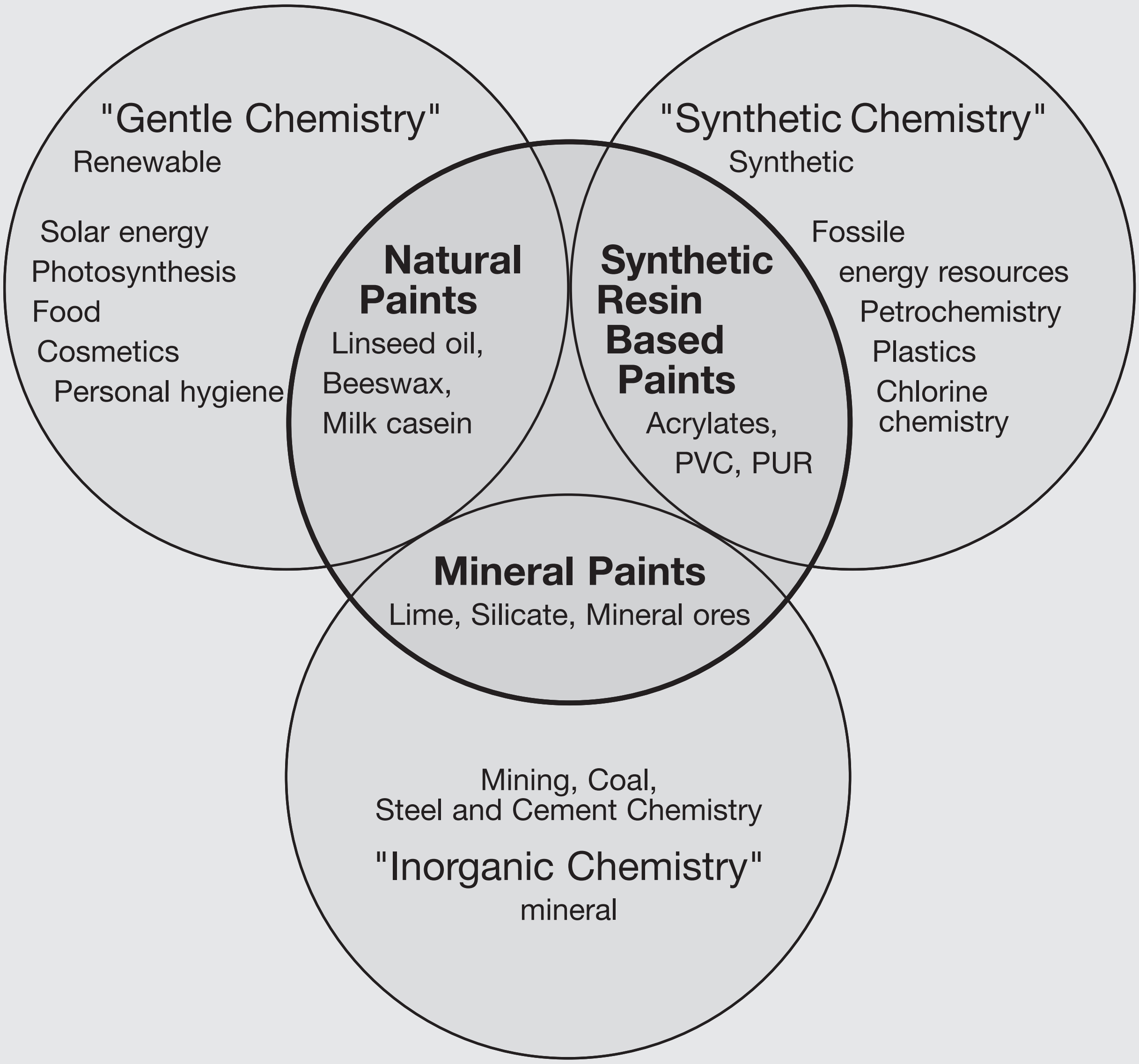
PAINTS AND LACQUERS

APPLICATION AND ECOLOGY



Paint Industry

Raw material base and interfaces with other chemical industries

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PAINTS AND LACQUERS

by Ralf Rieks

1. Introduction

Paints and lacquers are the protective, decorative and value-maintaining coatings on plasters, wood and metal. They are the decisive visual elements in our built-up environment, expression of our creativity or of a simple technical necessity, and they contribute to our quality of life. However, they also belong to a problematic class of products, often linked with allergies and wood preservative scandals. Since the use of coatings is often unavoidable and the number of products is huge, not allowing to easily differentiate between "toxic" and "non-toxic" products, a sophisticated approach that considers health, ecological and biological building aspects is recommended.

2. Historical Retrospect

Spanish and South French cave paintings are the oldest proof of human creativity using paints. They date back more than 15,000 years. With the use of umber and ocher colored earth, red chalk and bone black, hunting scenes and ritual motifs were turned into paintings. The architecture in later historical eras was already sophisticated: burnt lime, wetted and mixed with sand, was used as a durable mortar for colossal buildings. Lime milk was used for limewashing clay and stone. By adding powdered pottery shard, puzzolana earth or similar hydraulic (only solidifying when in contact with water) substances, water resistant, tough mortars were produced making e.g. the construction of port facilities possible. Limewashes were refined by adding milk casein or linseed oil making the paint less chalking while increasing the pigmentation take-up and providing a better durability.

Until far into the 20th century, lime technology prevailed. Another mineral paint type, based on waterglass (such as silicate paints), was developed and reached production maturity until the end of the 19th century, resulting in coatings of a yet unknown durability which quickly replaced limewashes – at least in a more noble ambience.

Only in the fifties and sixties of the 20th century, synthetic resin dispersions, omnipresent today, made their way to the market. A microfine distribution of polymer particles in water formed the basis of these products, the so-called polymer dispersion. The chemical industry produced these new materials on a very large scale. Since dispersion paints were relatively cost-effective and processing required less skills, they soon became the standard product for wall coatings indoors and outdoors, especially thanks to the postwar construction boom.

Our ancestors not only knew how to protect mineral surfaces like stone and plaster from water, weather impact and corrosion, but also materials like wood and metal. Lime and waterglass were too open-pored and brittle for this purpose. A water-repellent, relatively dense and flexible film was required, able to firmly stick to these substrates. Drying fatty oils, recovered e.g. from linseeds or the seeds of the tung oil tree met these requirements and allowed pigmenting. These oil based paints remained standard until the chemical industry was able to design synthetic resins for use in combination with drying plant oils (such as alkyd paints) or without any further additives (such as acrylic paints, state-of-the-art catalyzed lacquers). Powder and water-borne paints are more recent developments meeting solvent reduction requirements.

3. Ingredients of Paints and Lacquers

According to DIN 55945, a paint is defined as a liquid to paste-like coating material which is mainly applied by brush, roller or spray gun. It is, in general, composed of binder, solvent, filler, pigment and additives. Depending on the formulation, a high-quality wall paint for indoor use (washable according to DIN 53778) comprises about 10 to 15 different ingredients, not to mention initial products and accompanying substances. This complex chemical mixture has to meet all kinds of requirements: high storage stability, good processing qualities, short drying time, high resistance of the paint film against mechanical, chemical and biological attacks, low tendency to pick-up dirt and (in the ideal case) ecologically compatible degradability.

Specific visual and technical requirements make further additives necessary, such as film-forming additives for a uniform flow, special pigments for visual effects or additional biocides to provide fungicide properties.

The compatibility of these components with each other must be ensured. This also applies to a positive interaction with all kinds of surfaces, no matter whether smooth, rough, alkaline, damp or water-swellable plaster, concrete, paper wallpaper, wood-based light-weight building boards, old paint coatings etc. Further criteria are raw material prices, the manufacturing process and naturally the acceptance on the market. Ecological aspects gain more and more importance, too, since the public is increasingly aware of environmental problems. It is, therefore, no surprise that, with view to construction, there is a tendency to go back to nature and use more natural building materials (clay, wood). This, of course, includes the paint industry since the public has been sensitized for possible environmental and health hazards through discussions about critical products such as wood preservatives and solvents.

The following chapters will, therefore, name common formulation constituents and coating systems for buildings and describe, as far as possible, ecological alternatives.

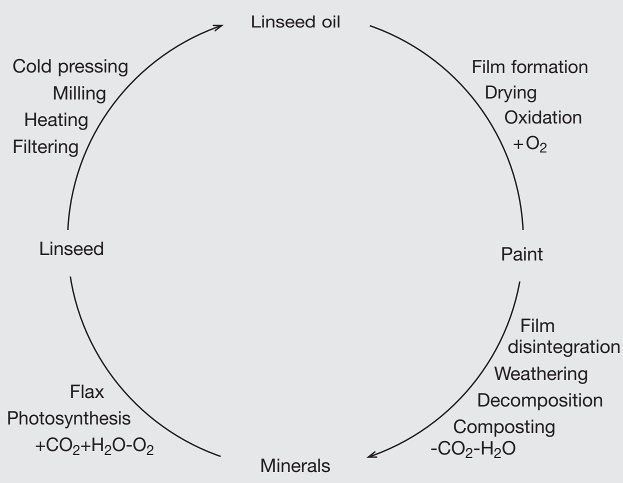
3.1 Binders

Binders (DIN 55945) are the non-volatile constituents of a paint providing adhesion to the surface. After drying, they enclose the other solids contents in a more or less dense matrix. Having released the solvent or water contained, physically drying binders bond to form a more or less dense film. A typical example would be a common dispersion paint for indoor and outdoor use.

Chemical drying or curing, however, describes a chemical reaction which the binder undergoes (in general during and after a phase of physical drying). Limewashes and silicate paints cure chemically through reaction with the carbondioxide from the ambient air, i.e. through transformation of the binder. Plant oil based oil paints also dry chemically through oxygen takeup. In two-pack catalyzed paints such as polyurethane or epoxy resins, the reaction takes place between the two components, i.e. the base and the hardener, as soon as the two are mixed together. Regarding polyurethane, these two components are isocyanates and polyalcohols, in case of epoxy resins, an epoxy group-containing resin and a polyamine.

The binder has a decisive impact on the paint's features which is why it finds expression in the classification of the coating material ("acrylic paint", "alkyd paint", "natural resin lacquers" etc.)

Linseed oil material cycle



3.1.1 Natural Organic Binders

Drying oils (chemically: triglycerides) are recovered from plant seeds. Drying is realized through physical film formation and subsequent chemical integration of oxygen from the ambient air in the reactive double bond of the esterified fatty acids (oxidation drying). After drying, speeded up through the use of drying agents, plant oils provide highly elastic, weather resistant and relatively diffusible coating films in terms of oil lacquers and oil glazes. Oils are often used in combination with natural resins (dammar, colophonium). Drying oils include, among others, linseed oil, soybean oil, safflower oil, dehydrated castor oil, wood oil (the latter from the fruits of the Chinese tung oil tree). Oils are recovered exclusively from renewable raw materials of plant origin through pressing, extraction etc. and are purified, deslimed etc. using simple physical processes. When heated under the exclusion of air, stand oils (DIN 55945) are obtained, sometimes offering improved performance characteristics.

From a toxicological point of view, they are generally recognized as safe and, therefore, ecologically recommended. After use (weathering of the paint, depositing), they find their way back into nature's cycle through composting (see figure). Unlike synthetic binders, they provide a zero CO_2 balance. Manufacturers of natural paints prefer oils from organically and regionally grown plants. Compared to conventional cultivation methods, the use of commercial fertilizers is minimized which ensures non-residual end products.

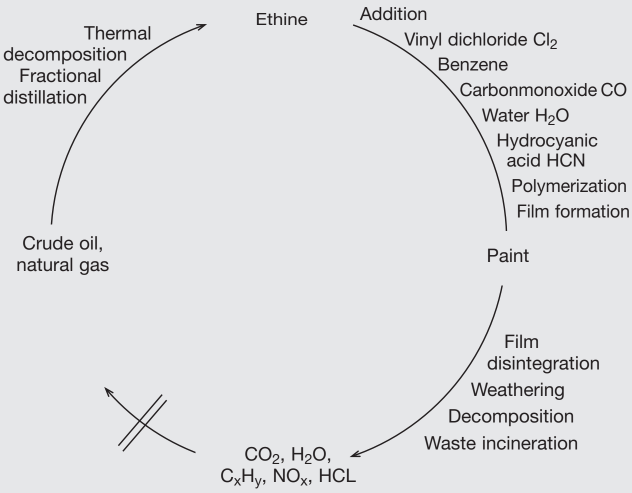
3.1.2 Synthetic Organic Binders

Synthetic organic binders are based on a synthetic organic polymer which, depending on its chemical configuration, may have versatile characteristics. Compared to oil lacquers, a greater hardness and scratch resistance are among the most important features. For special coatings, such as hard-wearing floor varnishes, heavy corrosion protection, chemical-resistant tank coatings etc., reaction resin lacquers are commonly used.

Synthetic organic binders include: acrylic lacquers (binder: polyacrylate), alkyd resin (DIN 53183), polyurethane and epoxy resins as catalyzed resins, PVC lacquers. They are made from raw materials such as crude oil and natural gas. Monomers recovered from cracked crude oil are polymerized, i.e. linked to become an organic macromolecule. Depending on the type of monomer (acrylic ester, vinyl acetate, styrene etc.) and the desired macromolecule (copolymerisate, terpolymer etc.), more than one synthesis step may be required. To obtain certain characteristics or to stabilize intermediates, additives such as preservatives, amines, solvents, antioxidants or plasticizers will be required. From a toxicological point of view, monomers are generally reactive compounds with a high toxic and often carcinogenic potential. More critical are residual monomers that are transformed during the polyreaction and, thus, outgas for a longer period of time from the coating and container. A large number of reaction resins out of the polyurethane (isocyanate) and epoxy resin classes are subject to identification requirements under the Hazardous Chemicals Ordinance. From the latter, it is specifically the hardener (amines) that has a high allergy causing potential. The highly irritating effect of partly volatile amines makes particular precautions for the processing of epoxy resin systems such as floor coatings in industrial facilities, basement garages etc. necessary.

From an ecological point of view, synthetic lacquers and dispersion binders are unnatural, fully synthetic products with high risks for the environment during recovery, processing and disposal. The material cycle of a synthetic resin shows a cut where an increasing CO_2 content inthe atmosphere stands in clear contradiction to a squeeze of fossile resources. The cycle remains unclosed since the process of returning CO_2 into mineral oil takes geological periods of time, i.e. millions of years, and can only take place under certain climatic, geological and biochemical conditions.

Synthetic Paint Material „Cycle“



The actual synthesis of resins for lacquers and varnishes includes intermediates and initial products labeled as hazardous substances. Even when processed in closed circuit systems, environmental risks such as accidents, averages or improper disposal cannot be excluded. Quite a number of the chemical elements used not only by the paint industry but also by the plastic, fertilizer and pesticide industries, are potential war gases (chlorine gas, phosgene) and highly toxic. Substances such as chlorohydrocarbons found in flame retardants, plasticizers and vinyl chloride based binders cause disposal problems: they are difficult to degrade, thus enter the food chain and concentrate especially in the fatty tissue of humans and carnivorous animals. When incinerated, dioxines are produced, i.e. highly toxic compounds of a carcinogenic effect causing chlorine acne. There is risk of dioxine formation with both regular thermal disposal in hazardous waste incineration plants and uncontrolled combustion, e.g. during an accident.

Recycling, i.e. reuse of paint resins is not feasible since the plastic material is not type-differentiated and there is no way to strictly separate accompanying substances.

3.1.3 Inorganic Binders

Inorganic binders play a role in lime and silicate paints and are, therefore, discussed in Chapter 4 where they are compared to synthetic resin binders.

3.2 Solvents

According to DIN 55945, solvents are liquids that are able to dissolve the binder and that are volatile while film forming. In everyday language, "solvent" means the volatile organic constituents, i.e. hydrocarbons in the broadest sense unlike water as a "solvent" in waterborne paints.

Among the most important solvent classes are:

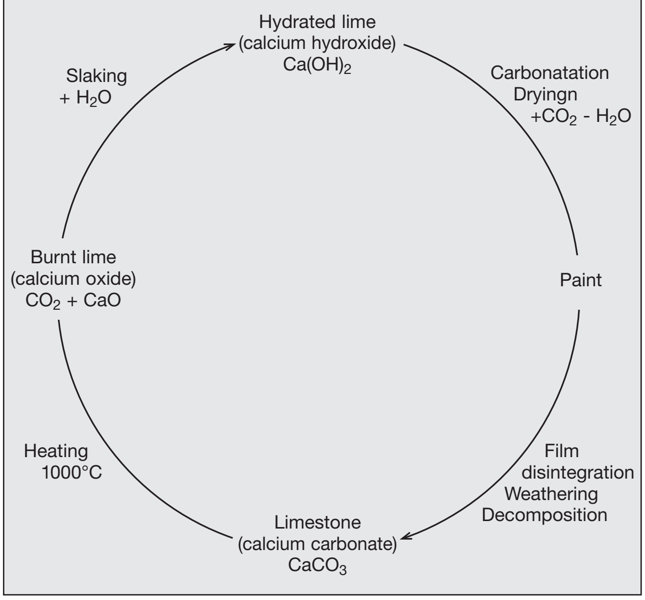
- Alipathic hydrocarbons such as white spirit ("gasoline"), isoalipathics
- Aromatic hydrocarbons such as toluene, xylene
- Glycols such as ethylene glycol, diethylene glycol
- Ethers such as dibutyl ether, some glycol ethers
- Esters such as butyl acetate, some glycol esters
- Ketones such as methyl ethyl ketone (MEK)
- Alcohols such as ethanol, methyl isoamyl alcohol
- Terpenes such as balsamic terpenes, citrus terpenes, orange peel oil.

From a working hygiene point of view, solvents are always to be considered potentially harmful for their fat-dissolving properties (skin protection !) and because of their narcotizing effect in case of longterm contact. Certain solvents such as xylene, isoaliphatics have been found, at least in animal tests, to have a carcinogenic potential. Solvents are mainly recovered through petrochemical methods and contribute to CO_2 accumulation in the atmosphere. Thus, they favor the global greenhouse effect, the local summer smog and the formation of ozone.

Besides road traffic, solvents used in coatings are the second biggest source of emission of hydrocarbons. An ecological alternative to crude oil based solvents are natural terpenes, found e.g. in the resin flow of pines (the so-called balsam or gum) or in the peels of citrus fruits. These terpenes are recovered and cleaned through pressing or steam distillation, respectively.

The essential difference to synthetic solvents is, on the one hand, the millenia-old familiarity with the human organism (turpentines in wood, coniferous woods, citrus fruits as a food), on the other hand, the zero CO_2 balance: During solvent degradation exactly the same amount of carbon dioxide is released into the atmosphere as was taken beforehand from the atmosphere by the plant when building up the terpene.

Material Cycle of Limewash



Plant terpenes are almost exclusively used in strictly natural paints. They are well compatible (pine oil is also used by the cosmetics and pharmaceutical industry) and show considerable advantages (CO_2 balance, plant reactor) compared to petrochemical solvents.

The paint industry aims at reducing solvents as far as possible. Thus, the solvent content of 50-70% once encountered in off-the-shelf paints has been reduced to a maximum of 10% in waterborne paints carrying the environmental sign and to 15% in high-solids paints. The reason for this trend is both a lacking customer acceptance and increasingly restrictive actions in connection with volatile organic compounds which find their expression in more and more restrictive statutory environmental and safety at work requirements.

3.3 Pigments

Pigments or colorants are the coloring elements of a paint and defined in DIN 55945 (or DIN 55943 and 55944). Certain pigments also take over the job of corrosion protection or UV absorption in a paint. In analogy to binders, pigments may be divided into inorganic and organic, natural and synthetic modifications.

3.3.1 Earth Color Pigments

Earth colors are natural, inorganic pigments (metal oxides) of an earthy undertone. They were used even in prehistorical times (cave paintings). Till the beginning of the 20th century, they were often the only pigments available in larger quantities. Regional deposits led to colorings typical for that region. Earth pigments are absolutely lightfast and extremely chemical and weather resistant. Examples of earth colors are: umber, ocher, Terra di Siena, bolus and Swedish red.

The raw materials for earth colors are recovered from natural deposits. Through treatment and cleaning including milling, sieving or washing, the earths are turned into dyes. Further treatment such as heating is common for certain types (e.g. burnt umber, Terra di Siena).

From a toxicological point of view, earth colors are absolutely safe as long as they are free of heavy metal impurities. From an ecological point of view, they are ideal since the natural materials can be used directly after simple milling and cleaning, not requiring any chemical processes such as transformation.
However, the fact that places of discovery are partly very limited may be considered a disadvantage. Among the problems resulting thereof are: assault on the landscape and risk of resource shortage in case of "rare earths". Under color psychology aspects, earth colors have a tranquilizing and harmonizing effect.

3.3.2 Mineral Pigments

Mineral pigments are synthetic inorganic pigments (metal oxides). They include titanium dioxide, chrome oxide green, iron oxide yellow, red, brown and black, ultramarine blue, nickel-titanium yellow. The ores they are recovered from come from natural deposits. Through simple chemical processes (e.g. precipitation, liberation) natural metal oxides are liberated from accompanying substances. When heated, iron oxides change their colors due to the escape of crystal water, a fact taken advantage of at industrial scale. Ultramarine blue used at large scale is recovered through melting from soda, clay and sulfur.

From a toxicological point of view, mineral pigments can be considered safe. They are free of soluble heavy metals. Compared to earth colors, they offer an alternative, especially for color tones blue, yellow and green. However, the decomposition processes used at commercial scale, e.g. for titanium ores, involve a higher risk for the environment since they require the use of highly concentrated mineral acids such as chloric or sulfuric acids. Closed-circuit plants for multiple acid concentration are standard. Even though ocean dumping of waste acid isn't a major issue any more, the use of huge amounts of chemicals and energy surely is a disadvantage. Titanium dioxide – an indispensible white pigment because of its excellent whiteness, covering capacity and outdoor durability – should nevertheless be used very sparingly since high brilliancy and whiteness requirements can only be met at the expense of the ecological balance.

3.3.3 Plant Color Pigments

Plant colors are natural organic pigments and dyes from plants. They provide many colors, however, of a low colorfastness. Examples of plant colors are: indigo, woad, alizarin red, reseda, alkanna violet and saffron. Raw materials for plant colors are leaves, flowers, fruits or roots of certain dyer's plants.

In some of the plants we find, in general, an initial stage of the pigment or dye which may be processed in several operations, e.g. for the blue of dyer's woad leaves through milling, fermentation and air drying according to traditional procedures.

From a toxicological point of view, they are safe. Plant colors are renewable raw materials of a high brilliancy and dyeing capacity. However, their use is restricted due to their lack of fastness, especially lightfastness. Availability, demand and actual market price will also have to be considered in this context. Plant colors started to gain importance when first used by Rudolf Steiner School teachers for glazing color design.

Regarding field cropping, certified organical growth methods should be preferred doing without the use of pesticides or artificial fertilizers. In recent years, woad cultivation has revived an ancient industry especially in Thuringia.

3.3.4 Synthetic Pigments

Synthetic pigments are artificial organic pigments and dyes. They can be synthesized in almost any shade, especially in very pure color tones and also with visual effects (daylight-fluorescent paints etc.). Examples are: azo, dioxazine and phthalocyanine pigments. Raw materials for synthetic pigments are crude oil, coal and tar.
From a toxicological point of view, they cause certain problems since azo pigments with their benzene nucleus (aromatic hydrocarbons) are known for their carcinogenic

potential. Entirely synthetic products are made from petrochemical base units in multistage process chains. Among the most important base substances are the compounds benzene, phenol and aniline, all of which are listed as toxic and carcinogenic. The individual synthesis steps produce intermediates, and since the yield is not 100%, hazardous waste of a nonuniform nature is being produced with every single step, finally requiring thermal treatment or dumping at special sites when being disposed of. The result is an environmental hazard through noxious substances (e.g. dioxins) and a shortage of disposal areas. When synthesizing one kilogram of azo pigment, about ten times the amont of hazardous waste is being produced Long-term effects on humans and the environment are unknown for many synthetic pigments of today as new substitutes are being brought to the market every day, still completely unknown to both the eco system and the human organism. A reintegration in natural cycles is impossible, at least for aromatic and chlorinated synthetic pigments, since they are, unlike plant colors, biologically heavily degradable and, unlike earth and mineral pigments, not mineralizeable.

3.4 Fillers

Fillers usually means fine powdered stones providing body and hardness to the coating material. Compared to pigments, they are not or only insignificantly chromophorous. Examples are: talcum, chalk and quartz. Filling facade paints contain larger, paints and glazes smaller amounts of fillers. From a chemical and biological point of view, powdered stones are more or less inert. Ecologically, only the landscape and energy consumption during recovery and processing of the fillers will have to be considered.

3.5 Additives

Auxiliary materials or additives are substances that are added to the coating material in small amounts in order to obtain certain qualities with view to storage life, processing or look. Additives as specified in DIN 55945 very much in chemical structure, effect and ecological importance. Therefore, some important classes are worth taking a closer look at:

Thickeners

are swellable in the solvent and control the consistency of the paint. Common types are synthetics of the polyurethane and acrylate classes. Modified natural substances are the bentonites (layer lattice silicate) and the cellulose derivatives. On a natural renewable basis and, therefore, of a better environmental compatibility are polysaccharides such as xanthan and tragacanth. Xanthan is not only used in natural paints and cosmetics, but also in food, e.g. in yoghurt.

Pot preservatives (Biocides)

Pot preservatives keep the paint from disintegration in the container, caused by mold or bacteria. Preservation is only required for waterborne systems such as dispersion or water-based paints. Commonly used are so-called formaldehyde retardants that continuously release small amounts of (cancer-causing!) formaldehyde. Aromatic and heterocyclic chemicals, partly halogenated with chlorine or bromine, are also among the standard biocides used. They represent some of the most important hazardous substances to the environment which is why they are subject to identification requirements under the Hazardous Substances Act. Despite their low share in the overall formulation (in case of dispersion or waterborne paints only about 0.1 to 0.3 weight percent), they really are a toxicological and ecological risk. These biocides are potentially hazardous to the human organism when inhaled, e.g. when volatile and released to the indoor air, or when the wet or dry paint comes in contact with the skin and the biocides reach the blood stream, thus potentially resulting in dangerous accumulations in the fatty tissue.

Problems encountered with biocides and their toxicological assessment are discussed in more detail in Chapter 5 (Wood Protection).

Another essential problem is the disposal: Whether product remainders reach the sewage system, are disposed of or incinerated as hazardous waste, they are always potentially harmful to the environment since they cannot be degraded by microorganisms.
Coating systems that do without the use of preservatives are a true alternative. Lime and silicate paints are naturally protected from microorganism attacks through their high alkalinity (pH value above 11). In natural paints, however, essential oils such as thyme, lavender and eucalyptus oil or boric salts are used for their disinfecting effect. Both families are characterized by human and environmental compatibility (e.g. boron as a trace element for humans and plants) and their ecological recyclability.

Wetting agents

Wetting agents, also referred to as dispersing agents, are important for wetting and for integrating pigments. Polycarboxylic acids, phosphoric acid esters and polyacrylates are among the common synthetic classes. Of plant origin are soy lecithin, Turkey red oil (sulfated castor oil) and olein, the oleic acid of a plant. Shellac, a versatile additive in natural paints, is recovered from the excrements of an Indian plant louse. Due to their chemical structure, wetting agents may be irritating to the skin. An advantage of plant-based products is the gentle recovery, the better degradability and a good and healthy compatibility. Soy lecithin, for example, is a constituent part of the soybean and contained in many foods.

Drying agents (Siccatives)

Drying agents are metal soaps, usually cobalt, barium, zirconium or manganese soaps of a carboxylic or naphthenic acid. Drying agents support the oxidation drying of oil-based paints and are, therefore, indispensible e.g in natural oil paints. Due to their heavy metal content, they represent a certain ecological and toxicological risk. However, siccatives that contain lead areintolerable today.

Plasticizers

Most synthetic resin paints contain plasticizers supposed to keep the synthetic resin's normally very brittle and cracking-sensitive polymer chains flexible and expandable. Commonly used are fatty acid esters (e.g. phthalic acid ester), sulfonic acid esters or amides and chlorinated paraffins. Non-polymerizable plasticizers, not integrated in a polymer chain, might exude or evaporate by nature, resulting in a release into the ambient air and in an accumulation in room textiles, stored food and the human organism. Even with a low acute toxicity, a steady contact with plasticizers that have proven carcinogenic in animal tests must be considered potentially hazardous.

Defoamers

Defoamers inhibit the foam formation of waterborne paints during manufacture and when being stirred up. Commonly used are surface-active compounds of the family of organosilicon chemicals as well as certain polymers and alcohols. One thing these substances have in common is their more or less water-endangering effect. Solvents or essential oils are often also characterized by a degassing effect and may, if required in the formulation for other reasons, minimize the addition of special defoamers or make them even superfluous.

Other additives

Other additives may include e.g. skin inhibitors, flow improvers, emulsifiers and initiators. In general, it can be said: The higher the requirements on the paint, the larger the number of additives used. The chemical affinity also has an impact: The less compatible two components are, e.g. organic polymers and water, the more additives will be required to eliminate the perturbating forces. For waterborne paints, this would be emulsifiers, defoamers, biocides, amines and film-forming aids. From a toxicological point of view, some additives are not harmless. However, when being added in very small quantities only, a direct impact on human health is rarely found.

What's more significant is the accumulation in the ecosystem and in the food chain. Many additives have only been on the market for a few years or decades which is why a final assessment with view to the impact on humans and the environment is not yet possible.

Almost unconsidered are the synergies that may result from the coexistence and interaction of very different additives.

4. Paint Systems

4.1 Limewashes

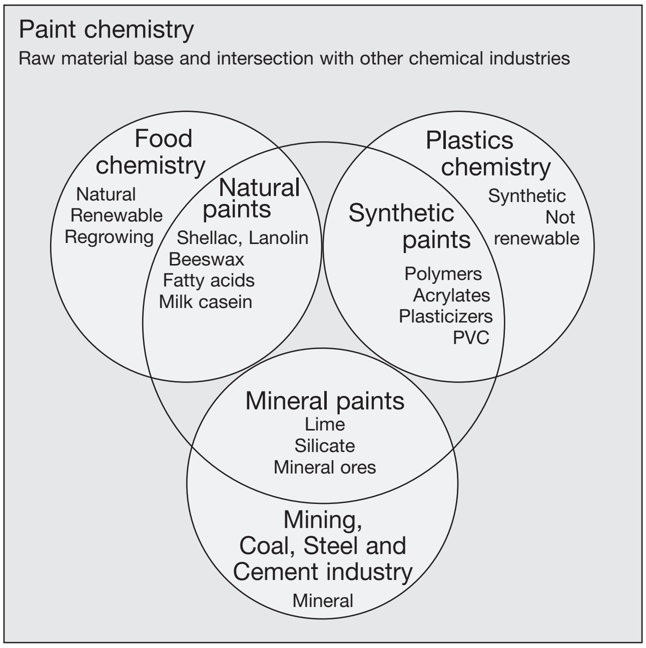
Today, lime is again being used more and more often for paints taking advantage of its excellent bactericidal and humidity control properties. Especially when used in combination with clay, the use of limewashes makes perfect sense. Since hydrated lime is highly water-soluble, limewash is the most simple paint type imaginable that can do without additives. Furthermore, limewash may also be used in terms of a pigment and a binder. For further features, see chart.

Because of the acid rain today, the use of lime based paints outdoors is no more recommended as they would require extensive maintenance. For indoors, manufacturers of natural paints offer washable distempers in the form of a powder which may be prepared very easily by the user. These distempers are open-pored and emission-free, i.e. recommended from an ecological and biological building point of view.

4.2 Silicate Paints

Pure silicate paints without organic (artificial) ingredients are supplied in terms of two components, the fixative (waterborne waterglass solution) and the powdered pigment (filler combination toned with earth and mineral pigments). Silicate paints offer excellent biological building features since they are perfectly water vapor permeable and free of organic ingredients (solvents, biocides, plasticizers etc.). With view to the preservation of monuments, they are absolutely ideal for old, often critical surfaces because they do not form film unliksynthetic resin systems.

Thanks to their excellent durability, silicate paints are



cost-effective (maintenance intervals of 20 to 25 years). Substrates, such as lime-containing plasters outdoors, also profit from the silicate paint because of its open-pored character and the silicification that takes place between the silicate paint and the lime. The chart details the most important differences found in waterborne facade systems. Unlike purely inorganic silicate paints, dispersion silicate paints have a maximum organic content of 5 weight percent, usually an acrylate dispersion. The advantage of this product type is its availability as a one-component product offering both good storage durability and easy processing on certain critical surfaces. However, the fact that most commercially distributed dispersion silicate paints are organically bound, i.e. film-forming and only insignificantly silification-active, may be considered a clear disadvantage.

Facade Paints for Mineral Surfaces
in accordance to VOB DIN 18363

	Mineral Systems			Synthetic Resin Systems	
	Limewash	**Silicate paint**	**Dispersion silicate paint**	**Synthetic resin dispersion paint**	**Silicone resin emulsion paint**
Binder	Lime hydrate	Potash waterglass	Potash waterglass and/or synthetic resin dispersion	Synthetic resin dispersion	Synthetic resin dispersion with silicone resin emulsion
Organic content	None	None	Max. 5 %	10-25 %	10-20 %
Drying/Curing through	Carbonatation	Silicification	Silicification and/or film formation	Film formation	Film formation
Film-forming	No	No	Partially	Yes	Yes
Water-vapor permeability	0.02	0.04 - 0.08	0.08 - 0.6	0.6 -1.5	0.1 -0.9
Raw material of the binder	Limestone	Quartz and potash	Quartz and potash/crude oil	Crude oil	Crude oil
Availability of the raw material	Unlimited, worldwide	Unlimited, worldwide	Unlimited, worldwide/limited	Limited, only for a few more years	Limited, only for a few more years
Organic solvents in the coating	None	None	Partially	Often	Often
Outgassings of the coating (solvents, residual monomers, plasticizers, amines)	None	None	Partially	Often	Often
Are defoamers, biocides, pot preservatives required	None	None	Partially	Often	Often
Degradation products of the binder	Powdered stone	Powdered stone	Powdered stone/ organic decomposition products	Organic decomposition products,partly toxic	Organic decomposition products, partly toxic
Flammability/Gas formation in case of fire	No	No	Low flue gas formation, partly with toxic gases	Flue gas formation, partly with toxic gases	Flue gas formation, partly with toxic gases
Chemicals and energy consumption during basic renovation	Low (brushing, cleaning)	Low (brushing, cleaning)	Low to high, depending on silicification activity	High. High-pressure water jet with hot water and chemical paint stripper required	High. High-pressure water jet with hot water and chemical paint stripper required
Durability of the coating (outdoors)	Low, especially in regions with acid precipitations	Very high, insensitive to aggressive atmospheric substances	Medium to high, depending on silicification activity	Low to medium, with a tendency to flake and embrittle	Medium, a little more durable than purely synthetic resin dispersion paints
Ecological and biological building - Overall evaluation	Good	Good	Average	Unsatisfactory	Unsatisfactory

4.3 Synthetic Resin Dispersion Paints

Synthetic resin dispersion paints are also covered by DIN 18363 and, thus, a frequent constituent of the VOB (contracting rules for the award of public works contracts). Indoors and outdoors, they are the most common family of wall paints. Essential differences to mineral paints are shown in the chart.

Synthetic resin dispersion paints are film-forming and, therefore, less open-pored, water vapor and carbon dioxide permeable than silicate paints. The result is a loss of indoor air quality since the natural indoor/outdoor water vapor exchange is being prohibited. Among the secondary effects found may be mold and mildew formation (affecting the respiratory system and possibly resulting in allergic reactions) or even a complete penetration of the building substance with moisture.

Another disadvantage of film formation is the fact that renovation coatings sum up and, after a few decades, will reach a total thickness that causes the coating to flake due to stress. This will cause another problem: the removal of the coating from the facade with high-pressure water jet using hot water or through a chemical paint stripper. Paint strippers are usually hazardous to health with a high solvent content and partly chlorinated hydrocarbons that require identification through labeling. Improper disposal, e.g. the introduction of stripping residues into the sewage system, constitutes a severe environmental offense. The energy and chemical requirements for renovating a facade that has been treated to form film are very high. Depending on the formulation, synthetic resin dispersion paints will emit solvents (unless solvent-free), plasticizers, residual monomers and, if applicable, other low-volatile ingredients for years. This may result in a contamination of the indoor air and cause health problems. Another group of synthetic resin dispersion paints are silicone resin emulsion paints, i.e. silicone resin-modified, binder-reduced synthetic resin dispersion paints. DIN 18363 neither specifies requirements nor minimum or maximum values for ingredients affecting the quality. As can be taken from the chart, this paint type shows no difference to synthetic resin dispersion paints from an ecological and biological building point of view which means that it can be considered nothing but another, not exactly defined version of these paints.

4.4 Waterborne Paints – „The Blue Angel“

The environmental sign "Blue Angel" is assigned by the Bundesumweltamt (German Federal Environmental Agency) together with the RAL (German Institute for Quality Assurance and Labeling, a non-profit organization) for products that - compared to other products for the same purpose and considering aspects of environmental protection including an economic use of resources – are characterized by their environmental friendliness without their fitness-for-use or safety being reduced.

In the paint industry, the environmental sign is only awarded to these two families of products: waterborne paints with a maximum 10 weight percent organic solvents content without toxic heavy metals, as well as water-thinnable paints with a high solids content and a solvent content of no more than 15%. Regarding the reduction of solvents, this restriction to only two products may be considered positive. However, it still remains hard to understand. In contradiction to its high claims, the environmental sign only considers the "solvent" aspect while completely leaving aside factors such as raw material requirements, renewability and ecological material balance.

Awarded the environmental sign because of low content of noxious substances' may well refer to the end product but does not include the synthetic chemicals used in the course of its manufacture. As explained in Chapter 3 "Ingredients", a waterborne paint carrying the environmental sign may be actively involved in producing and releasing synthetic chemicals such as chlorine gas, phenol, benzene, aniline, phosgene and carcinogenic monomers. Disposal through composting is impossible due to components such as biocides, chlorinated and aromatic hydrocarbons. Instead, disposal in a special waste incineration plant will be required, resulting in the release of dioxins and furans.

Therefore, the environmental sign is unsuitable as a tool to clearly identify systems that are envi onmentally friendly by nature, such as linseed oil or lime based products, or their ecologically unsafe counterparts polyurethane or synthetic resin dispersion paints.

4.5 Natural Paints

Natural paints are composed of plant or animal, renewable or mineral ingredients. The individual raw materials are not at all or only slightly modified, thus keeping their natural character.

The basic idea to produce safe, ecological paints from available natural materials was, on the one hand, a reaction to the wood preservative scandal of the 70s and 80s. On the other hand, the upcoming ecological understanding made some pioneers recognize that proven lime, shellac or plant oil based systems were replaced more and more often by petrochemical products with inherent problems regarding raw material recovery, disposal and biological building aspects.

The alternative is a production of some millions of tons of balsamic terpenes from plants every year. Natural resins, vegetable oils and milk casein (from cow's milk) are produced and again degraded in large amounts without causing any disposal problems.

The trend towards natural paints started with innovative small-size companies. In 1986, some natural paint manufacturers founded the Association for Natural Colors (AGN) and set up quality requirements for the natural paints that were produced at that time. Petrochemical constituents, whether in terms of solvents or other formulation components, are not accepted. With the full declaration of each and every ingredient, raw materials no longer remain a secret. Chemically sensitive and environmentally ill persons are thus prepared to avoid those ingredients that may cause a life-threatening allergic shock.

Example of a full declaration of a natural paint:

Interior wall paint of an AGN member, washproof according to DIN 53778, covering white and solvent-free. For universal indoors use on plaster, wallpaper, lightweight building boards and recoatable old coatings.

[1]: Tap water (L), Titanium dioxide (P);
[2]: Aluminum silicate (P), Diatomaceous earth (P), Zinc white (P), Beech cellulose (F), Talcum (F), Caolin (F), Dehydrated castor (stand) oil (B), Dammar (B), Refined linseed oil (B);
[3]: Beeswax soap (W), Shellac (W), Boric salt (W), Borax (W), Turkey red oil (W), Milk casein (W).

B Binder
L Solvent
P Pigment, Filler
W Active agent, Auxiliary agent, Additive

Key to the ingredients according to weight percentage:

[1] Raw material rate in the product > 10 wt.%
[2] 1-10 wt.%
[3] < 1 wt.%

However, the full declaration also shows how natural, renewable organic animal (casein, shellac) and plant materials can be combined with natural mineral substances to form a fit-for-use product.

5. Wood Protection

The wood preservative scandals of the 70s and 80s essentially contributed to a more critical use of chemical products that used to be applied rather thoughtlessly, such as wood preservatives containing PCP and lindane. Slowly but surely, people understand that preventive wood protection doesn't necessarily mean chemical wood preservation.

DIN 68800 Part 3 – Preventive Chemical Wood Protection – takes this development into account and specifies which chemical wood protection will be required for which exposition grade (grade 0 to 5 depending on weathering) and against which wood pest types (fungi, insects) this wood protection must be effective. The lack of chemical wood protection requirements for exposition grades 0 and 1 is of a high significance since it covers virtually any interior wood in service under normal living conditions. Wood preservatives contain biocides. There is, however, a tendency to replace general purpose active agents such as the insecticide lindane with substances that aim at inhibiting the development of potential pests. From an ecological point of view, this trend is highly welcome as it counteracts the distribution of ubiquitous substances that are harmful to the environment.

The effectiveness of wood preservatives is checked by the Institute for Building Engineering, Berlin, resulting in a certification mark. The test report specifies the ranges of application and the preservative retention and details how to carry out the wood protection work. Of a similar nature is the RAL quality label awarded by the Association for Wood Preservative Quality Labels.

In its information sheet on wood preservative handling, the Industrial Association for Construction Chemistry and Wood Preservatives, a non-profit organization, declares quality labeled products non-hazardous to health and environment when used according to instructions, based on an assessment by the National Department of Health (Bundesgesundheitsamt) for biocidal agent clearance. However, among experts, this declaration is somewhat controversial because of the test criteria. The determination of upper limits, for example, is based on numerical values which can hardly be understood from a human toxicological point of view since these values are usually obtained in tests through short-term feeding to animals. From the lethal dose thus obtained a still tolerable daily allowance for humans is calculated. A short-term oral intake of substances may, however, affect the test animals in another way than will the long-term inhalation or skin absorption of the same substance by humans. The risk of chronically pathogenic effects is especially high in outgassing wood preservatives. Among others, we already know of nerve damages, concentration problems, liver and skin damage (chlorine acne) and even cancer.

With a purpose, we do not indicate limit values, threshold limit values or maximum indoor air concentrations for common wood preservative biocides. They merely reflect the actual classification with the above mentioned restrictions which is why they should not be considered absolute or generally valid. The fact that there are clearly different classifications in the hazardous substances registers of our neighboring countries should worry us.

Pyrethroides, the durable synthetic imitation of the natural phytotoxin pyrethrum from the chrysanthemum flower, were long considered a "gentle" insecticide but are lately massively criticized. They are strong neurotoxins which may result in chronic damages or even anaphylactic shock (death caused by a spontaneous allergic reaction).

A real alternative, i.e. toxicologically harmless and environmentally friendly mineral based wood preservatives, are the boric salts. Common boric salt impregnations contain boric acid and borax in an aqueous solution. These active agents are natural boron compounds occuring in salt lakes in the United States and in Turkey.

Of particular interest is their low toxicity: For humans they are an essential trace element and, when taken orally, about as harmless as common salt (similar threshold limit values). Since they do not outgas or form decomposition gases, they do not affect the indoor air. Boric salts are known for their preventive effect against fungi and insects and, as far as non-fixated water-soluble salts are concerned, are perfect for supporting wood constructions indoors. They are, however, not suitable for directly weathered areas outdoors such as wood windows, formwork etc., even when painted or otherwise coated. Boric salts offer another advantage: They lower the flammability of wood. Thus, the use of traditional halogenated polymer based flame retardants may be minimized.

6. Hazardous Substances Ordinance

The November 10, 1983, Hazardous Substances Ordinance requires that all hazardous substances are identified. In the field of paints and lacquers, the following classes are of particular importance:

F+
Extremely flammable

E.g.: vinyl chloride, methane, ethene, ethine and carbon monoxide.

F
Flammable

E.g.: benzene, ethanol and acrylonitrile

T+
Very toxic
E.g.: phosgene and hydrocyanic acid

T
Toxic
E.g.: phenol, benzene, vinyl chloride, chlorine, acrylonitrile, carbon monoxide, zinc chromate, aniline, formaldehyde

C
Corrosive
E.g.: hydrochloric acid, potassium hydroxide and ammonia

Xi
Irritating

E.g.: acrylates, triethylamine and dichlorofluanide.

Xn
Harmful
E.g.: xylene, toluene, polychlorinated biphenyles, styrene and butyl glycol.

Identification requirements are usually depending on concentrations which means that the lack of the corresponding label doesn't necessarily mean that the product is entirely free of dangerous substances. Special care must be taken whenever the skull and crossbones symbol is used: The corresponding formulations may cause irreversible damages to health or even death.

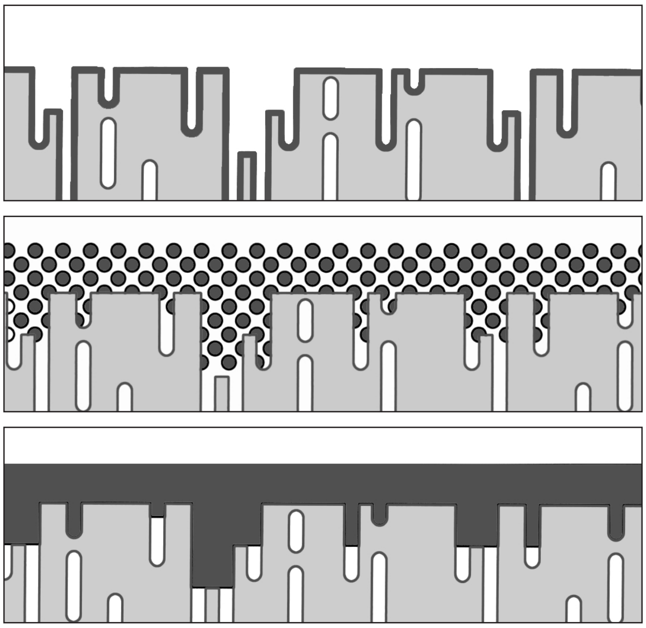
7. Room Climate

Building biology has started at a very early stage to stress the manifold interrelations between the building material, the room climate and the quality of living which cannot be limited to technical-abstract numerical values, limit values and physical characteristics.

One example: If the outgassing rate of a wood preservative used in a kindergarden exceeds a set value by only a few ppm (parts per million), authorities will promptly initiate the reconstruction or shutdown of the facility. If values remain only slightly below the limit, no action will be required by law. However, it is highly improbable that the few ppm that make the difference between leaving the facility open or shut it down, constitute a significantly higher toxicological risk for the infants and the staff.

Therefore, building biology requires the use of building materials that are both natural to the largest extent possible and residue-free. These building materials, such as wood or linseed oil, are not at all sterile or emission-free. They continously release small amounts of (chemically analyzable) compounds, in the case of wood e.g. wood vinegar, terpenes, etc. The fact that human organisms have been exposed to these outgassings for thousands of years makes an acute toxic effect very improbable. It would surely make no sense to determine threshold limit values for natural wood emissions although any substance may be hazardous to health starting from a certain concentration. Threshold limit values for synthetic compounds completely unknown in living nature can be no more than recommendations, but do not have the quality of absolute values.

The porosity of a coating may also have an impact on the indoor air quality: Open-pored paints are capable of taking up part of the air humidity and release it to the (usually absorbent) substrate of plaster, stone or wood. As the humidity of the air decreases, part of this pore water is again released into the room air. Intercalated water also counteracts an electrostatic buildup which may become unpleasant in case of large metal and plastic surfaces whenever the humidity of the air is low. In rooms that lack any or a proper heat insulation and in vaults etc. with a high humidity of the air, a particularly open-pored (mineral) paint is the only way to obtain an acceptable room climate. The more dense and less water vapor permeable a film-forming coating is under such conditions, the sooner and more severe damages will become evident such as mold formation and damages due to excessive moisture which may finally result in chronic respiratory diseases, allergic reactions and rheumatic symptoms. Wood, cork and open-pored ceramic tiles are also moisture controlling as long as they are not sealed with impermeable films. Oils and waxes will maintain the natural porosity to a large extent.



Pictures from top to bottom:
When treated **with oils and waxes**, the pores are lined but not clogged.
Diffusible paint on a porous substrate.
When **sealed**, the pores are clogged and become gastight.

Natural paints are, in general, suitable for interior design purposes as they are usually absorbent and diffusible. For a large number of applications, they are a true alternative to very dense film-forming products. The layer thickness of a conventional sealing may be about 80 µm while a wax treatment will be less than 10 µm. The advantage: Building material pores are not clogged, but lined and, thus, remain naturally diffusible.

8. Coating Recommendations (Using Environmentally Friendly Paints)

The following list states alternatives to traditional coating systems on surfaces meeting practical requirements:

Outdoors

Mineral facade plasters of mortar groups PI to PIII (DIN 18550), none or low water repellency

- Traditional systems:
  Synthetic resin dispersion paints, silicone resin paints (DIN 18363)
- Recommendation:
  Pure silicate paint (DIN 18363), alternatively:
  Dispersion silicate paint (DIN 18363).

Wood windows and sidings outdoors, constructive wood protection measures (roof overhang, drainage, wood grade etc.)

- Traditional systems:
  Alkyd paints and glazes, acrylic paints and glazes, emulsion paints (DIN 55945). Primer with biocide-containing wood primer.
- Recommendation:
  Diffusible pigmented oil based glaze, alternatively:
  Oil varnish (DIN 55945) from renewable plant materials.

Indoors

Interior wood formwork, planed or unplaned.

- Traditional systems:
  Acrylic paints and glazes, water thinnable.
- Recommendation:
  Diffusible oil glaze, water thinnable and solvent-free, alternatively:
  Milk casein/shellac based glaze, pigmented or colorless; or oil primer and subsequent waxing with beeswax or carnauba wax.

Parquet floor, cork or open-pored ceramic tiles in living areas.

- Traditional systems:
  Polyurethane, alkyd or acrylic resin based sealing.
- Recommendation:
  Oil based primer and subsequent treatment with carnauba wax, alternatively:
  Oil based primer and subsequent treatment with natural hard resin lacquer.

Interior plasters (mortar groups according to DIN 18550), paper wallpapers, recoatable old coatings in living areas.

- Traditional systems:
  Synthetic resin dispersion paint (DIN 55945), washable and wear-resistant according to DIN 53778:
- Recommendation:
  Natural resin wall paint
  (washable according to DIN 53778), alternatively:
  Washable distemper.

High traffic interior walls in public and commercial buildings such as hospitals and kindergardens.

- Traditional systems:
  Synthetic resin dispersion paint (DIN 55945), wear-resistant according to DIN 53778 ("latex paint").
- Recommendation:
  Natural resin wall paint,
  wear-resistant according to DIN 53778.

Interior walls in vaulted basements, stables or historical buildings with a high humidity of the air, substrate: lime plaster.

- Traditional systems:
  Synthetic resin dispersion paint, washable according to DIN 53778, fungicidal through the use of biocides.
- Recommendation:
  Limewash, alternatively:
  Silicate paint or silicification-active silicate paint for indoor use.

9. Painting Work

In general, when processing paints or other coating materials, some precautionary measures should be taken. Products that contain solvents should be applied only in well ventilated areas while a mobile or stationary exhaust unit will be required for a number of commercial applications. This also applies to natural, renewable solvents which, despite of their good environmental and human compatibility, may in larger concentrations and after longer exposure cause dizziness and irritation of the mucosa. More details about the personal protection to be used are given by employer's liability insurance associations, consumer associations and paint manufacturers. Special care must be taken when using working materials that are subject to labeling requirements.

When used in private homes, make sure that paints are stored out of the reach of children. The disposal of paint residues, empty containers etc. is specified in state laws. Since material recycling of paint residues is impossible for technical reasons because they are neither type-specific nor separable from accompanying substances, law requires that such residues are disposed of as hazardous waste in incineration plants. Natural paints that are, principally, compostable are, for the time being, not stated separately in the actually valid list of waste codes.

There will be a chance to realize recycling in a gentle way through composting as soon as criteria such as biodegradability, water hazard class or limit values will have been established for critical ingredients (e.g. heavy metals). Then, products would have to be separated, based on their ingredients, in products that may be composted and products that require thermal disposal.

10. Evaluation

To sum up, it can be said that for most applications there is a petrochemistry based status quo, i.e. a synthetic resin paint in a broader sense, on the one hand, with an environmentally-friendly, mineral or plant based alternative, on the other hand. An obvious, but in the end completely unsatisfactory classification in "toxic" and "non-toxic" paints has been avoided since such classification would fail to meet ecological requirements. Essential criteria are, however, the raw material availability, the extent of the chemical transformation, the health compatibility and the reintegration in nature's cycles.

The depletion of crude oil resources is only a question of time depending less on how we manage to recover them, but rather on how reasonably we will use the resources that are left. Concerning energy, a thermal protection ordinance was realized with the objective to save fossile energy resources while releasing less CO_2 and other noxious gases into the atmosphere. The mechanism is the same in any petrochemical product: Not only are raw material resources running out but the use of petrochemical products also causes more and more environmental problems with view to climatic changes, accumulation of airborne pollutants and growing amounts of waste.

Renewable plant raw materials save fossile energy resources. At the same time, they offer a perspective to agriculture through an as far as possible regional supply of biological-dynamically grown useful plants. The fact that useful plants do not only provide paint raw materials but also fibers (flax), wood (pine) or citrus fruits, has another positive effect on the economical and ecological balance. Plant raw materials offer one more alternative to fossile resources since the shortage of the latter will sooner or later result in a significant price increase.

Material cycles depicted in Chapter 3.1.2 "Synthetic Organic Binders" show a considerable number of hazardous substances wherever synthesis steps are carried out under potentially hazardous conditions. Comparatively troubleless are the cycles and transformations encountered in mineral paint production. CO_2, for example, is released during heating, but is again taken up by the chemically reactive binder during drying. This "gentle chemistry" is also the basis for natural paints which almost completely do without chemical transformation processes and, thus, avoid both the risk of accidents and highly toxic intermediates during production. The exclusive and consequent use of natural paints also assures that no "traditional" toxins such as formaldehyde, aromatic or chlorinated hydrocarbons are introduced into your home.

Indoor air analysis confirms a higher indoor air quality, i.e. quality of living, with less noxious substances and a lower risk to health.

Many of the techniques have actually survived, e.g. in the restoration business, where linseed oil varnish or casein paints are still used the traditional way for architectural monuments and historical buildings and where low maintenance confirms the technical suitability of these methods and materials.

Standards:

DIN 18363
VOB Verdingungsordnung für Bauleistungen, Teil C: Allgemeine Technische Vertragsbedingungen für Bauleistungen (ATV), 1992.

DIN 55945
Beschichtungsstoffe
(Lacke, Anstrichstoffe und ähnliche Stoffe), 1988.

DIN 68800 Teil 3
Holzschutz, vorbeugender chemischer Holzschutz, 1990.

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