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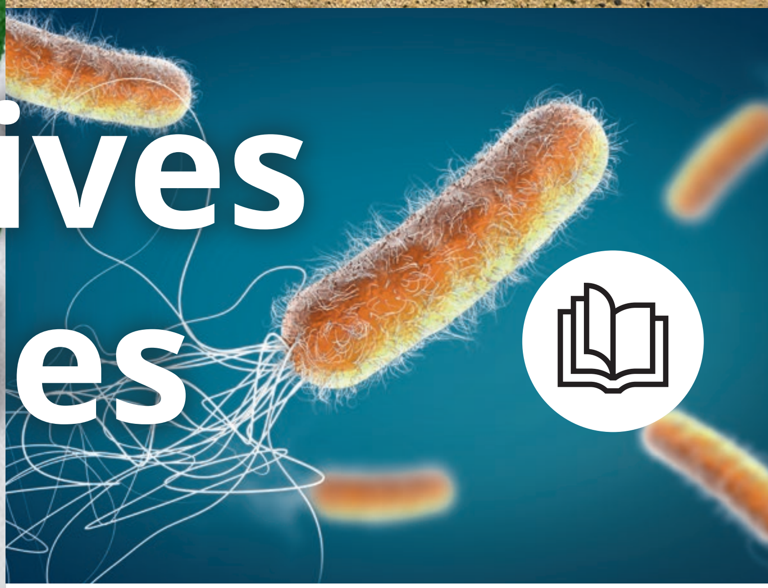

Alternatives to Biocides

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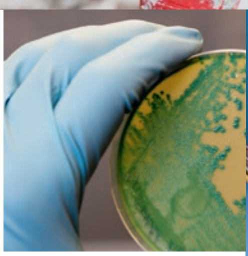

VINCENTZ

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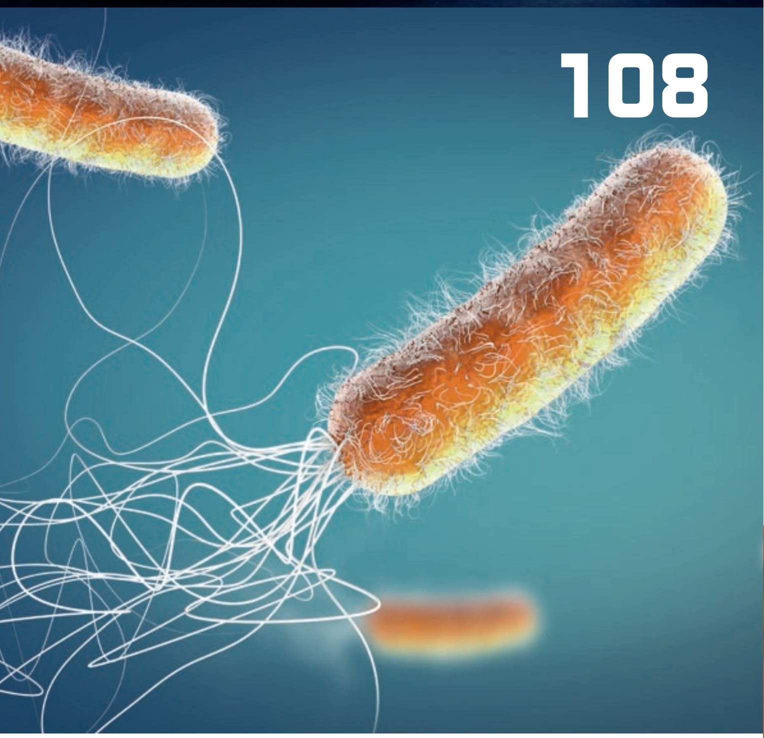

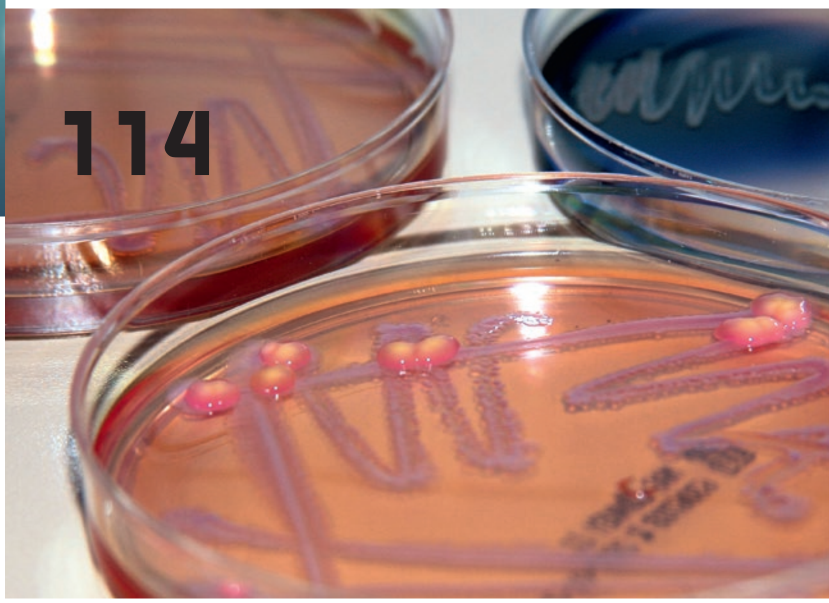

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COATINGS PRESERVATION

One of the biggest trends in the microbicide market is a desire for more eco-friendly products. Find here the basic knowledge about in-can and dry-film preservation.

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2 Coatings preservation

Microbicides are used in a variety of applications, including paints and coatings, stuccoes/plasters, polymer emulsions, adhesives and sealants, inks, plastics, wood treatments and many more. The coatings industry has to cope with a triangle of conflicting priorities between the various demands of technical solutions for contamination problems, increasingly stricter regulatory requirements, and commercial constraints. Regulations governing the production and application of microbicides affect the various markets in a number of ways, as they often restrict the use of certain microbicidal products while increasing the cost of time-consuming regulatory support. As a result, a number of microbicides are being withdrawn from some applications and traditional chemistries are being replaced by new products. While the regulations in Europe, America, Asia and other parts of the world are becoming more stringent, officials are agreed that these changes will benefit all stake-holders in the long term.

One of the biggest trends in the microbicide market is a desire for more eco-friendly products which have for example little or no VOC content and whose components exhibit minor ecological toxicity, and a desire for more cost-effective alternatives. This feeds directly into the need for a deep understanding of the intrinsic properties of microbicidal actives and the corresponding chemistries. Consequently, making the right selection from a range of legally accepted microbicides is key to protecting paints and coatings from microbial attack whilst simultaneously ensuring environmental sustainability. In this connection, the variety of potential chemical compounds is quite restricted and the proper allocation of products is becoming a more and more sophisticated task that requires a balancing act in terms of product design.

The extent to which the application of a microbicidal product poses a risk to human health and the environment depends on the manner of application. In general, risks can be reduced either by using a microbicide which has a low potential to cause harm or by applications that lead to low exposure levels.

Ideally, the microbicide should
- Offer a broad spectrum of activity against the target species
- Be stable, even under challenging environmental conditions (e.g. pH, UV light)
- Be compatible with the substrate to be protected
- Not pose a risk to human health
- Be environmentally sound
- Be cost-effective

Most commercially available microbicides do not meet all of these requirements. The choice of microbicidal product for a specific purpose often represents a compromise between expectations and reality. It is not always necessary to offer a full range that covers all species of microbes. Consequently, it is highly recommended that preliminary laboratory pre-trials be conducted on the suitability of the chosen microbicidal product for the intended purpose (see also Section 4).

All water-borne coatings typically contain organic components (e.g. binder, additives) which serve as nutrients for germs and are therefore susceptible to microbial degradation. In

Coatings preservation

the absence of appropriate preservation in the wet state, the coatings become unusable and give rise to customer complaints. In addition, cured coatings come under microbiological attack from fungi, algae and lichens, particularly if the degree of atmospheric humidity is increased. Dry-film preservatives serve to prevent spoiling in and on the applied, cured paint film. Bio-deterioration of coatings is caused especially by the microbial groups illustrated in Figure 2.1.

These germs have only simple requirements for growth and proliferation, but these requirements are usually met during manufacturing processes, in storage, during transportation, and after application of water-borne products.

2.1 In-can preservation

Spoilage in the wet state is mainly due to bacterial and fungal growth. The product might develop a bad odour, discolouration, broken emulsions, a loss of viscosity or a decrease in pH. Evolution of carbon dioxide as a metabolite of microbiological action often causes the product containers to bulge until eventually the product is no longer sellable. The resulting economic loss is exacerbated by the ensuing need for waste disposal, which will incur additional costs.

Plant hygiene also requires the use of appropriate preservatives for the wet state (see Section 2.3)

The structural degradation of industrial fluids is usually attributable to complex microbial communities consisting of bacteria, fungi and yeasts. Ideally, for optimum efficacy, the microbicide will match the microbial species and its likelihood of occurrence in a given product. The following key factors should also be considered in the search to identify the best solution to a contamination problem:

- Type of product to be preserved
- pH & temperature at the point of dosage
- pH & temperature in the final product/in storage
- Typical or expected storage time of the product in question
- Requirements of specific regulations and approvals (e.g. eco-label, food contact)
- Exclusion of specific chemistries (e.g. sensitising agents)
- Currently employed microbicide(s), dosages and costs
- Known problems with microbicide(s) already in use
- Degree of service expected

Figure 2.1: Primary microorganisms responsible for the bio-deterioration of coatings

Table 2.1: EU work programme for the processing of applications under the biocides regulation[182]

Priority	**Existing active substances for PT's**	**eCA to submit AR's and conclusions to ECHA**	**ECHA to start preparation of its opinion (submission to Commission max. 270 days later)**
1st priority list	8, 14, 16, 18, 19, 21	31st Dez, 2015	31st Mar, 2016
2nd priority list	3, 4, 5	31st Dez, 2016	31st Mar, 2017
3rd priority list	1, 2	31st Dez, 2018	31st Mar 2019
4th priority list	6, 13	31st Dez, 2019	31st Mar, 2020
5th priority list	7, 9, 10	31st Dez, 2020	31st Mar, 2021
6th priority list	11, 12, 15, 17, 20, 22	31st Dez, 2022	30st Sep, 2023

AR = Assessment Report; eCA = evaluating Competent Authority; ECHA = European Chemicals Agency; PT = Product Type

Very often, different actives are combined in order to complement their microbicidal spectra (e.g. a very fast acting microbicide which kills the majority of germs in a short time frame, but which might be rapidly consumed due to its action, can be combined with a long-lasting microbicidal active which maintains protection during protracted storage of an industrial fluid). Moreover, standard laboratory test methods (see Section 4) are available that help to decide whether a selected antimicrobial product is appropriate for the intended purpose (Figure 2.2).

Although the initial Biocidal Product Legislation came into force at European level[181] back in 1998, even today, more than 18 years later, many actives for which an application has been filed are still awaiting final approval for the intended use – as indicated in the form of a so-called ‘product type’ (PT). Meanwhile, Commission Delegated Regulation (EU) No. 1062/2014 of 4th August 2014[182] foresees finalisation of the work programme in 2024, as shown in Table 2.1, i.e. some 26 years after the initial step.

However, some scepticism might be allowed as to whether even these significantly delayed timelines will be met.

The European Chemicals Agency (ECHA) regularly publishes on its website a list of biocidal active substances, also known as the ‘Art. 95 List’[180], for which a dossier has been submitted by the relevant applicants, either under the former Biocidal Products Directive 98/8/EC (‘BPD’)[181], or under its successor, the Biocidal Products Regulation (EU) No. 528/2012 (‘BPR’)[126]. As

Figure 2.2: Standard laboratory test methods for choosing the right microbicidal products

of 9 May 2017, the Art. 95 List contained 52 different active substances for product type 6 (in-can preservation). Not all of them are utilised solely in the coatings area; some are also used in other areas, such as in-can preservation of glues and adhesives. The following sections discuss the most relevant and prominent actives for coatings designated for in-can preservation, grouped by chemistry.

2.1.1 Formaldehyde and formaldehyde-releasing compounds (FA-R)

Formaldehyde is an endogenous chemical compound that naturally occurs as a metabolite in humans and animals[183] and is also essential for the synthesis of amino acids, which are building blocks for important proteins in living creatures. Formaldehyde naturally appears in the troposphere as an intermediate oxidation product of hydrocarbons[184]. The latter are ultimately transformed into carbon monoxide, carbon dioxide, hydrogen and water. Finally, formaldehyde is naturally present in vegetables and is also formed in the early stages of the decomposition of plant residues in soil[184]. Given this, formaldehyde can be regarded as a chemical compound which is ubiquitous in the environment and which is additionally characterised by a very short half-life.

Regulation (EC) No. 1223/2009 of the European Parliament and of the Council on cosmetic products, the so-called 'Cosmetic Products Regulation'[185], allows the use of formaldehyde and selected formaldehyde releasers in cosmetics under specific conditions. According to this regulation, labelling of the finished cosmetic products is currently not required if the formaldehyde concentration does not exceed 500 ppm[185].

With regard to its mode of action, formaldehyde is an electrophilic substance and an alkylating agent (see also Table 1.3, Section 1). It can react with different nucleophilic elements of the cell, such as amino, amide and thiol groups, and is capable of inactivating enzymes via reaction with the amino acids of their constituent proteins. Finally, formaldehyde can affect essential biomolecules, such as proteins, RNA and DNA via cross-linking reactions[127, 131, 143].

According to the Art. 95 List[180], the active substance formaldehyde itself is not supported under the BPR for in-can preservation purposes (product type 6), but there are several applications in this regard for formaldehyde releasers under European biocides legislation. Formaldehyde releasers (FA-R) are chemicals which act as carrier systems for formaldehyde and are designed to release the inherently microbicidal active under use conditions after a time delay. In their undiluted form, they are quite stable but, in dilutions with water (e.g. in water-borne paints), they decompose more or less rapidly as a function of specific reaction kinetics and the molecular structure involved, as well as of further factors, such as pH, temperature and matrix properties[186].

Formaldehyde-releasing compounds vary substantially in physical appearance and chemical properties. They range from solid to liquid materials, from water-soluble to oil-soluble compounds, and have alkaline, neutral or slightly acidic properties. They enable formaldehyde to be used for applications which would otherwise be inaccessible to the active substance formaldehyde itself on account of its unfavourable properties[127]. As shown in Figure 2.3, formaldehyde releasers can be arranged into groups of O-formals and N-formals.

The bond strength of formaldehyde units is much greater in N-formals than in O-formals. Formaldehyde is therefore released from N-formals much more slowly than from

O-formals, and this leads to a considerably lower content of free formaldehyde in the corresponding formulations and subsequently in fewer undesirable side-effects, such as pungent odour or the need for classification and labelling. Figure 2.4 shows the situation for two examples of O-formals.

A set of active substances based on N-formal chemistry that is frequently encountered in coatings is illustrated in Figure 2.5.

Formaldehyde releasers are fast-acting bactericides/fungicides that are also efficacious against spores but whose effectivity spectrum against several fungi has some gaps. Thanks to their properties, they are very economical in use and are pH, temperature and redox stable. Formaldehyde itself is chemically reactive and so the active substance is consumed as it unfolds its microbicidal action. The typical dosage is within the range of 100 to 1000 ppm totally available formaldehyde content (see further). Figure 2.6 shows the stepwise release of formaldehyde, starting with the formaldehyde-releasing compound (ethylenedioxy)dimethanol (EDDM), in an industrial fluid.

1 mole (ethylenedioxy)dimethanol (EDDM) can theoretically liberate a maximum of 2 moles formaldehyde; the equilibrium of this reaction lies to the right. The percentage of formaldehyde in the molecule can be calculated as follows:

Molecular weight of (ethylenedioxy)dimethanol = 122.12 g/mol
Molecular weight of formaldehyde = 30.03 g/mol
Percentage of formaldehyde in the molecule = 2 * 30.03/122.12 * 100 = 49.2 %
i.e. nearly 50 % of the molecular weight of EDDM is potentially available formaldehyde.

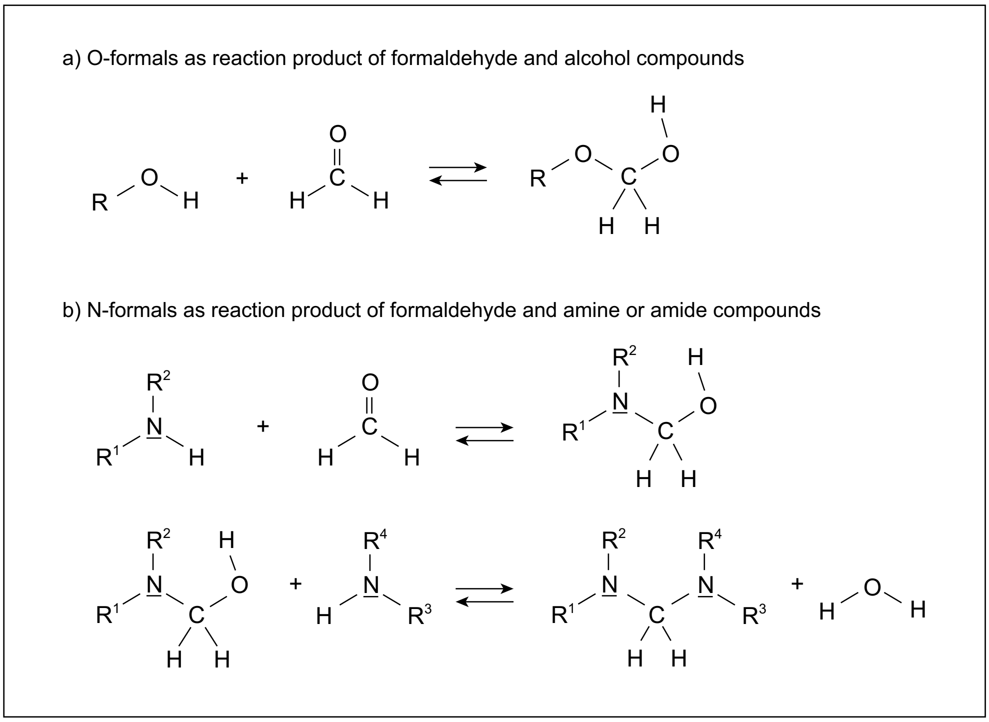

Figure 2.3: Schematic description of a) O-formal and b) N-formal constituents

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The following calculation shows how the maximum available formaldehyde content in an industrial fluid to be protected is determined when a microbicidal product containing a formaldehyde releaser is added for in-can protection purposes. This value should not be confused with the free formaldehyde content in such a formulation, as there is always an equilibrium between the initial releaser compound and the corresponding reaction products. Consequently, the **free formaldehyde** content in a water-borne formulation is often substan-

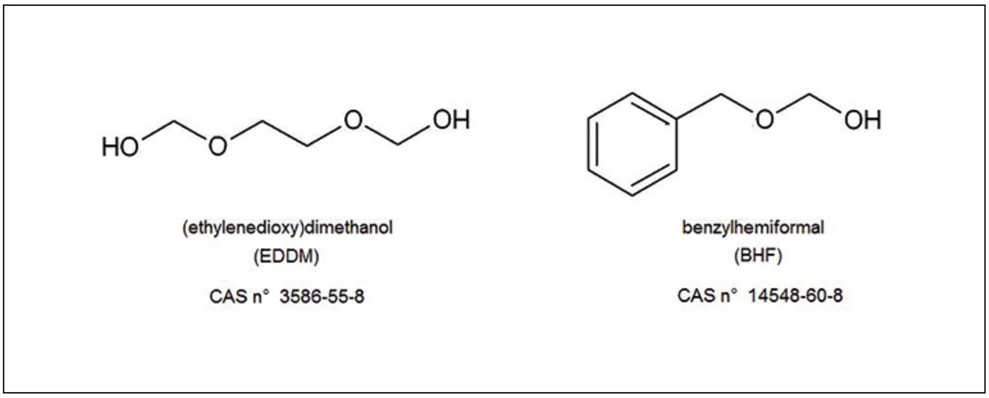

Figure 2.4: Examples of O-formals used in coatings (short forms in parentheses)

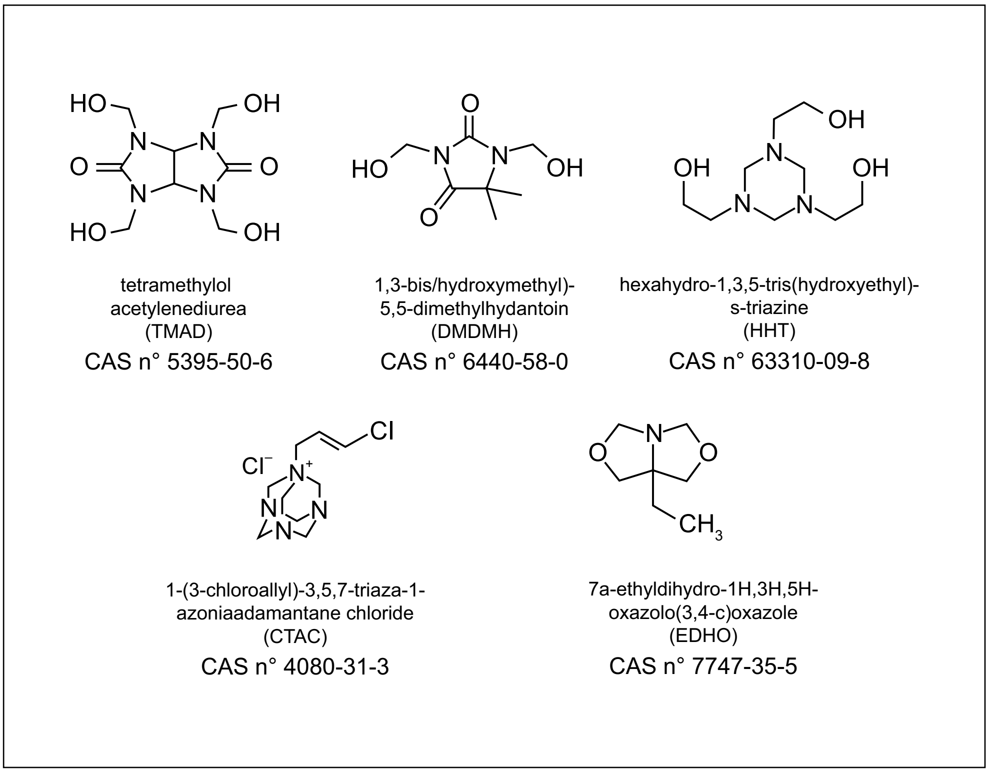

Figure 2.5: Examples of N-formals used in coatings (short forms in parentheses)