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Durability of Biocidal Agents in Facade Coatings and their Release Under Real Climatic Conditions

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ABSTRACT

Growth of algae and fungi is a well known phenomenon on exterior building surfaces. Modern façade coatings, especially coatings based on organic resins, therefore contain antimicrobial agents. The biocides are meant to inhibit or at least to delay microbiological growth significantly. Visible microbiological activity in the form of coloured spots is accepted as deficit in German prevailing law cases. Besides juristic aspects the leaching of biocidal ingredients from coatings may also have environmental effects and points out the necessity for product optimisation to minimize the impact of biocides on water and soil.

In a four year outdoor study the behaviour of façade coatings equipped with different biocidal agents was examined. Special test specimen based on external thermal insulation composite systems (ETICS) were designed and furnished with different façade coatings. The coatings contained four different mixtures of biocides. In sum, 20 different types were exposed to real climatic conditions at two locations in Germany. At defined times the biocide content of the coatings was analyzed by high performance liquid chromatography/tandem mass spectrometry (LC/MS-MS). Additionally, the run-off water from the specimen was collected and analyzed. In all coatings the concentrations of the active ingredients declined depending on the type of the ingredient and the matrix. In the run-off water the highest concentrations were found within the first three months of exposure. The results show clearly that the decrease of the antimicrobial ingredients in the coatings can not only be explained by leaching. Other ways of release are also possible, as well as the formation of transformation or degradation products.

KEYWORDS

Façade coatings, microbiological growth, antimicrobal agents, weathering-experiment, run-off water

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1 INTRODUCTION

The design of building façades shows a wide variety related to regional habits and changes permanently due to technological reasons and fashionable trends. For the choice of the coatings the substrate and the potential appearance have to be considered. This results in different requirements for the preservation of the coatings [Lindner 2005].

Modern coating materials show reduced amounts of heavy metals, many components are bio-degradable, and biogene ingredients are used. Because of this, microbiological growth can develop more easily than in former days. There are different antimicrobial agents applied in organic bound façade coatings. In general they are added to the coating as an appropriate formulation, i. g. as a powder, solution or dispersion. For the protection against microbiological growth in the wet state of a coating in-can preservatives are used. Dry film preservatives are applied for the protection of the finished coatings. Both types of conservatives should possess a broad spectrum of activity and a convenient cost effectiveness as well as being easy to handle. They must not interact with other ingredients of the coatings or influence the workability. Additionally, they must be stable at pH-values up to 13 which is important for example in silicate-based paints. Generally, in-can preservatives should have a high water solubility, i. e. a low partition coefficient pKow and a rapid way of action. In contrast, dry film preservatives should show low water solubility and high partition coefficients. Dry film preservatives have to be stable under the influence of weathering conditions and show a long lasting activity against microorganisms. Therefore, low volatility and water solubility are important aspects concerning the durability of the protection. Common dry film preservatives generally are organic molecules with molecular masses between 200 and 500 g/mol, water solubilities from 2 to 300 mg/L and partition coefficients from log 2,5 bis log 4 [Lindner 2000]. Normally combinations of several active ingredients are used because of the specific way of action of most biocides.

2 MATERIALS AND METHODS

In a four year outdoor study the behaviour of façade coatings equipped with different biocidal agents was examined. Two plasters with inorganic binders and three plasters with organic binders were selected. A lime cement plaster, a silicate plaster and three plasters with organic binders based on styrene acrylate, terpolymer and silicone resin were used. Dispersion type silicate paint, an emulsion paint (styrene acrylate based) and a silicon resin based paint were also examined. The renders were applied without a paint coating. The paints were applied on different biocide free plasters. All coatings were special, but realistic formulations. One of four different biocide combinations was added to every coating. Every mixture consisted of three active ingredients: terbutryne (CAS 886-50-0), OIT (CAS 26530-20-1) and a third ingredient which was either carbendazim (CAS 10605-21-7), DCOIT (CAS 64359-81-5), IPBC (CAS 55406-53-6) or zinc-pyrithione (CAS 13463-41-7) (Table 1). The biocide combinations were added in concentrations of 0.5 mass-% to the plasters and 1.0 mass-% to the paints.

Approximately 350 test specimen based on external thermal insulation composite systems (ETICS) were exposed to real climatic conditions at two locations in Germany, most of them in Holzkirchen, located approx. 25 km south of Munich in Upper Bavaria on a plateau at an altitude of 680 m above sea level. The climate is characterized by three main factors: at foehn conditions, when warm winds from the south blow over the Alps, temperature differences within one day may reach up to 35 K. Radiation at night causes surfaces temperatures to fall below the dew point frequently. Especially in summer heavy thunderstorms with intense rainfalls occurs which lead to high exposure to driving rain.

At defined times the biocide content of the coatings was analyzed by high performance liquid chromatography/tandem mass spectrometry (LC/MS-MS). Additionally, the run-off water from the specimen was collected and analysed.

Table 1. Properties of the biocides used in the study.

active ingredient (CAS-numberr)	*substance category*	*properties*
IPBC (55406-53-6)	carbamate	broad spectrum of activity, fungicide, unstable under UV-radiation, high pH-values and presence of catalysts (metalls like Co)
carbendazime (10605-21-7)	benzimidazole-derivative	fungicide, high activity (but not against *Alternaria*), chemically stable
OIT (26530-20-1)	isothiazolinone	broad spectrum of activity, high water solubility and mobility
DCOIT (64359-81-5)	isothiazolinone	broad spectrum of activity, high volatility, unstable, hydrolysis at pH-values > 8,5
zinc-pyrithione (13463-41-7)	pyridine-derivative	very broad spectrum of activity, fungicide and algicide, in alkaline systems possiblity of complexation with calcium, possibility of discolouration with other metalls, hydrolysis at pH-values > 9
terbutryne (886-50-0)	triazine-derivative	algicide, high activity, sublimation possible, dependent on the microorganism partly high concentrations necessary, otherwise metabolizable and possibilty of fomation of resistances

3 RESULTS

3.1 Biocide contents in coatings

The active ingredients show strong differences in their durability within the examined façade coatings. Depending on the type of the coating, recoveries can be widely spread (Figure 1). The upper limit of the range corresponds to the highest found recovery, the lower limit to the minimal found recovery within all examined coatings. It becomes obvious that the biggest loss of active ingredients takes place within the first year of exposition.

The biocide carbendazime possesses a high durability in all coatings. In some coatings there is no decrease of the content detectable within the observation period. Partly concentrations above 100 % are found. This probably is due to migration within the coating. Terbutryne also shows high recoveries. In the worst case observed, the terbutryne content drops below the analytical detection limit after three years. For IPBC, OIT, DCOIT and zinc-pyrithione this is the case already after one year. IPBC and OIT are very similar concerning their durability. Recoveries of DCOIT are little lower. After one year, Zinc-pyrithione can be found only in one coating with a very low recovery.

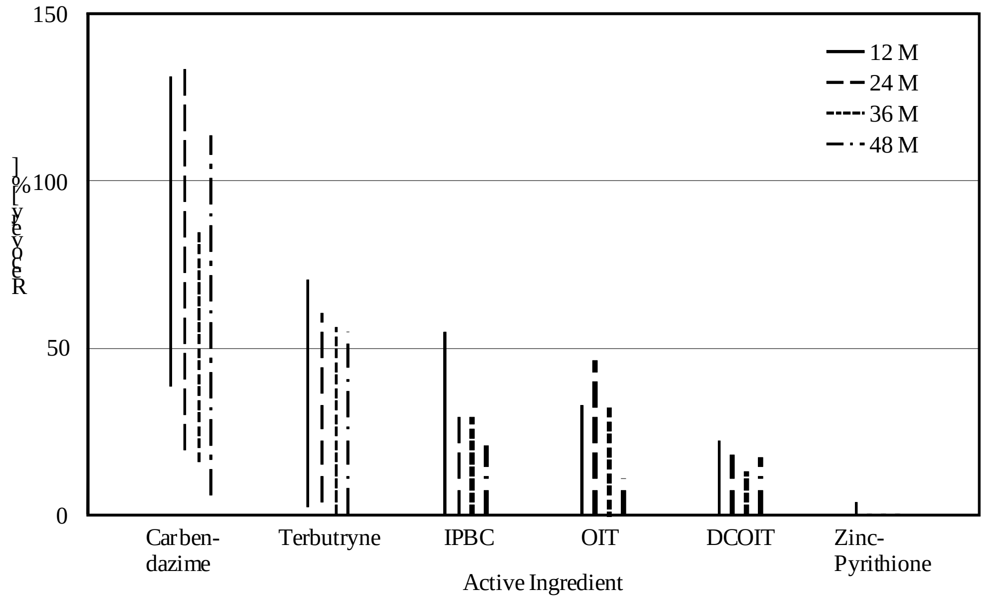

Figure 1. Durability of the biocides in the coatings. Ranges of recoveries within all examined coatings after 12, 24, 36 and 48 months of exposition.

3.2 Biocide contents in run-off water

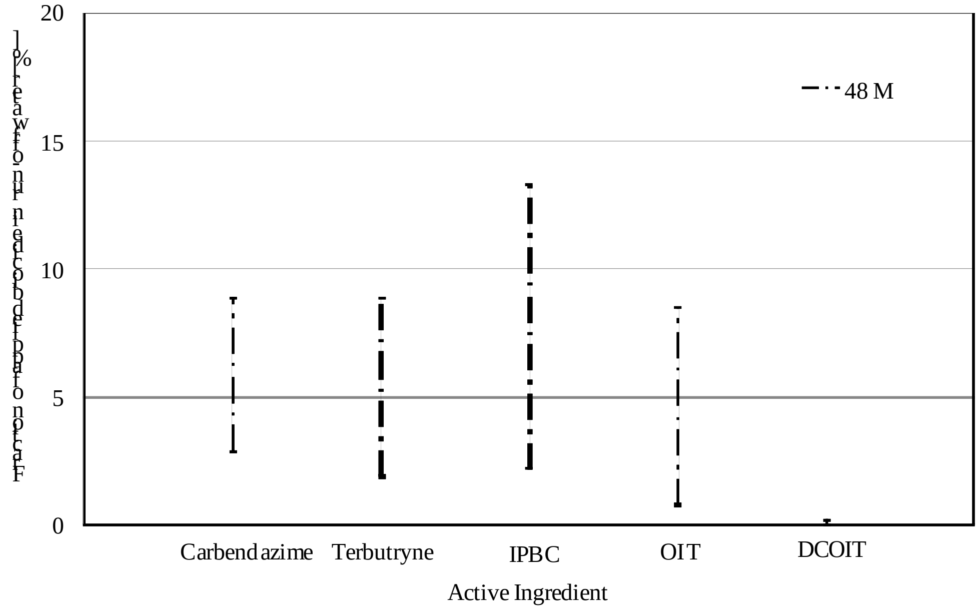

Figure 2. Accumulated amounts of the biocides originally applied in the coatings which is found in run-off water within 48 months of exposition. Ranges of recoveries over all examined coatings.

The active ingredients may be released from the coatings because of the influence of driving rain. In this context mainly the first months of the exposition are relevant. The highest contents of biocides (OIT, IPBC, DCOIT, terbutryne) in run-off water are measured within three months after application of the coatings. In the following, no changes in the total amounts are observed. Carbendazime is washed off significantly for six months and shows permanently small release in the ongoing time.

In sum there were fractions between maximum 0.2 % (DCOIT released from terpolymer based plaster) and 13.3 % (IPBC released from silicone resin based paint applied on lime cement plaster) of the originally used biocides released by rain water after four years (Figure 2).
Analysis of zinc-pyrithione in water is not conducted due to its high reactivity and its short half-life.

3.3 Biocide content in the coating vs. content in run-off water

Considering the applied amounts of biocides, the contents in the coating and the release by run-off water partly very high gaps of balance appear (Figure 3). In the case of carbendazime the largest range of a possible gap is found. In some coatings like the styrene acrylate based plaster or the silicate plaster no reduction of the carbendazime content is observable whithin four years, at the same time only small amounts are measured in the run-off water. This results in an equalized balance (gap of balance 0 %). In the lime cement plaster the carbendazime content has decreased down to 6 % after four years. At the same time no significant release by run-off water could be measured. This leads to a gap of balance of 85 %. For terbutryne, the gap of balance lies between 46 % and 95 %, IPBC shows a gap of balance between 75 % and 93 %. The isothiazolinones OIT and DCOIT show gaps of 83 % to 99 % and 100 %, respectively. This means that in some cases there is no biocide measurable after four years and at the same time also is not released with water.

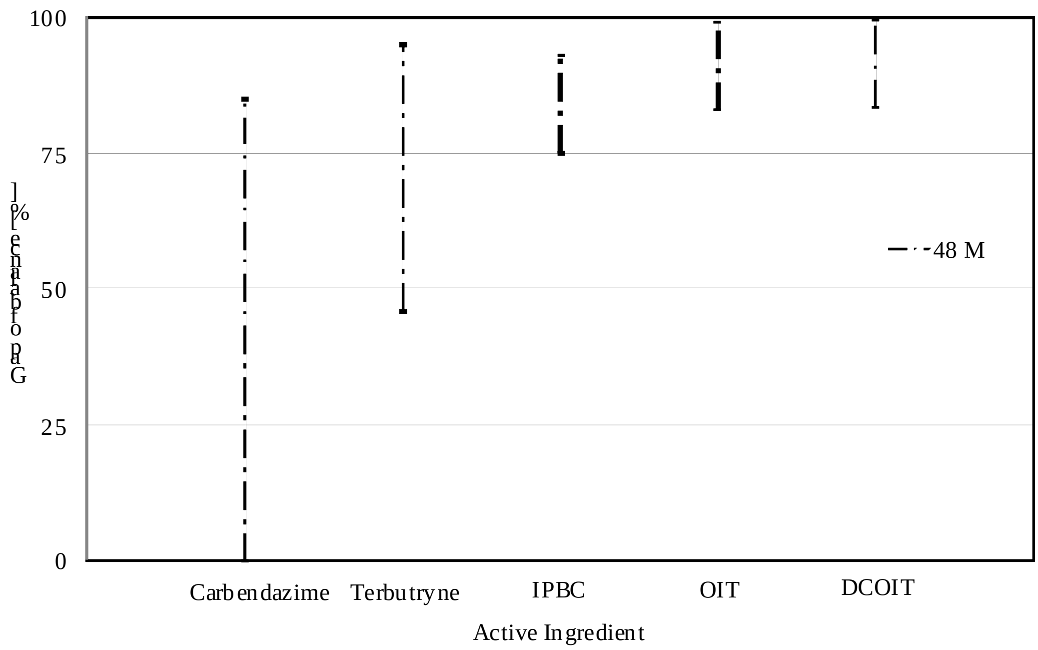

Figure 3. Gap of balance of the biocides in the coatings. Ranges within all examined coatings after 48 months of exposition.

4 CONCLUSION

The biocides show strong differences concerning their durability in façade coatings. In relation to the type of the coating, the recovery rates spread over a wide range. Carbendazim is very consistent in the coatings, followed by terbutryne. IPBC and OIT are less durable but they show recovery rates higher than those of DCOIT. After one year zinc-pyrithione can be detected only in one coating (terpolymer based plaster), in the following years the ingredient can not be determined any more.

The type of the binder has strong influence on the durability of the biocide. Carbendazim is very consistent in all coatings apart from the lime cement plaster. The other active ingredients show high contents in the styrene acrylate and the terpolymer based plaster, followed by the silicate plaster. For the silicon resin plaster the recovery rates are significantly lower. The lowest recovery rates are found for the lime cement plaster.

The substrate influences the durability of the biocides in the applied paint. Within the paints the emulsion paint applied on styrene acrylate based plaster shows the highest recovery rates. Applied on lime cement plaster, the same paint has significantly lower recovery rates. The recovery rates of the silicon resin base paints and the dispersion type silicate paint are even lower.

The active ingredients of façade coatings can be released by run-off water. The highest concentrations of biocides in water are found within the first six months of weathering. Only carbendazime shows a continued release of small percentages during the entire observation time of four years. The minimum cumulated fraction of biocide after four years is found for DCOIT with 0.2 %, the maximum for IPBC with 13.3 %.

The results show that the decrease of the antimicrobial ingredients in the coatings can not only be explained by leaching. In some cases there exist gaps of balance of over 90 %, meaning that over 90 % of the originally applied biocides are neither found in the coating nor in the run-off water. This becomes especially significant for the active ingredients OIT and DCOIT plus the silicon resin plaster. This means that for the decrease in the coatings, additional mechanisms have to be taken into account. On the one hand, other ways of release like sublimation are also possible, as well as migration of ingredients in deeper layers of the facades. On the other hand, the formation of transformation or degradation products under the influence of high temperatures, UV-radiation, oxidation or hydrolysis in the complex matrix of a coating has to be considered. Mechanisms like these may lead to potent metabolits which possess antimicrobial activity themselves, so that the coating may be protected against microorganism in spite of the decrease of the parent biocide. The biocide content is not alone decisive for the susceptibility to development of biological growth on a coating.

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