Coating Preservation - Biocide Issues

Dr. Houshang Kheradmand (ERMA Director)

Abstract:

Coatings contaminated products could have serious impact on company reputation and product quality.

The preservation of aqueous coating materials is increasingly challenging for industries driven to:

- Produce more sustainable and environmentally friendly products
- Participate in markets with increased restrictions on preservatives

Micro-organisms can adapt to a range of extreme environments and when conditions are optimal, they can grow. Contamination occurs in most cases from the environment or from an already contaminated substrate or product. Many waterborne systems such as paints are susceptible to microbiological contamination and require the inclusion of an in-can preservative to provide protection during manufacture and an appropriate shelf life and film protection after application.

Coatings product preservation becomes more and more difficult due to the increasing restrictions such as BPR, CLP, Ecolabels, Exposure limitations [(1)].

Strong R&D organization is necessary for innovative solutions and to demonstrate the benefits of new and innovated solutions during product life cycle via Life Cycle Assessment methodology.

Introduction

Microorganisms play an essential part in human health, wealth and happiness. The world as we know it cannot function without microorganisms. Every human and every animal hosts countless millions of bacteria vital to digestion and nutrition, all soil fertility and natural recycling of materials depends on microorganisms and much of the air we breathe is regulated by microbial action. Many foods and drinks and medicines need microorganisms in their production.

Almost all manufactured goods and raw materials can be attacked by microorganisms and a wide variety of wastes can be treated and re-cycled by using microorganisms. Microorganisms are ubiquitous and all pervasive, intimately bound up with our very existence, but the knowledge of the general public tends to be restricted to association with disease, decay - and food production**!**

Each year tens of thousands of coating types are manufactured and used worldwide (estimated global production of 30 million tons in 2009). Their main functions are to protect, decorate and stabilise the surfaces to which they are applied. They are composed of four main components: the binder, pigments and extenders, solvents, including water, and thickeners, with other ingredients making up less than 5% of the product. Paints and coatings are susceptible to bacterial and fungal growth when in the liquid state but prone to colonisation, especially by fungi, algae and cyanobacteria after application; components such as residual thickening agents are the most abundant carbon source [(2)].

Biocides Regulation

The regulatory basis for European biocides evaluation changed from September 1, 2013 and the Biocidal Products Regulation BPR (528/2012) replaced the Biocidal Products Directive. This opened new opportunities such as a union authorization for biocidal products but also brought changes in the formal authorization process and the legal basis. Moreover, the evaluation criteria became stronger and the exclusion of products showing the properties like CMR (Carcinogenic, Mutagenic or Toxic for Reproduction) PBT (persistent, bioaccumulative and Toxic) or vPvB (very persistent and very bioaccumulative) is foreseen.

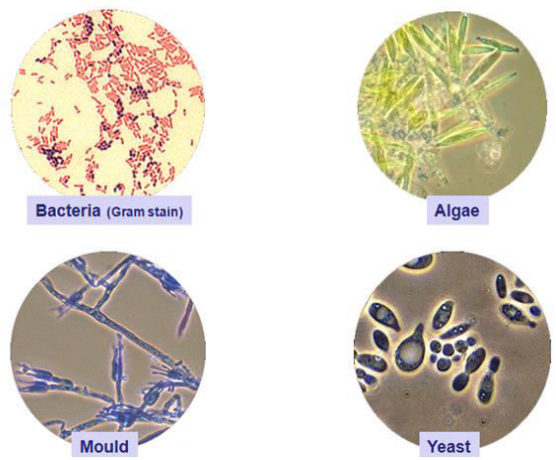
The Biocidal Products Regulation (BPR) aims to improve the functioning of the biocidal products market in the EU, while ensuring a high level of protection for man and the environment. To this end detailed risk assessments need at present a better knowledge on exposure estimation,

improved methods of risk management and in depth efficacy testing. In addition, the assessment of mixture toxicity is a new challenge for product authorizations.

Microorganisms:

The three main classes of microorganisms that can colonize paints and surface coatings or contaminate surfaces in general are:

- Fungi
- Algae
- Bacteria



Typical aspect under a microscope (x1000)

Fig 1: Example of Microorganisms

All microorganisms need both water and nutrients and some, like algae, also need sunlight.

Microorganisms have the potential to grow in liquid paint before it is applied and also on paint films after application. Paint manufacturers may use biocides in their products in order to prevent these organisms developing. The biocides that are used for this purpose can be divided into three main classes:

- In-can biocides designed to prevent the growth of microorganisms during storage.
- Film biocides designed to protect applied paint films by preventing microbial growth.
- Film biocides designed to impart antimicrobial activity to the coating (to produce a hygienic or antimicrobial coating).

Biocides are also added to other materials, either to preserve it (for example wood), or to provide it with antimicrobial properties (for example certain plastics).

These biocides can be further sub-divided into those which have anti-fungal, anti-algal and anti-bacterial properties, namely fungicides, algicides and bactericides.

Waterborne Coatings & Micro-organisms adaptation

Water-based industrial products (polymers, dispersions, emulsions, suspensions, glues, paints, raw materials, slurries, surfactants, etc.) are susceptible to bio-deteriorations.
In this presentation we will develop the sources of contamination and propose the best practical approach for efficient preservation and minimizing trends for marketed products.

The use of chemical preservatives (biocides) is the sustainable answer to the problem of microbial contamination of water based products. Briggs (1980) recommended an integrated approach of prevention and treatment, consisting of three main parts [(3)]:

- Identification and treatment of contamination sources (water, raw materials, inherent production plant infection, poor production hygiene)
- Improved plant hygiene/cleanliness including frequent and thorough cleaning
- Use of an effective broad activity spectrum biocide

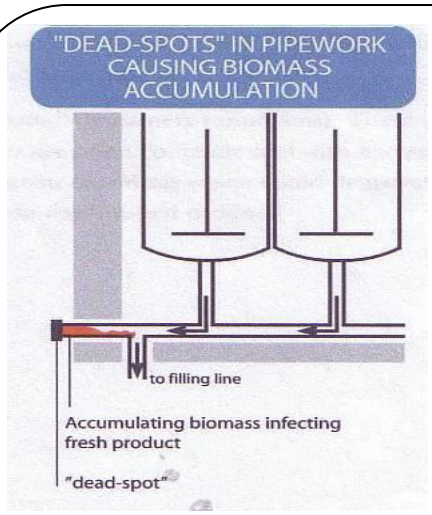


Fig 2: Example of contamination

Impacts of a product contamination

As noted the water-based paint is susceptible to bacterial contamination due to its aqueous nature and organic components which provide the ideal environment for many bacteria to grow and multiply. The presence of bacteria can interfere with the final paint properties and change its physical and chemical properties resulting in a spoilt product.

Paint is one of the essential items of construction materials in modern times, whether it is meant for residential purposes, or industrial applications. It is obvious thought that paint-life, as dry film, has to be as long as possible. The technology has advanced many folds in recent years to achieve this aim, with many new advances in binder systems available for innovative formulation. The efforts focus to improve better chemical properties of formulated paints, so that paint films would give extended life to the satisfaction the users including for microbial stability of paints, since any such growth on painted surface is known to deteriorate the functional usage of paints.

A contaminated batch of paint could create serious economic consequences for paint manufacturers given the cost of the raw materials, production effort and man hours wasted, as well as the logistics of product recall. Perhaps even more importantly a contaminated batch has a detrimental effect on the brand's reputation and customer confidence in the paint manufacturer. Bacterial contamination can occur during the paint manufacturing process but can also develop during storage after canning. The addition of biocides (agents that kill bacteria) is the only effective way to prevent the proliferation of bacteria and maintain an environment hostile to bacterial growth to ensure a satisfactory shelf life after canning. It is therefore essential to ensure that biocides are effective and present in the right concentrations in critical situation as vast majority of wet-state biocides used in paints are based on only five main active agents and this restricted numbers are the result of regulatory, health and safety restrictions.

The selection of an appropriate in-can preservative is an important factor in the development of a paint formulation and failure to prevent spoilage due to microbiological growth can result in the development of foul odours, discoloration, loss of structure and the generation of gasses that might distort / damage the final packaging. The protection provided includes the interval during manufacture as well as storage both within the plant and prior to sale. The protection should be sufficient to provide a shelf life suitable for the product and may be extended to allow storage of part-used containers by the end user.

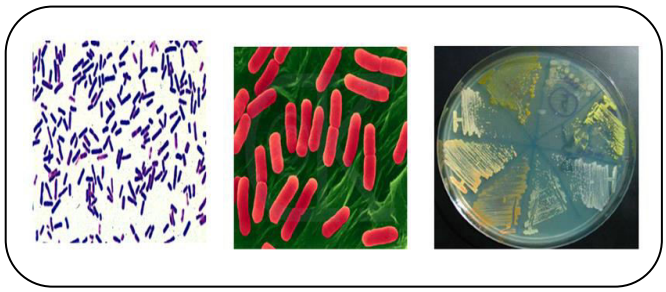


Fig 3: Bacteria -A common cause of spoilage

Fig 4: Example of contaminated paint

Biocide package development

The worldwide annual cost of the biodeterioration of susceptible non food products was estimated as $4 billion in 1973, revised in 2009 to $40 billion per annum (Allsopp).

There are many techniques used to preserve materials such as:

- They may be Physical - such as good building construction,
- Chemical (examples: biocides addition), this approach to preservation is by far the most

common, with about 1000 active substances being identified as having biocidal properties. However, the European regulations on Biocidal Products (BPR) requires a significant ecotoxicology /toxicology and efficacy package and it is likely that when fully implemented there will be very limited authorized substances (only 98 Substance dossiers have been reviewed and approved as per May 27th 2015.

- Biological (enzymes addition).

With the introduction of regulations to limit Volatile Organic Compounds (VOC's), the use of organic solvents has been significantly reduced and most have been replaced by water. One consequence of this change is a greater requirement for wet state preservation to protect these now susceptible materials [(3)].

The product protection from attack by microorganisms is an area of the coatings formulation that is often not well understood. Contamination of coatings such as paint, by microbial growth in it, in either the wet state or on dried film can destroy the functions of the paint, leading to both aesthetic and physical degradation of the painted surface.

As noted the types of microbial attack that are of concern to the paint industry are bacterial, fungal and algal.

- Bacteria, which are small, single-celled organisms, grow readily in unpreserved water-based systems.

- Fungi are unicellular or filamentous organisms that are devoid of chlorophyll and attack the dry paint film.
- Algae, are unicellular or filamentous organisms that require light.

A can of waterborne paint is an ideal environment for bacteria to grow in due to the available nutrient sources (surfactants, thickeners, de-foamers, minerals etc.), available water supply, adequate oxygen supply, and suitable pH (3.0–10.0).
Product bacterial contamination specially "in the can," may originate from a number of sources and may be influenced by several factors, including the formulation and plant design and overall manufacturing cleanliness.
The largest source for carrying the contamination further is water, particularly recycled water, or stored water.

Air, specifically in the paint factory, will contain a variety of microorganisms on dust. This is particularly true in the case of dusty environments where starches, cellulosic thickeners, pigment powders and fillers are used. The typical plant environment is not sterile.

Accumulation of dried product, waste raw materials, and general refuse in the production and storage areas will act as a reservoir for microorganisms that may later cause contamination.
Only waterborne coatings are susceptible to bacterial contamination in the can, both water- and solvent borne coatings are prone to attack on the dry film by fungi and algae, in latter case after the paint has weathered to some extent.
Once a waterborne paint has been contaminated, its physical and chemical properties change. When introduced into paint, microorganisms start to multiply and attack organic components in the paint
system. One of the first signs of microbial activity is viscosity loss, which is caused by microorganisms releasing enzymes that can destroy traditional cellulosic thickeners. These enzymes, which are capable of functioning independently of the cells that produce them, are large proteinaceous molecules that attack the polymer chains of the thickener and break them down into [(4)]

There is a need to protect the products against of fungi and algae growth typically when a freshly painted white façade becomes grey, black, green or orange after only a short time. In addition to the undesirable colour changes, damage to the substrate also occurs due to the increase in water uptake. Furthermore, adhesion loss of the paint and plaster (blistering and flaking) can occur, as well as partial damage to masonry, concrete, sandy limestone, fibrous cement, concrete roofing slabs and joints giving rise to failure of the coating. While the initial pH of cementitious substrates or with silicate- based coatings may be too high to

prevent initial colonisation, weathering and erosion of the coating with time will allow fungi and algae to grow [5].

Fig 5: Example of contaminated materials

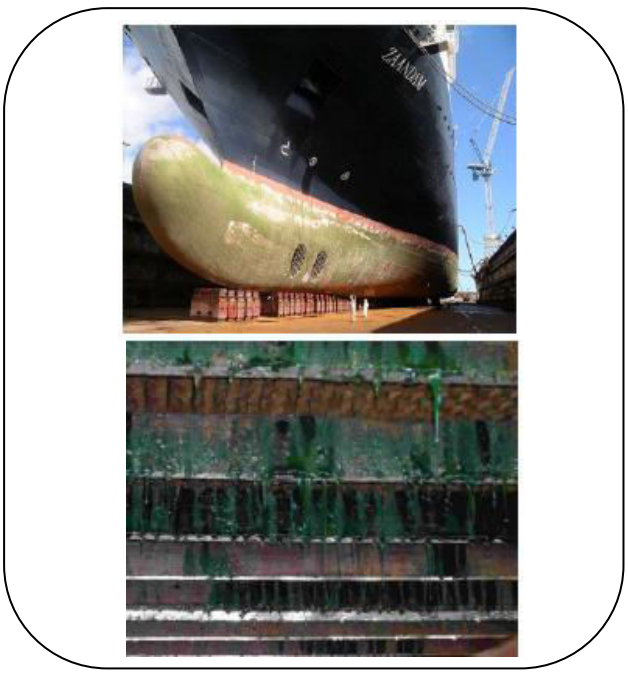


Fig 6a: Example of impacts on materials

The first step in developing an optimum preservative package is selecting an appropriate biocide active ingredient and assessing its stability in the coatings product. Once biocide stability has been established then a preservative efficacy test (PET), or challenge study, may be used to determine the efficacy of a preservative package versus an unpreserved blank.

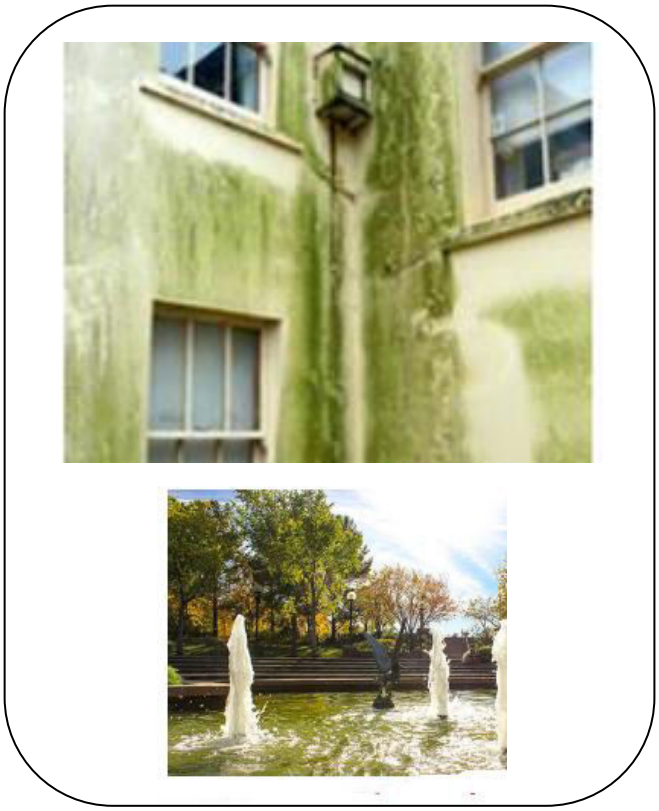


Fig 6b: Example of impacts on materials

Product labelling:

Labelling is an important and effective communication tool, which should be viewed as an integral part of the marketing of a product and is right way to share the information from raw material suppliers through to end-users.

It's also vital that the industry is aware of regulatory developments, which affect what should be displayed on labels and what adaptations can be made to formulations, which take into account these changing requirements.

As an example with the second adaptation of the CLP Regulation 1272/2008 to technical and scientific progress (Commission Regulation 286/2011), the conditions for labelling of mixtures such as paint containing sensitizing substances are changing.

The regulation is designed to address the needs of that part of the population that has developed skin and respiratory allergies, and are more sensitive to subsequent exposure.

- The levels for elicitation are lower than the level for sensitization.

- A big part of biocides used for water borne products preservation are classified as sensitizer.
- Product should have specific label “EU H208” from 0.1% of normal substance classification.

Conclusion:

Micro-organisms can adapt to a range of extreme environments and when conditions are optimal, they can profile. Contamination occurs in most cases from the environment or from an already contaminated substrate or product.

Many waterborne systems such as paints are susceptible to microbiological contamination and spoilage and require the inclusion of an in-can preservative to provide protection during manufacture and an appropriate shelf life and film protection after application. Biocidal active ingredients (ai’s) possess a range of both physicochemical and biological properties which make them more or less suitable for certain formulation types and manufacturing processes. From the consumers view point, it is to maintain the aesthetic aspects of the coating, thereby, stopping the premature discolouration of painted facades and surfaces.

References

1. H.Kheradmand “To label or not label” PPCJ August 2014
2. J.GillattK. “An Atlas of Biodeterioration –P27” 2013
3. Briggs, MA. “Emulsion Paint Preservation - Factory Practice and Hygiene”,Paint Research Association Technical Report TRi 81 78, May 1980.
4. Dr.Pathare “Saving the Paints from Constant Threat of Microbial Attack” – Melzer 2009
5. E.Yvon, P.Wood “Sustainable and novel microbial control dry film concept” PPCJ-August 2014