# Handbook of Coatings Additives
## Second Edition

edited by
**John J. Florio**
**Daniel J. Miller**
*King Industries, Inc.*
*Norwalk, Connecticut, U.S.A.*

MARCEL DEKKER, INC. NEW YORK • BASEL

**Library of Congress Cataloging-in-Publication Data**
A catalog record for this book is available from the Library of Congress.

**ISBN: 0-8247-5626-6**

This book is printed on acid-free paper.

**Headquarters**
Marcel Dekker, Inc., 270 Madison Avenue, New York, NY 10016, U.S.A.
tel: 212-696-9000; fax: 212-685-4540

**Distribution and Customer Service**
Marcel Dekker, Inc., Cimarron Road, Monticello, New York 12701, U.S.A.
tel: 800-228-1160; fax: 845-796-1772

**Eastern Hemisphere Distribution**
Marcel Dekker AG, Hutgasse 4, Postfach 812, CH-4001 Basel, Switzerland
tel: 41-61-260-6300; fax: 41-61-260-6333

**World Wide Web**
http://www.dekker.com

The publisher offers discounts on this book when ordered in bulk quantities. For more information, write to Special Sales/Professional Marketing at the headquarters address above.



Current printing (last digit):

10 9 8 7 6 5 4 3 2 1

**PRINTED IN THE UNITED STATES OF AMERICA**

# Contents

# 8

# Biocides: Wet State and Dry Film

**Paul S. Kappock**
Arch Chemicals, Inc., Cheshire, Connecticut, U.S.A.

## 8.1 INTRODUCTION

### 8.1.1 Historical Perspective

Microbes have been defacing paints films ever since the first binders and pigments were mixed and applied as crude protective coatings. Up until and into the 20th century, solvent-borne coatings utilizing seed oils for binders were used almost exclusively. The most common seed oil used was linseed. All that is needed for the growth of fungus on paint films is sufficient moisture. This is supplied by precipitation and condensation. The paint surface provides the necessary nutrients. These nutrients are provided by the organic materials that compose the paint film and/or are provided by airborne organic debris. Natural oil binders are low-molecular-weight materials that are easily metabolized by fungi. With the development of alkyds, higher-molecular-weight binders resulted in paint films with more resistance to the growth of fungi, although the long oil alkyds that are used for architectural exterior paints are still quite susceptible. Generally, materials with molecular weights of less than 600 are readily metabolized. Higher-molecular-weight organic materials are broken down by enzymes and acids released by the micro-organisms to smaller units that can then be metabolized by the organism.

These early coatings received some protection against the growth of fungus from metallic pigments that contained zinc, mercury (cinnabar, vermilion), or chromium (green cinnabar). Later, organometallic materials such as phenyl mercuric oleate (PMO), phenyl mercuric acetate (PMA) and TBTO (bis-tributyltin oxide) were used with greater success, especially with the mecurials. However, the mercury compounds were eventually forbidden for use in paints by the U.S. EPA (Environmental Protection Agency) because of toxicity, ecotoxicity, and environmental persistence. TBTO is no longer being used in antifoulant paints because of ecotoxicity and environmental persistence, but it is still used in some wood preservative preparations and coatings. Today, there are a number of effective products on the market for preserving dry paint films. These will be discussed in a later section.

High-quality waterborne coatings did not become available until the development of styrene butadiene emulsions during the 1940s. With the growing volume of waterborne coatings came a greater demand for preservation of the paint in the wet state. The abundant water available in the wet state, along with the low-molecular-weight organic additives, presents an ideal environment for the growth of bacteria. Fungi (molds and yeasts) can also grow in paints in the wet state, but it is mostly the bacteria of the genus *Pseudomonas* and *Enterobacter* that cause the most damage. Bacteria grow much faster than fungi under ideal conditions, doubling in population as quickly as every 20 min.

Phenyl mercuric acetate was widely used for wet state preservation in the United States until banned by the EPA for use in paints. PMA would function as both a wet-state and dry-film preservative. Formaldehyde-releasing compounds replaced PMA for the most part and are still widely used in paints. Because formaldehyde is recognized as a carcinogen and a VOC (volatile organic compound), there has been a move away from formaldehyde-releasing bactericides and toward isothiazalones. The isothiazalones have their own problems, such as being sensitizers, poor stability in paints, and most isothiazalones are sensitive to amines and sulfides. Among the simplest formaldehyde-releasing compounds are the condensates of amines and formaldehyde. One of the first to be synthesized was the condensate of ammonia and formaldehyde in the 1800s to yield hexamethylene tetramine (HTA). HTA and similar amine formaldehyde condensates will go back to the starting materials ammonia and formaldehyde under acidic conditions. In practice, acidic conditions are encountered in alkaline paints in the localized environment of bacteria that will release acidic metabolites. The released formaldehyde kills the bacteria. The pH dependency of formaldehyde release can be eliminated by quaternizing HTA [1]. Formaldehyde release then becomes pH independent.

These early bactericides were originally developed to be used by the medical profession as disinfectants. However, some like 1-(3-chloroallyl)-2,5,7-triaza-1-azoniaadmantane chloride are widely used in preserving aqueous coatings today. The effectiveness of formaldehyde-releasing bactericides can generally be determined by the amount of formaldehyde that can be measured by the Tannenbaum method [2]. This method uses the reaction of dilute aqueous bactericide solutions with phenylhydrazine and potassium hexacyanoferrate.

## 8.1.2 Consequences of Biodeterioration

Microbes were the first forms of life on Earth. Their presence goes back about three and a half billion years. It is safe to say they will be around for many more years. Microbes exist practically everywhere and their destructive activity is basically unavoidable, but can be inhibited. Using microbicides can be viewed as protecting the environment. Allowing materials to last longer prevents them from being disposed of and also uses less electrical power and raw materials to replace the degraded objects. If uncontrolled, microbes will contaminate coatings in the dry and wet states, leading to degradation of the wet paint and destruction of the paint film. Not having to dispose of spoiled paints and not having to repaint objects as often contributes to protection of the environment.

Understanding some of the basic biocide terminology is important for understanding the discussions that will follow in this chapter.

- Biocide: any compound that is capable of killing living organisms.
- Microbicide: any compound capable of killing microbes.
- Bactericide: any compound that kills bacteria.
- Fungicide: any compound that kills fungi.
- Algaecide: any compound that kills algae.
- Microbistat: any compound that inhibits the growth of microorganisms without necessarily killing the organism.
- Microbicides at very low concentrations could also function as microbistats.

There are many microbicides that are available for many different industries, but only a limited number are suitable for use in coatings. Microbicides that are used commercially are targeted to the organisms that cause the damage with minimal impact on higher organisms. The microbes of interest to the coatings industry are bacteria, fungi (mold, mildew), yeasts (unicellular fungi), and algae.

Bacteria are the principle degraders of paint in the wet state. Fungi and yeasts also are capable, but are usually much less of a problem. Many of the organic materials in paints can serve as nutrients. Some of the indications of contaminated paint include foul odor, drop in pH and viscosity, generation of gas, color changes, can corrosion, lumping and stringiness of the latex, and gelation of the paint. Bacteria can even degrade and detoxify the dry-film preservative added to the paint to protect against the growth of mildew on the paint film. The production of enzymes by the organisms makes it almost impossible to recover spoiled paint. Even if a bactericide is added and kills all the bacteria in the paint, the enzymes still remain and can break down materials in the paint. Springle studied the effects of the enzyme cellulase on the cellulosic thickeners common in aqueous paints [3]. Concentrations as low as 0.00001 mol/mm can lead to degradation of the thickener.

The cost of damaged paints can be quite high when all the incidentals are taken in to account. In addition to the cost of the paint itself, there is the cost of returning the spoiled paint to the manufacturer, the cost of disposal, lost profit, loss of future sales because of diminished reputation, and the legal costs of claims of illnesses caused by individuals exposed to the spoiled paint. The costs to the manufacturer of spoiled paint could be substantial, running as high as $200.00 per gallon or more, when all these consequences are considered.

Preservation of the dry paint film against microbial growth is also necessary for most exterior and some interior applications. In the home, bathrooms, kitchens, and basements are often damp enough to support the growth of mildew on paint films. In industry, dairies, breweries, bakeries, and food processing need to have mold-resistant walls for hygienic reasons. These even coatings on the market for hospitals that claim to resist the growth of mildew and bacteria on the dry film.

Hygienic issues aside, most dry-film preservative use is in outdoor applications for esthetic reasons and extending the useful life of the coating. Mildew and algae grow on paint films when sufficient moisture is present. Nutrients are supplied by organic materials in the paint film and also by airborne organic debris that has settled on the film. Some types of fungus, such as *Aureobasidium pullulans*, can grow under fairly harsh conditions, but algae generally require more moisture than fungi. Both will contribute to degradation of the paint film. The fungi produce acidic metabolites and enzymes that actively degrade the paint film. Algae cause problems indirectly by keeping the paint film moist. Loss of adhesion, decay, or corrosion of the substrate, allergic responses, and release of toxic gasses (mycotoxins) have been attributed to fungal growth on and in buildings.

## 8.1.3 Current Trends

### 8.1.3.1 Government Regulations

Much of the drive behind current trends affecting the biocidal products that are available is government regulations. There are several major initiatives that will be slowly adopted over the next decade. In the United States, the regulation of biocides for the coatings industry falls under the jurisdiction of the EPA. Congress gave the EPA responsibility under the Federal Insecticide Fungicide and Rodenticide Act (FIFRA). All bactericides, fungicides, and algaecides used in coatings are classified under FIFRA as pesticides. In 1988, the congress passed an amendment to FIFRA that subjected all pesticides registered before 1984 to data recall. Congress realized that the data used to assess the effects of pesticide exposure to humans and the environment had become outdated in some cases. Newer methods of detection and assessment were developed that would shed a clearer light on the hazards of using pesticides. The EPA grouped all registered pesticides into 600 cases. These 600 cases comprised ~1150 active compounds and 45,000 formulated products. With so many products to review, along with many other EPA responsibilities, it is likely that the process will take a very long time. The first data recall procedure did not occur until 2001 and is not expected to be completed for several years.

The type of data required for supporting registration varies by product and intended use patterns, toxicity, availability to the environment, rate of degradation in the environment, and composition of degradants. The inevitable consequence of the data recall would be higher costs and less products to choose from.

In Europe, the unification of the economies to form the European Union has led to the Biocides Product Directive (BPD). It was realized that regulation of pesticides could be a trade barrier and that to avoid the barrier, a unified set of regulations was needed. The whole process is expected to take over a decade to be fully implemented. In Europe, blends of biocides are commonly used in coatings. The practice is not common in the United States due to the need to have each blend registered with the EPA. In Europe, only the actives needed to be registered and could be used in blends without the blends themselves needing registration. That will change with the BPD. With the high cost of registration and uncertain future, some of the European blenders chose to be acquired by biocide producers in the United States. A few of the common European blends for coatings have been registered in the United States and are available commercially. Development of new blends for the US market is the focus of product development by suppliers looking for new opportunities. A few have been registered and more are likely to become available.

Another major regulatory initiative is the international ban of tin compounds in antifoulant paints. The International Maritime Organization (IMO) passed the resolution and was approved by a diplomatic conference in 2001. When countries that account for 25% of the world's ship tonnage ratify the treaty, it will become international law. The treaty provides for banning the application of tin-containing paints by 2003 and banning the presence of tin-containing paints on ships hulls by 2008. Tin compounds such as tributyl tinoxide (TBTO) and tin copolymers are used in antifoulant paints to control the growth of algae. Tin compounds are not very effective against hard fouling such as barnacles. Copper, as cuprous oxide, is used to control hard fouling. The compounds that are replacing tin in anitfoulant paints are also effective in controlling the growth of algae in architectural paints.

Most dry-film preservatives on the market in the United States are not effective against algae, only fungi. A few of the replacements for tin in antifoulant paints, zinc pyrithione and 4,5 dicloro-2- *n*-octyl-4-isothiazalin, are effective against both fungi and algae in architectural paints. Thus, the manufacturers of architectural paints have benefited from the tin ban by having more dry-film preservatives to choose from that likely would not have been available if tin were still allowed to be used in antifoulant paints. The suppliers of these compounds would not have gone through the expense of U.S. EPA registration unless there was a large market and opportunity that the tin ban provided.

### 8.1.3.2 Indoor Air Quality

It has long been known that people have allergic reactions to fungal spores. More recently, organisms have been implicated in causing more severe damage to humans such as central nervous system damage and death. The outbreak of *Legionella pneumophila* in 1976 was the beginning of media attention to building related illnesses and sick building syndrome (SBS). The World Health Organization has defined sick building syndrome as a situation where 20% of a building's occupants complain of physical problems that occur soon after entering the building, the problem gets worse while they are in the building, and the problem ceases after they leave the building [4]. Obviously, discomfort caused by temperature and noise would not be caused by micro-organisms, but allergens and toxins produced by fungi could cause discomfort or worse. Thus, the definition is vague and the contribution of micro-organisms not well documented, with the exception of well-known infectious contaminants. When the indoor humidity is above 60% for extended periods of time, microbial growth can occur on materials in the building that hold the moisture and provide a nutrient source [5]. Although it is unlikely that the painted surfaces in most buildings would be a significant source for microbial growth that would lead to illness, there are interior paints available that provide protection of the dry film against the growth of bacteria and fungi. The increase in availability of these paints is invariably the result of heightened awareness to the problem of indoor air quality brought about by media attention. As mentioned earlier, some buildings such as breweries and food processing plants need to have fungicides in the paint films because the high moisture levels and nutrients that settle on the paint film provide an excellent environment for fungal growth.

It is the airborne spores and the mycotoxins produced by the fungi that cause the problems with indoor air quality. There are about 20 common genres of airborne fungi, with *Cladasporium*, *Alternaria*, *Penicillium*, *Aspergillus*, *Fusarium*, and *Aureobasidium* being the most common [6]. All are capable of causing allergic reactions in susceptible people [7]. *Alternaria*, *Aspergillus*, and *Penicillium* have been identified as mycotoxin producers [8]. However, it is *Stachybotrys chartarum* that is the fungus receiving a lot of attention in the media. Recently, its occurrence and implication in building-related illnesses is being intensely investigated and reported on. Under the right conditions, *Stachybotrys* can produce mycotoxins that are inhibitors of DNA, RNA, and protein synthesis [9]. Studies of the effects of exposure to *Stachybotrys* in water-damaged buildings have not conclusively proved that the organism caused health hazards. However, the studies have brought more attention to the presence of this and other organisms that have not been extensively acknowledged previously as toxigenic fungi [10–13].

## 8.2 TECHNICAL CONSIDERATIONS

### 8.2.1 Basic Causes for the Spoilage of Paint in the Wet State

Because waterborne coatings consist of water and organic materials, bacteria and, to a lesser extent, fungi can thrive and multiply quickly to spoil the paint. Also, because contamination of the paint by these organisms is practically unavoidable, a wet-state preservative must be used if the paint will not be used within a few days.

Contamination can arise from raw materials such as extender pigments and slurries. The water supply itself will have a significant amount of bacteria present unless run through a sterilization procedure.

Contamination from equipment is a major source of bacteria being introduced to paint. Tanks and lines that are rinsed out after a batch of paint is made can become breeding grounds for bacteria, especially in dead areas where water collects. Splash areas on mixing shafts and tank lids also provide ideal surfaces for micro-organisms to proliferate. Condensation and drippings from these areas into the paint are common sources of contamination. Recycled wash water must be treated to prevent bacteria from growing and contaminating fresh paint. Dust particles will also carry micro-organisms that can end up in the paint. Sometimes, when a batch of paint is being held up waiting for the quality control (QC) department to make adjustments, a layer of water is added to the surface to prevent skinning. Sometimes, this layer is left overnight. A bactericide must be added to this layer to prevent bacteria from growing because the bactericide added to the paint will not defuse into the water layer in sufficient quantity to have much of an effect.

Plant hygiene is an essential part of the process for preventing paints from spoiling. Because equipment configurations vary greatly, individual customized plant audits should be performed periodically by the biocide supplier.

## 8.2.2 Conditions That Affect the Growth of Micro-organisms on Paint Films

The type and extent of microbial growth on paint films is influenced by many factors. This makes predicting and preventing growth at a reasonable cost difficult. An understanding of the conditions that influence growth can help in formulating paints resistant to the growth of micro-organisms. Some of these variables are climate, air quality, building design, substrate, landscaping, and paint formulation. Mildew (fungus) and algae have both similar and different requirements for growth. Both require moisture, oxygen, carbon, and nitrogen nutrients, trace minerals, and temperatures between 15°C and 35°C for optimal growth. Algae require light for photosynthesis, whereas mildew does not. Mildew must obtain the necessary nutrients from the substrate; algae can fix carbon from the carbon dioxide in the air. Many species of algae can also fix nitrogen from the air. The ideal pH range for mildew is neutral to acidic; algae grow better on neutral to alkaline substrates. Often the conditions for the growth of both mildew and algae are present together and both can be seen growing on a building. For the species of algae and fungi that grow on painted surfaces, algae generally require more moisture than fungi. On very wet surfaces, algae usually will grow alone. On drier surfaces, usually only fungi grow [14].

The climate has a great influence on the type and degree of microbial growth on buildings. Higher temperatures generally favor greater microbial growth. High humidity and/or considerable rainfall will accelerate growth. Temperature extremes such as warm humid days and cool nights can lead to condensation on walls. Heavy rainfall will extract materials from a paint film and also the substrate if the film is porous enough. These materials can be nutrients or toxins and will be discussed in more detail. The season the paint is applied can also effect how quickly and severely the film is infested with growth. A paint film is most susceptible to growth soon after it is applied because the low-molecular-weight organic materials (thickeners, dispersants, etc.) are readily available as nutrients to mildew. If the application of the paint coincides with a wet season, rapid growth of micro-organisms may occur if the paint is not sufficiently protected with an algaecide/fungicide. Prevailing winds can also effect the growth of micro-organisms. Soil (farming or excavation activity), vegetation, and bodies of water are all sources of spores and propagules. If a building is downwind from these sources, chances for deposition and growth on the building is increased. North and Davis reported recovering a greater diversity of micro-organisms in the air during the spring and summer months in Florida and speculated that this was due to increased farming activity [15]. Cultivated soils typically produce higher concentrations and greater diversity of spores than noncultivated soils [16].

Desiccated soil, easily blown about by the wind, can carry spores of fungi and algae and also nutrients to the surface of a paint film. Pollution can also deposit carbon and nitrogen onto a paint film, providing nutrients to fungi. Pollen and detritus from dead vegetation can settle on a painted surface and provide nutrients to micro-organisms. Another source of airborne nutrients that find their way onto painted surfaces are bird and insect droppings.

Building design can have a profound effect on the amount of water to which a painted surface is subjected. Runoff from roofs, sills, and balconies onto painted surfaces is sure to lead to the growth of algae or mildew no matter how much biocide is added to the paint. If the building does not have a properly designed vapor barrier, moisture transmission from outside to inside can occur if the building is air conditioned. This may lead to condensation of water on the inside wall, increasing the chance for mildew growth. If the building is heated, moisture vapor transmission will move from inside to outside and may lead to condensation on the outside wall. Air conditioned buildings could also have condensation on the outside walls if there is poor insulation and the outside air is warm and moist. This is a common observation on gloss white concrete residential roofs in Florida that do not have good insulation. Overnight condensation can remain on the roof into the afternoon.

Roofs that do not overhang the walls and do not have gutters will allow excessive water to run down the walls and also splash up onto the walls after hitting the ground, carrying spores from the soil onto the walls. Insufficient or improper expansion and control joints on masonry buildings will lead to cracks in the surface. These cracks will collect nutrients, spores, and moisture and lead to the growth of micro-organisms.

The substrate is a very important consideration when deciding on the amount and type of biocide to add to a paint. Wood has a lower pH, usually 4–5, and is more favorable to the growth of fungi. Fungi generally grow faster than algae on surfaces where the pH is lower than 8 [17]. Wood is also a very good source of nutrients for fungi. These nutrients can migrate through a paint film, especially a film with a high PVC (pigment volume concentration). Very often, wood is already supporting the growth of fungi before it is painted and the fungi can grow through the film from the substrate. Wood retains moisture. Even kiln-dried lumber has a 15% moisture content. Wood is dimensionally unstable. It will expand and contract with changes in moisture and temperature. This could lead to cracking of the paint film and expose the wood to micro-organisms. Nutrients and moisture will also collect in the cracks.

Masonry is more resistant to the growth of mildew because it is alkaline. The pH is usually around 12 when it is new, dropping to near neutral after several years, depending on the amount of rainfall, if it is painted, and the type of paint. The alkaline salts can migrate through the paint film and inhibit the growth of mildew. Algae will tolerate a higher pH and often grow on masonry surfaces in the absence of fungi. The rough texture of masonry encourages the deposition of airborne dust, spores, and propagules.

The type and extent of landscaping around a building can influence the growth of micro-organisms. Trees and shrubbery near a building provide a moist microclimate, attract birds and insects, and are a source of organic debris and sap. Algae and fungi thrive on vegetation and can be blown by the wind from trees and shrubs onto a building. Wood chips and mulch are a good source of fungal spores. Debris from cutting grass and shrubs can blow onto a building and serve as a nutrient source. Any digging and disruption of the soil will release fungal and algal propagules into the air, increasing the chances of deposition onto a building nearby.

The paint formulation itself will have an impact on the resistance to growth of micro-organisms, both in the degree of primary infestation and secondary infestation. Primary infestation is growth that occurs on the paint film that is directly enhanced by materials that are in the paint film that can serve as nutrient sources and are readily available to the organisms. Such materials found in emulsion paints are thickeners, particularly the cellulosics, dispersants, defoamers, and wetting agents. In addition to being nutrients, some of these materials are also hydrophilic and will keep the film moist for a longer time after a rainfall. The more porous the paint film, the more readily these materials will leach out. The susceptibility of the paint film to primary infestation usually will last up to 6 months, depending on the rainfall, film porosity, and the type and quantity of leachable organic material. Inorganic leachable materials will facilitate algal growth. These materials include tripolyphosphates, such as KTPP and NaTPP, and carbonates, such as calcite and dolomite. Primary infestation is a complex interaction of paint formulation, substrate, climate, and local species of micro-organisms. The local community of micro-organisms include bacteria, fungi, and algae. The succession of these organisms on painted surfaces has had limited investigation. O'Neill concluded that initial infestation by bacteria degrades materials in the paint film, paving the way for fungal infestation [18].

Secondary infestation of paint film occurs when materials in the film break down such as the polymer and/or airborne nutrients are carried to the paint surface and are deposited. The binder may degrade by hydrolysis, photolysis, and oxidation. Acids and enzymes secreted by microbes also accelerate the degradation of the binder to lower-molecular-weight fragments that can be metabolized by the organisms. Acrylics are generally more resistant to degradation than the vinyl acrylics and usually support less growth of micro-organisms. Hard polymers are normally more resistant to collection of dirt and microbial propagules than soft polymers and, therefore, support less growth of micro-organisms.

Alkaline pigments such as calcium carbonate will inhibit the growth of fungi but may allow an increase in the growth of algae because there is no competition from the fungi and the calcium is a necessary nutrient for algae.

The PVC of the paint may also influence the degree of microbial growth on paint films [19]. Low-PVC paints will collect more dirt and spores if the binder is soft and thermoplastic. More growth of micro-organisms on low PVC paints is likely unless the binder is hard and hydrophobic. For masonry paints, choosing a hard styrene acrylic will improve the resistance of the coating to microbial growth. High-PVC paints also collect dirt and spores easily because the surface is rough and porous. Flat and matte finish paints should be formulated to the lowest possible PVC to minimize surface texture and porosity.

Because the thickness of a paint film has a direct effect on the resistance of the film to the growth of micro-organisms, the volume solids of the wet paint and the rheology are important considerations when formulating for maximum resistance to growth. Dry-film preservatives must migrate out of the paint film to be effective. They must migrate slowly to have long-term protection. A thicker film will have a higher concentration of preservative per unit area and, therefore, will provide longer protection against microbial growth than a thin film of the same formulation.

The ideal dry-film preservative will have a broad spectrum of activity against algae and fungi, will migrate out of the paint film at a rate that provides a toxic concentration to the surface of the film, but will not migrate so fast that long-term efficacy will suffer. The paint formulation will also have a substantial influence on the rate of migration of a given dry-film preservative. The inherent solubility of the preservative in water and leachable components of the formulation together with the chemical and physical properties of the coating will determine how well and for how long the dry-film preservative will perform. Chemical and physical stability and uniform distribution of the dry-film preservative in the dry paint film are also desirable characteristics. No one product works well in all formulations under all conditions.

The growth of micro-organisms on buildings is a complex interaction of climate, airborne matter, building design, building substrate, local community of micro-organisms, the paint formulation, and application. Knowledge of the influence of these factors is important in formulating a high-quality product and satisfying the expectations of the building owner.

## 8.3 TYPES OF ADDITIVE: WET-STATE PRESERVATIVES

The primary need for most aqueous coatings is protection against bacteria. Fungi usually will not grow in coatings with the exception of occasional yeast contamination. Gram-negative bacteria (gram-negative bacteria do not absorb a standard dye, iodine/crystal violet, and become stained) have cells walls that are less permeable than gram-positive bacteria (will absorb a standard dye) and are, therefore, more difficult to kill with toxicants.

*Pseudomonas aeruginosa* is the most common bacterial organism that spoils paints. Often, there are other bacterial organisms as well such as *Enterobacter* sp. *Bacillus subtillus*, and other *Pseudomonades*. Anaerobic bacteria could also be present [20]. Therefore, in addition to activity against the standard spoiling organisms, a wet-state preservative must also have broad activity against the less common organisms as well.

The most common types of bactericide used in coatings are the formaldehyde-releasing products and the isothiazalone (isothiazalin-one)-based compounds. Formaldehyde itself does not work well as a wet state preservative for coatings because it is too volatile and too reactive. It reacts with amines and is easily oxidized. Compounds that release formaldehyde slowly or under certain conditions are most frequently used in coatings. It is the electrophilic character of formaldehyde that makes it effective, reacting with nucleophilic cell components that have amino or thiol groups. Formaldehyde blocks the synthesis of methionine by reacting with homocysteine that the cell produces as a methionine precurser [21,22].

The range and variety of compounds that release formaldehyde is enormous. However, most of the compounds used in the coatings industry are condensates of formaldehyde and amines. These include the triazines, the quaternary hexaminium salts, and the oxazolidines.

## 8.3.1 Triazine

One of the simplest and highest in available formaldehyde of the common coatings preservatives is hexahydro-1,3,5-tris(2-hydroxyethyl)-*s*-triazine (also known as just triazine). It is formed by the condensation and trimerization of ethanolamine and formaldehyde. This compound is sometimes inaccurately referred to commercially as 2-(hydroxymethyl)amino ethanol, which is really just an intermediate that quickly trimerizes to the triazine structure. It is stable at alkaline pH, but releases formaldehyde under acid conditions. Normally, aqueous coatings are on the alkaline side, but bacteria will release acidic metabolites and trigger a localized release of formaldehyde in the presence of triazine.

Triazine may contribute a slight yellowing in a white paint due to breakdown to ethanol amine. Ethanol amine will develop an amber color over time. The reaction of amine with monomer and/or residual redox activator is also a possible cause of yellowing. This problem is overcome by using an amine that is color stable such as amino methyl propanol.

## 8.3.2 Oxazolidines

When secondary amines like 2-amino-2-methyl propanol are reacted with formaldehyde, oxazolidines are formed—in this case, 4,4 dimethyl 1,3 oxazolidine. This is a widely used preservative in the coatings industry. Like the triazine compound, it is sometimes inaccurately referred to as something else in commercial products. The 4,4 dimethyl 1,3 oxazolidine is sometimes referred to as 2(hydroxymethyl)amino-2-methyl propanol. The true structure is the 1,3 oxazolidine. Oxazolidines are more color stable than triazine (hexahydro-1,3,5-tris(2-hydroxymethyl)-*s*-triazine) but not quite as effective due to slightly less available formaldehyde. The oxazolidines are also slightly higher in cost than triazine. Like triazine, oxazolidines release formaldehyde under acidic conditions.

### 8.3.3 Quaternized Salts of Hexamethylenetetramine

One of the first synthesized formaldehyde-releasing compounds was hexamethylenetetramine (HTA). This was the simple condensation reaction of mixing ammonia with formaldehyde. To increase effectiveness in alkaline media, the HTA is quaternized [23]. The quaternized hexaminium salts release formaldehyde in aqueous solutions independently of the pH. Although the quaternized hexaminimium salts have a weak cationic character, they are compatible with anionic compounds and have been used for many years in aqueous paint formulations. Traces of monomer will react with the amine and lead to slight yellowing of white paints. Quaternized hexaminium salts do not partition into the organic phase. .The triazines and oxazolidines will partition into the organic phase to a slight degree. The most common quaternized hexaminium salts used in coatings are 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride and methyl-3,5,7-triaza-1-azoniaadamantane chloride.

### 8.3.4 Bronopol

Bronopol (2-bromo-2-nitropropane-1,3-diol) is a compound that has a minor role as a preservative in coatings in the United States. In Europe, it is more common and used in blended products, usually in conjunction with isothiazalones. Bronopol will slowly release formaldehyde in alkaline environments. The activated bromine also acts as a toxophoric group. Some discoloration and corrosion may occur on degradation and release of bromide.

The formaldehyde-releasing preservatives have good efficacy against the bacteria that causes spoilage in aqueous paints. However, because formaldehyde is toxic and a suspected carcinogen and not very effective against fungi, other non-formaldehyde-releasing compounds are often used in paints instead.

### 8.3.5 Isothiazalones

The isothiazolone (isothiazolin-one)-based compounds do not release formaldehyde. The most common isothiazolones used in coatings are 2-methyl-4-isothiazalin-3-one, 5-chloro-2-methyl-4-isothiazalin-3-one, and 1,2-benzisothiazalin-3-one. Usually the 2-methyl-4-isothiazalin-3-one (MIT) and 5-chloro-2-methyl-4-isothiazalin-3-one (CMIT) are used as a mixture. The CMIT is much more effective against fungi and bacteria than the MIT, but it is also a much more potent sensitizer than MIT. Concentrations as low as 20 ppm of the mixture are often enough to preserve an aqueous paint. Stability of isothiazolones is not very good. Amines, sulfides, sulfites, thiols, and oxidizing and reducing agents all deactivate MIT and CMIT. The chemical stability of MIT and CMIT is greatly increased by adding a small amount of metal salts, copper being the most effective. Copper salts have also been found to increase the activity of CMIT [24]. Thermal decomposition of both MIT and CMIT starts at about 55°C. Thus, the value of the mixture is for a formaldehyde-free preservative that will protect the paint until it is opened. Once the paint has been opened and used, contamination of the unused portion may occur.

Benzisothiazolone (1,2 benzisothiazolin-3-one), also known as BIT, is much more stable than MIT or CMIT both chemically and thermally; however, its activity is not as good. Somewhat higher concentrations must be used, but stability in the paint is generally better. BIT is also a skin sensitizer, although not as potent as CMIT. However, BIT must be used at higher concentrations than CMIT to achieve desired preservation performance. Chlorination of isothiazolones results in greater potential for skin sensitization.

### 8.3.6 1,2 Dibromo-2,4-dicyanobutane

A non-formaldehyde-releasing, non-isothiazolone preservative that finds some use in coatings is 1,2 dibromo-2,4-dicyanobutane (DBDCB). The solubility in water is low (3.8 g/L) for an aqueous preservative, but still finds use in some applications. It is stable up to about pH 9. It does not have the toxicity and sensitization issues of the formaldehyde releasers and isothiazolones, respectively, but, typically, it is not as effective in most coatings applications. DBDCB is often blended with other wet-state preservatives such as bronopol or isothiazolones.

## 8.4 TYPES OF ADDITIVES: DRY-FILM PRESERVATIVES

Dry paint films, especially exterior paint films in most climates, need to be protected against the growth of micro-organisms. In North America, fungi cause most of the problems with discoloration and degradation of exterior paint films, particularly over painted wood. Masonry is less susceptible to fungal growth because of the alkaline nature and lack of nutrients. On the other hand, masonry is likely to support algae growth due the higher tolerance to alkalinity and lack of competition from fungi.

The number of suitable organic dry-film preservatives for decorative coatings is not very large and none will last more than a few years under harsh conditions. Inorganics are more durable, but efficacy is not as good. Using both often results in good performance. Most dry-film preservatives only have activity against fungi; a few are active against both fungi and algae, notably the pyrithiones and isothiazolones. The toxicity of the preservative together with its solubility in water and water-miscible components of the paint, and the porosity and hydrophobicity of the paint film will determine how well the film remains free of microbial growth. A recent trend in the United States has been to follow the Europeans in blending products to broaden the spectrum of activity.

## 8.4.1 Carbamates

### 8.4.1.1 3-Iodo-2-propynyl butylcarbamate

One of the most commonly used dry-film fungicides for coatings is 3-iodo-2-propynyl butylcarbamate (IPBC). It is suitable for both waterborne and solvent-borne architectural coatings and wood treatments. IPBC has a very broad spectrum of activity against the fungi. It is very effective against yeast, mold, stain fungi, and rot fungi. Against algae, IPBC has some weak activity.

3-Iodo-2-propynyl butylcarbamate is available in a number of solvent carriers at various active concentrations as well as a 97% active powder. Typical concentrations used in coatings range from 0.1% to 0.4% active on the weight of wet paint. The use levels for wood treatment products are typically slightly higher. The type of solvent carrier will have an effect on the following:

- The package stability of the IPBC
- How the IPBC partitions between the water and polymer in water-based coatings
- How deep the IPBC penetrates into the substrate
- The migration out of the paint film
- The distribution of IPBC through the paint film

The type of solvent used to dissolve the IPBC should be considered a formulation variable that will affect the performance of the coating. Aqueous preparations of IPBC as dispersions or emulsions are possible but generally do not perform quite as well as the solvent-borne versions.

Degradation of IPBC usually leads to formation of a yellow to brown color, depending on the degradation products and the coating formulation. Degradation can occur on storage and/or by exposure to light. The degradants are usually elemental iodine, iodides, and multiple iodo propynyl butylcarbamate products (di and tri iodo propynyl butyl carbamate). Because of the sensitivity to light, IPBC should be used in pigmented products or in products than will penetrate into the substrate. Roof coatings and elastomeric coatings are often formulated with only 0.25–0.50 lbs of titanium dioxide as the only pigment, which runs the risk of turning a pale yellow within hours in bright sunlight.

### 8.4.1.2 Carbendazim

Carbendazim is chemically *N*-benzimidazolyl-2-carbamic acid methyl ester (BCM). Carbendazim is one of the most widely used dry-film preservatives around the world, but is not used much in the United States. Carbendazim is a low-cost agricultural fungicide that has been used mostly in blended products. Because carbendazim is not effective against one of the most common types of fungi growing on paint films, *Alternaria alternata*, it is usually blended with 2-*n*-octyl-4-isothiazolin-3-on (OIT). Typically, the amount of OIT in the blended product is not very high, 4–5% plus 10–15% carbendazim. The OIT is much more expensive than the carbendazim. Because algae is recognized as a problem in Europe and Asia, algaecides are usually also included in the blend with carbendazim and OIT. Newer products are available where the OIT have been replaced with IPBC, also at low concentrations. The major attraction of carbendazim is its low cost and exterior durability (8 ppm water solubility). The major drawback is the lack of activity against *Alternaria alternata*.

## 8.4.2 Chlorothalonil

Chlorothalonil (2,4,5,6 tetrachloroisophthalonitrile) is a common dry-film fungicide used in both waterborne and solvent-borne architectural coatings. It has broad activity against most stain and mold fungi, but it is not as effective as IPBC against rot fungi. Chlorothalonil is also effective against algae, but has poor efficacy against *Chlorella* sp., some of the most common species of algae growing on paint films. Chlorothalonil is available as an aqueous dispersion as well as powdered forms. The powdered forms have to be dispersed using high-shear equipment. The dispersion forms may be added to the letdown.

Chlorothalonil reacts with nucleophilic microbial cell entities, such as thiol groups, and is deactivated in doing so. Hydrolysis occurs at high pH, about 8.5, and increases with increasing pH. At pH 9.0, the half-life is 38 days. Aqueous paints that contain chlorothalonil must be formulated no higher than 8.5 and should not be applied over alkaline substrates such as masonry.

The water solubility is very low, about 1 ppm at neutral pH. Therefore, resistance to leaching from the paint film would be expected to be good. However, the solubility in common paint solvents such as propylene glycol and coalescent agents can be several percent, and could contribute to early loss due to leaching of some of the chlorothalonil.

The major negative in using chlorothalonil for coatings is the tendency to cause erosion (chalking) of the paint film on exposure to light for long periods of time. For this reason, chlorothalonil is used mostly in white and off-white paints and seldomly used in colored paints, unless at low concentrations.

### 8.4.3 Folpet

Folpet (trichloromethylthiophthalimide) is a fungicide that is only used for solvent-borne coatings. Folpet is easily hydrolyzed, and the rate increases with increasing pH, so it is unsuitable for waterborne products. It is widely used as a surface fungicide in conjunction with IPBC for wood treatment products such as transparent and semitransparent wood stains. The IPBC penetrates into the wood, due to its solubility in the hydrocarbon carrier, and the folpet remains on the surface. Solvent-borne paints that use Folpet should be low in moisture content because folpet will hydrolyze easily, even with a small amount of water.

### 8.4.4 Isothiazolones

Methyl and chloro methyl isothiazolones are used for preservation of paints in the wet state and are water soluble. By increasing the length of the alkyl chain on the N atom, the water solubility is significantly reduced, allowing use for dry-film preservation of exterior paints. The water solubility can be further reduced by chlorination. Chlorination also increases the toxicity. However, at the same time, chlorination increases the potential for skin sensitization.

#### 8.4.4.1 2-*n*-Octyl-4-isothiazolin-3-one

The most common isothiazolone used for film preservation is 2-*n*-octyl-4-isothiazolin-3-one (OIT). It has been used for many years and is not known to discolor paint films like some of the other dry-film fungicides available. The problem with OIT is stability and water solubility. Stability in the presence of primary and secondary amines as well as oxidizing and reducing agents is not very good. Zinc oxide is used to stabilize OIT in the presence of amines, usually at a concentration of about 2–2.5% of the weight of the wet paint. The water solubility of OIT is somewhat high for exterior applications, about 460–480 ppm. The OIT can leach out of a porous paint film if exposed to substantial rain. Lengthening the alky chain will decrease the water solubility, but at the expense of antimicrobial activity. OIT is also quite soluble in common paint solvents like propylene glycol and common paint coalescent agents. Additional OIT loss can occur with the leaching out and evaporation of the glycols and coalescent agents in typical coatings. Because of the alkaline instability, paints that contain OIT should not be applied over alkaline substrates, like new masonry or cement fiberboard.

#### 8.4.4.2 Dichloro-2-*n*-octyl-4-isothiazolin-3-one

Substitution of the isothiazolin-one ring with chlorine led to the development of 4,5 dichloro-2-*n*-octyl-4-isothiazolin-3-one (DCOIT) [25]. DCOIT has a much lower water solubility than OIT (about 2 ppm) and is more likely to remain in the paint film on weathering. Because of the activated chlorine, DCOIT may be more toxic than the OIT, but also more of a skin sensitizer. DCOIT, like OIT, is not very stable in the presence of amines or in alkaline environments.

### 8.4.5 Pyrithiones

#### 8.4.5.1 Zinc Pyrithione

The most common pyrithiones used in coatings are the zinc and copper pyrithiones (2-mercaptopyridine–*N*-oxide or 2-pyridinethiol-*N*-oxide): Zinc pyrithione is used in both architectural and antifoulant coatings. Copper pyrithione is almost exclusively used in antifoulant coatings because of its green color. Zinc pyrithione is white. Both are very effective fungicides and algaecides with very low water solubility. The solubility of dry-film preservatives in water and in the common solvents used in emulsion coatings (coalescent agent, glycols, surfactants, and defoamers) adversely affects the durability of the preservative in the coating, allowing the preservative to leach out more quickly.

The water and solvent solubility of zinc pyrithione is among the lowest of all the dry-film preservatives available. This is contributing factor to the very good long-term performance of zinc pyrithione compared to many other compounds.

Pyrithiones complex strongly with transition metals, copper being the most stable. Zinc pyrithione is close in formation constant value to ferric pyrithione and cobalt pyrithione. Therefore, when iron or cobalt is present in a coating formulation, some transchelation may occur. Zinc pyrithione is not used in alkyd paints due to the presence of a cobalt drier catalyst. Extender pigments such as calcium carbonate may contain several hundred parts per million of iron. Dissolution of that iron could occur and react with zinc pyrithione to cause discoloration. Ferric pyrithione is blue/gray in color. Some latex emulsions also have small amounts of iron present. Iron(II) sulfate heptahydrate is often used as an activator for redox initiator systems. Prevention of ferric pyrithione formation in the coating is easily accomplished by the addition of about 0.05% zinc oxide [26]. Zinc oxide is more soluble at alkaline pH than zinc pyrithione and prevents transchelation, most likely by the common ion effect. Zinc pyrithione is also sold commercially by Arch Chemicals, Inc. with an appropriate amount of zinc oxide mixed in. The product is Zinc Omadine ZOE Dispersion.

Pyrithiones are alkaline stable, which makes them a good choice for use in masonry paints. Most organic dry-film preservatives are not stable at pH much greater than 9.0. Typical dosage for zinc pyrithione is 0.2–0.4% active by weight of wet paint.

### 8.4.5.2 Sodium Pyrithione

Sodium pyrithione is also used as a dry-film preservative as well as for preserving in the wet state. Sodium pyrithione is water soluble and effective against bacteria when used in coatings at over 600 ppm active. If zinc oxide is also present in the coating formulation, then the sodium pyrithione will react with the zinc oxide to become an insoluble zinc complex that will provide dry-film protection against the growth of both fungi and algae [27]. For dry-film protection, more than 600 ppm is necessary—usually at least 1600 ppm is required. By using sodium pyrithione at over 1600 ppm (active) and zinc oxide at over 2.0% by weight on wet paint, effective wet-state and dry-film preservation can be achieved without adding any VOC to the coating formulation.

## 8.4.6 Azoles

Tebuconazole and propiconazole are fungicides used mostly for preservation of wood against wood-destroying (decaying) fungi. They are less effective against the staining fungi. Because they are only moderately effective against *Alternaria alternata*, one of the more prevalent invaders of paint films, their use is mostly restricted to wood treatment products.

Thiabendazole (TBZ) also is not very effective against *Alternaria alternata*. It works best if used in combination with fungicides that are effective against *Alternaria alternata*. Also, the high cost of thiabendazole limits its use in coatings.

### 8.4.7 Diidomethyl-*p*-tolylsulfone

Diiodo-*p*-tolylsulfone is a broad-spectrum fungicide, effective against the common organisms that grow on paint films. The very low water solubility, about 1 ppm, is good for exterior durability. Unfortunately, discoloration due to the iodine content makes it a poor choice for white and light-colored paints. Its alkaline stability is good up to about pH 10.

### 8.4.8 Blends of Dry-Film Preservatives

For many years, blends of dry-film preservatives have been used in Europe and Asia in preference to single actives. The main reason blends that have not been used in the United States has been due to regulatory costs. In the United States, each blend would have to be registered separately with the EPA. Blending broadens the spectrum of activity of the preservative product. A typical blend would have a low-cost fungicide such as Carbendazim, a higher-cost fungicide to address the activity gaps of the Carbendazim, and an algaecide. Another reason that blends have been popular outside the United States is testing philosophy. Europe and Asia have typically put more faith in laboratory test results than field test results. The rationale has been to have better control of the experiment. U.S-based workers have typically put more faith in field test results, believing that actual dynamic weathering conditions cannot be accurately duplicated in the lab. Standard, repeatable laboratory tests using the same organisms for all the testing is conducive to designing blended products to pass the lab tests rather than perform well in the field. As in the previously mentioned example of the blend of carbendazim, OIT, and algaecide (Diuron), the OIT is added at a low level (typically 4–5%) to cover the gap in the Carbendazim activity against *Alternaria alternata*. The 4–5% of OIT is sufficient to pass the laboratory test, but is not likely to provide much protection for the paint film in actual outdoor conditions. Many of the blends available are similar to the above example. Sometimes, OIT is replaced with IPBC and Diuron is replaced with another algaecide (herbicide). Blends are becoming more widely available in the United States as an attempt to offer new products to the paint industry because it is unlikely that any new molecules will be coming along soon.

### 8.4.9 Algaecides

Both the pyrithiones and isothiazalones are effective algaecides as well as fungicides. The most common use of algaecides in coatings is for the antifoulant market. Algae commonly grows on painted buildings, but is not as widely recognized as a problem as mildew growth is.

The only purely algaecidal compound registered in the United States for coatings applications is 2-methylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine. It has a low water solubility of about 7 ppm, so it is suitable for antifoulant coatings. Use in architectural coatings could cause problems because as an herbicide, damage to plants may occur from leaching out of paint films and into gardens. Usually, the better choice would be zinc pyrithione or DCOIT because neither is a herbicide and both have good activity against fungi as well as algae. 2-Methylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine is used in some blended products and it is also available as a single active.

## 8.5 TEST METHODS

### 8.5.1 Wet State

For aqueous coatings, bacterial contamination is much more of a problem than fungal contamination. ASTM D2574, Standard Test Method for Resistance of Emulsion Paints in the Container to Attack by Microorganisms is commonly used to determine if the coating is susceptible to microbial growth. *Pseudomonas aeruginosa* and *Enterobacter* sp. are specified in the method to be the test organisms, but may be substituted with other organisms if appropriate. These two organisms are generally regarded as common in paints [28]. Other variations include acclimating the organisms to the paint by inoculation of unprotected paints and using the paint itself as the inoculum for the test samples. Alternately, naturally spoiled paint could also be used for the inoculum. Multiple challenges are suggested, usually two to six. Viability of the bacteria is determined 1 day and 1 week after each challenge. Once it has been determined what concentration of bactericide is adequate to protect the paint, a safety factor of 2–3 should be used to finalize the correct dosage to provide protection under most conditions.

### 8.5.2 Dry Film

For laboratory evaluations, ASTM D5589-97, Standard Test Method for Determining the Resistance of Paint Films and Related Coatings to Algal Defacement, and ASTM D 5590-94, Standard Test Method for Determining the Resistance of Paint Films and Related Coatings to Fungal Defacement by Accelerated Four-Week Agar Plate Assay are the two most common agar plate methods for determining the effectiveness of dry-film preservatives. They are quick and have good reproducibility. The option of preleaching the samples for several days is described in the two standards. Preleaching is a good idea for any type of coating that will be subjected to rain or wet conditions. A standard inoculum is suggested, but flexibility to use other organisms is provided for. An additional organism that should be considered for testing is *Alternaria alternata* because it is well known to be among the first colonizers of paint films [29]. For agar plate methods, the inoculum is directly applied to the test specimens.

A slower method, but one that naturally inoculates the test specimens, makes use of an environmental chamber. ASTM D3273-86, Standard Test Method for Resistance to Growth of Mold on the Surface of Interior Coatings in an Environmental Chamber. This method suggests a test period of 4 weeks, but up to 10 weeks is not uncommon because growth on negative controls often does not start for several weeks. The inoculum uses the same organisms as the ASTM D 5590 protocol, but instead of direct inoculation, the organisms are added to soil in the bottom of the chamber and inoculation occurs by airborne spores. There is no mention of preconditioning of the samples, but for testing exterior coatings, leaching before running the test could provide more realistic results.

The benefit of laboratory evaluations is that they can be controlled and results are usually repeatable, especially the agar plate methods. However, because growth of organisms on paint films is a dynamic event, where growth is occurring simultaneously with weathering, laboratory testing cannot accurately simulate actual outdoor conditions. Products may perform very well in laboratory testing and not well in actual outdoor testing. Laboratory tests are good for screening because if a product performs poorly in the lab test, it likely will not perform well in actual use. However, the reverse is not always true.

Actual outdoor exposure of painted panels is generally considered to be the best indicator of what to expect of a dry-film preservative. The importance of carefully designing and preparing a field exposure of paint panels cannot be overemphasized. Valuable information about the performance of a paint film under actual conditions takes much time and work and should reward the experimenter with good, useful data. ASTM D 3456, Standard Practice for Determining by Exterior Exposure Tests the Susceptibility of Paint Films to Microbiological Attack and ASTM D 1006-93, Standard Practice for Conducting Exterior Exposure Tests of Paints on Wood provide very good background information for designing a proper exposure study. The substrate and primer can have a significant effect on the degree of microbial growth on the surface of a paint film.

Careful selection of the types of substrate, layout of the paints on the panels, and appropriate use of primers will help in minimizing the biases they can cause in the results.

### 8.5.2.1 Wood

Wood substrates contain nutrients, are porous, and retain moisture, typically 15–25% by weight. The sapwood is more conducive to mildew growth than the heartwood due to the greater concentration of nutrients and the lower dimensional stability of the sapwood. The lower-dimensional stability can lead to microcracking of the paint film and, therefore, greater access to the substrate. The nutrient value, degree of moisture absorption, and dimensional stability will all influence the degree of fungal growth on the surface of the paint. These variables can be quite different from one piece of wood to another of the same species and can also vary along the length and width of a 6 in. by 36 in. board!

To minimize the influence of variability of the wood substrate, at least three boards are always recommended, with all the paints to be compared applied on the same board. A positive control, negative control, and up to four experimental paints can normally be applied to a 3-f board.

White pine is commonly used, unprimed, with two coats of each paint applied at equal spreading rates. White pine (Ponderosa) is used mostly for millwork and building details such as facia boards, soffits, and wood columns. It is also sometimes used for clapboard siding. White pine has a higher nutrient content than cedar or redwood, is also more dimensionally unstable, and will mildew faster than cedar or redwood. Cedar is a very common siding material and should be included in any mildewcide study as well as pine. Cedar must be primed to prevent bleeding of water-extractive tannins in the wood. One coat of primer and one topcoat of the experimental paint is a common practice. The primer should not contain a fungicide, unless the study is designed for evaluating a system.

Boards are flat-sawn, quarter-sawn, or somewhere in between (bastard-sawn). Quarter-sawn are the most dimensionally stable and should be used whenever possible. ASTM D 358-93 Standard Specifications for Wood to Be Used as Panels in Weathering Tests of Coatings provides good suggestions for selecting wood for exposure testing.

### 8.5.2.2 Masonry

Masonry does not provide any organic nutrients for mildew. It does provide trace minerals that algae and fungus need. The high pH and low moisture retention of masonry inhibits the growth of micro-organisms. The high pH can accelerate the hydrolysis of some dry-film preservatives. This can lead to yellowing and loss of efficacy. Because masonry is a common building material, especially in geographic areas most prone to mildew and algal growth, masonry panels should also be included in a study that evaluates dry-film preservatives. Masonry is much more consistent in composition than wood. Usually, two replicates are sufficient to provide consistent results. However, again, it is a good idea to have all of the experimental paints in a group on the same panel because position on a rack (height off the ground) can influence the growth of mildew and algae. Calcium silicate boards or stucco-coated calcium silicate boards are commonly used masonry substrates for outdoor exposures. Two coats of the finish paint with no primer is the preferred system for evaluating pH stability of the mildewcide. Priming the stucco panels with an acrylic sealing primer that contains no fungicide is a good way to determine the performance of a fungicide in a paint film without a significant influence from the substrate or the primer.

Recoat of weathered paint panels is also a good suggestion for evaluation of mildewcides because most painting projects will actually be repainting of walls that were previously painted and weathered.

## 8.6 SUMMARY

For most house paints, the mildewcide additive represents the third most expensive component of the formulation, after the pigment and binder. Typically, \$0.40–\$0.60 per gallon is spent on dry-film preservative. Most of the preservatives on the market have a broad spectrum of activity and are toxic to micro-organisms at low concentrations. However, the behavior of the products in different formulations can vary dramatically. Intuitively, the solubility of the molecules in water and in the various organic materials in the formulation will affect rate of migration of the product out of the paint film and, therefore, affect the durability and efficacy of the product. Ideally, the migration will be fast enough to provide an effective dose of the product on the paint film surface, but slow enough to provide years of service.

Cornish et al. [30] recently reported on the leachability of various fungicides with water and how solubility affects fungicide performance. The paint film becomes susceptible to fungal growth at the point of fungicide depletion. The porosity of the paint film was also studied for the effect on fungicide loss. Porosity of the paint film and water solubility of the fungicide undoubtedly are major factors in the loss of fungicide from the paint film during weathering. Other factors such as the solubility of the preservative in organic additives could also have a dramatic effect on the durability of the fungicide. For example, propylene glycol is present in most latex formulations at 3–6% by weight on wet paint. The solubilities of several common fungicides in propylene glycol at 25°C are as follows:

| | |
|---|---|
| 3-Iodo-2-propynyl butyl carbamate | >20% |
| 2-*n*-Octyl-4-isothiazalin-3-one | >45% |
| Chlorothalonil | 2100 ppm |
| Zinc pyrithione | 200 ppm |

Because the propylene glycol will be slow to evaporate, the more soluble fungicides could be rapidly depleted from the paint film if there is rain soon after application of the paint to a building. Also, migration of the propylene glycol to the paint film surface during evaporation could create a concentration gradient of fungicide through the paint film. One study measured the concentration gradient of IPBC in a paint film for an acrylic house paint [31]. The IPBC was found to be more concentrated at the surface of the paint film. As a consequence, the IPBC would be more rapidly weathered away than if uniformly distributed through the thickness of the film. The short-term performance would be very good at the expense of the longer-term protection of the paint film.

Other materials in the formulation could also effect the distribution and migration of the fungicide such as coalescent, defoamer, and even surfactants. IPBC is over 20% soluble in octylphenoxypolyethoxyethanol (hydrophobe/lipophobe balance = 13.5).

With all the possible formulation and drying condition variables, it becomes apparent that the more soluble the fungicide is in the various organic additives, the more random the fungicide distribution and migration rate out of the paint film will be. One type of fungicide is not likely to perform best under all conditions in all paint formulations. If the influence of the substrate is also taken into consideration, the situation becomes more complex.

Choosing a dry-film preservative that is not very soluble in any of the organic additives and is relatively low in water solubility would improve the long-term presence of the fungicide in the paint film. Thus, minimize the randomness of the distribution of the fungicide in the film. Still, the fungicide would have to migrate out of the paint film fast enough to maintain a toxic level on the surface of the paint film. The dry-film preservative zinc pyrithione has low solubility in all of the common organic paint additives and also has a low water solubility of 8 ppm at neutral pH. Zinc pyrithione typically provides very good long-term protection in flat paints. However, in gloss paints, a fungicide like IPBC that migrates faster generally provides better protection than zinc pyrithione due to the lower porosity of the film.

## APPENDICES

**Appendix 8.1** Common Wet-State Preservatives for Coatings: Bactericides

| Compound | Common name(s) | Trade names(s) | Company | Properties | Dose range (% by wt.) |
|---|---|---|---|---|---|
| 2-Bromo-2-nitropropane-1,3-diol | Bronopol | Bioban BPM (99%) | Dow Chemical | Formaldehyde release | 0.1–0.5% |
| | | Bioban BP 40 (40%) | Dow Chemical | | |
| 1,2 Benzisothiazolin-3-one | BIT | Acticide BW20 (20% | Acti-chem (Thor) | Isothiazolone more stable than CMIT/MIT blend | 0.1–0.3% of 20% solution |
| | | Proxel GXL (19.3%) | Avecia | | |
| | | Mergal K10N (9.5%) | Troy Chemical | | |
| | | Nipacide X (18%) | Clariant Corp. | | |
| | | Nuosept 495 (19%) | ISP | | |
| Mix 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazoloin-3-one | Kathon CMIT/MIT | Acticide DC | Acti-chem (Thor) | Blend of isothiazalones | 0.1–0.3% of 1.5% solution |
| | | Busan 1078 | Buckman Labs | | |
| | | Bioban 2000 | Dow Chemical | | |
| | | Kathon 886 MW 1.5% | Rohm & Haas | | |
| | | Mergal K9N | Troy Chemical | | |
| | | Nipacide CI 15 | Clariant Corp. | | |
| 4,4 Dimethyl 1,3 oxazolidine | | Bioban CS-1135 (76%) | Dow Chemical | Formaldehyde releaser | 0.1–0.4% |
| | | Nuosept 101 (77%) | ISP | | |
| | | Troysan 186 (68%) | Troy Chemical | | |
| | | Troysan 192 (74%) | Troy Chemical | | |
| Oxazolidine mixture | | Nuosept 95 (50%) | ISP | Formaldehyde releaser | 0.1–0.4% |

**Appendix 8.1** Continued

| Compound | Common name(s) | Trade names(s) | Company | Properties | Dose range (% by wt.) |
|---|---|---|---|---|---|
| Hexahydro-1,3,5-tris(2-hydroxyethly)-*s*-triazine | Triazine | Triadine 174 (78%)<br>Troysan 174 (78%)<br>CanGuard 454 (78%)<br>Nuosept 91 (78%) | Arch Chemicals<br>Troy Chemical<br>Dow Chemical<br>ISP | Formaldehyde releaser | 0.1–0.4% |
| 1-(3-Chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride | | Dowicil 75 (64%) | Dow Chemical | Formaldehyde releaser | 0.05–0.2% |
| Methyl-3,5,7-triaza-1-azoniaadamantane chloride | | Busan 1024 (18%) | Buckman Labs | Formaldehyde releaser | 0.1–0.5% |
| 1,2 Dibromo-2,4-dicyanobutane | DBDCB | Tektamer 38 (98%) | BASF | Non-formaldehyde; Non-isothiazolone | 0.1–0.5% |

**Appendix 8.2** Common Dry-Film Preservatives for Coatings: Single Actives

| Compound | Common name(s) | Trade names(s) | Company | Properties | Dose range (% by wt.) |
|---|---|---|---|---|---|
| 2,4,5,6 tetrachlo-roisophthalonitrile | Chlorothalonil | Acticide C40 (40%)<br>Acticide C 98 (98%)<br>Busan 1192 (98%)<br>Busan 1192D (40%)<br>Nuocide 404D (40%)<br>Nuocide 960 (96%)<br>Nopcocide N-40-D<br>Nopcocide N-98 | Acti-chem (Thor)<br>Acti-chem (Thor)<br>Buckman Labs<br>Buckman Labs<br>ISP<br>ISP<br>Cognis<br>Cognis | Slight yellowing; possible pinking with formaldehyde donors; chalking and fading on weathering | 0.5–1.2% as active |
| 2-*n*-octyl-4-isothiazolin-3-one | OIT<br>Octyl isothiazalone | Skane M-8 (45%)<br>Acticide 45 (46.5%) | Rohm & Haas<br>Acti-chem (Thor) | Degraded by sulfides and amines | 0.1–0.4% as a 45% solution |
| Trichloromethyl-thiophthalimide | Folpet | Fungitrol 11 (88%)<br>Fungitrol 11-50 (44%) | ISP<br>ISP | Solvent-borne only; hydrolyzes easily | 0.5–1.2% as active |
| 3-Iodo-2-propynyl butylcarbamate | IPBC | Omacide IPBC 20<br>Omacide IPBC 30<br>Omacide IPBC 40<br>Omacide IPBC 100<br>Fungitrol 420 (20%)<br>Fungitrol 430 (30%)<br>Fungitrol 440 (40%)<br>Fungitrol 400 (98%)<br>Polyphase P20T (20%)<br>Polyphase AF-3 (30%)<br>Polyphase AF-1 (40%)<br>Polyphase P100 (98%) | Arch Chemicals<br><br>ISP<br><br><br><br><br>Troy Chemical | May cause yellowing in wet state and dry film; can corrosion possible | 0.2–0.5% based on active |

**Appendix 8.2** Continued

| Compound | Common name(s) | Trade names(s) | Company | Properties | Dose range (% by wt.) |
|---|---|---|---|---|---|
| Sodium 2-pyridinethiol-1-oxide | Sodium pyrithione NaPT | Sodium Omadine (40%) | Arch Chemicals | Should use with zinc oxide; for waterborne coatings only | 0.1–0.5% as active (0.25–1.25% as supplied) |
| Zinc 2-pyridinethiol-1-oxide | Zinc pyrithione | Zinc Omadine (95%) | Arch Chemicals | Powder for antifoulant coatings; FPS and ZOE for waterborne only; fungicide, algaecide, and bactericide. | 2.0–4.0% active for antifoulant |
| | ZPT | Zinc Omadine FPS (48%) Dispersion | | | 0.1–0.5% active for architectural |
| | | Zinc Omadine ZOE (38%) Dispersion | | | |
| Dichloro-2-*n*-octyl-isothiazolin-3-one | DCOIT | Sea Nine 211 (30%) | Rohm % Haas | Severe sensitizer | 1.0–3.0% active for antifoulants |
| | Kathon 930 | Rosone 2000 (20%) | | | 0.115% active maximum for architectural |
| | C-9211 | | | | |

| | | | | | |
|---|---|---|---|---|---|
| *n*-Benzimidazolyl-2-carbamic acid methyl ester | Carbendazim BCM | Mergal BCM (99%) | Troy Chemical | Poor against *Alternaria alternata*; used mostly in blends. | 0.1–0.5% |
| Diiodomethyl-*p*-tolylsulfone | | Amical 48 (95%) Amical 50 (75%) | Dow Chemical | Yellowing in wet state and dry film | 0.2–0.6% on an active basis |
| 2-(4-Thiazolyl)-benzimidazole | TBZ | Metasol TK-100 (98.5%) | BASF | Poor against *Alternaria alternata* | 0.1–0.3% |
| 2-methylthio-4-tertbutylamino-6-cyclopropylamino-*s*-triazine | Irgarol | Irgarol 1071 (98%) Nuocide 1071 | Ciba Chemicals ISP | Algaecide only | 0.3–2.0-% |
| Zinc dimethyl-dithiocarbamate | Ziram | MZ-96 (96%) | RT Vanderbilt | Discolors with trace of metals | 1.0–3.0% |

**Appendix 8.3** Common Dry-Film Preservatives for Coatings: Blends

| Compound | Common name(s) | Trade names(s) | Company | Properties | Dose range (% by wt.) |
|---|---|---|---|---|---|
| 3,4-Dichlorphenyl-1,1-dimethylurea (19%) and 2,4,5,6 tetrachloroisophthalonitrile (14.7%) | Diuron Chlorothalonil | Acticide PM | Acti-Chem (Thor) | Algaecide and fungicide | 0.5–2.5% |
| 3,4-Dichlorphenyl-1,1-dimethylurea (19%) and 2,4,5,6 tetrachloroisophthalonitrile (8.8%) and 2-*n*-octyl-4-isothiazolin-3-one (6%) | Diuron Chlorothalonil OIT | Acticide SR-1216/6 | Acti-Chem (Thor) | Algaecide and fungicide | 0.5–2.5% |
| 3,4-Dichlorphenyl-1,1-dimethylurea (19%) and *n*-benzimidazolyl-2-carbamic acid methyl ester (9.9%) and 2-*n*-octyl-4-isothiazolin-3-one (2.5%) | Diuron Carbendazim OIT | Mergal S-89 | Troy Chemical | Algaecide and fungicide | 0.4–2.0% |
| 2-Methylthio-4-tertbutylamino-6-cyclopropylamino-*s*-triazine(4.9%) and *n*-benzimidazolyl-2-carbamic acid methyl ester (9.9%) and 2-*n*-octyl-4-isothiazolin-3-one (4.5%) | Irgarol Carbendazim OIT | Mergal S-90 | Troy Chemical | Algaecide and fungicide | 0.4–2.0% |
| 2-Methylthio-4-tertbutylamino-6-cyclopropylamino-*s*-triazine (15%) and 3-iodo-2-propynyl butylcarbamate (15%) | Irgarol IPBC | Polyphase 587 | Troy Chemical | Algaecide and fungicide | 0.4–2.0% |

| | | | | | |
|---|---|---|---|---|---|
| 2-Methylthio-4-tertbutylamino-6-cyclopropylamino-<br>*s*-triazine (10%) and<br>3-iodo-2-propynyl butylcarbamate (20%) | Irgarol<br>IPBC | Polyphase 588,<br>Polyphase 600 | Troy<br>Chemical | Algaecide and<br>fungicide | 0.4–2.0% |
| 2-methylthio-4-tertbutylamino-6-cyclopropylamino-<br>*s*-triazine (24%) and<br>3-iodo-2-propynyl butylcarbamate (4.8%) | Irgarol<br>IPBC | Polyphase 598 | Troy<br>Chemical | Algaecide and<br>fungicide;<br>mostly an algaecide | 0.4–2.0% |
| 2-Methylthio-4-tertbutylamino-6-cyclopropylamino-<br>*s*-triazine (4.0%) and<br>3-iodo-2-propynyl butylcarbamate (4.0%) and<br>*n*-benzimidazolyl-2-carbamic acid<br>methyl ester (12.0%) | Irgarol<br>IPBC<br>Carbendazim | Polyphase 662 | Troy<br>Chemical | Algaecide and<br>fungicide | 0.4–2.0% |
| 3-Iodo-2-propynyl butylcarbamate (5.0%) and<br>*n*-benzimidazolyl-2-carbamic acid<br>methyl ester (15.0%) | IPBC<br>Carbendazim | Polyphase 678 | Troy<br>Chemical | Fungicide | 0.4–2.0% |
| 3,4-dichlorphenyl-1,1-dimethylurea (15%) and<br>3-iodo-2-propynyl butylcarbamate (3.0%) and<br>*n*-benzimidazolyl-2-carbamic acid<br>methyl ester (9.0%) | Diuron<br>IPBC<br>Carbendazim | Polyphase 663 | Troy<br>Chemical | Algaecide and<br>fungicide | 0.4–2.0% |

## REFERENCES


1. Jacobs, W.A.; Heidelberger, M.; Bull, C.G. The bactericidal properties of the quaternary salts of hexamethylenetetramine. J. Exp. Med. **1916**, *23*, 577–599.
2. Tannenbaum, M.; Bricker, C.E. Microdetermination of free formaldehyde. Anal. Chem. **1951**, *23*, 354–357.
3. Springle, W.R. Enzymatic Liquefaction of Emulsion Paint and Cellulosic Thickeners. Chemspec Europe 89 BACS Symposium, WHO: Norlingen, Germany, 33–37.
4. *Indoor Air Pollutants: Exposure and Health Aspects*, Report on WHO Meeting, Norlingen, June 8–11, 1982.
5. Scarry, R.L. Looking into sick buildings. Heating/Piping/Air Conditioning 63–65, July, 1994.
6. Al-Doory, Y.; Domson, J.F. *Mould Allergy*, Lea and Febiger: Philadelphia, 1984.
7. Horner, W.E.; Helbling, A.; Salvaggio, J.E.; Leher. S.B.; Fungal allergens. Clin Microbiol. Rev. **1995**, *8* (2), 161–179.
8. Sorenson, W.G. Fungal spores: Hazardous to health? Environ. Health Perspect. **1999**, *107*, 469–472.
9. Ueno, Y. Trichothecene mucotoxins—Mycology, chemistry, and toxicology. Adv. Nutr. Res. **1980** *3*, 301–353.
10. Croft, W.A.; Jarvis, B.B.; Yatawara, C.S. Atmos. Environ. **1986**, *20*, 549–552.
11. Johanning, E.; Biagini, R.; Hull, D.; Morey, P.; Jarvis, B.; Landsbergis, P. Health and immunology study following exposure to toxigenic fungi (*Stachybotrys chartarum*) in a water-damaged office environment. Int. Arch. Occup. Environ. Health. 1996; 68: 207–218.
12. Hodfson, M.G.; Morey, P.; Leung, W.Y. Building-associated pulmonary disease from exposure to *Stachybotrys chartarum* and *Aspergillus versicolor*. J. Occup. Environ. Med. **1998**, *40*, 241–249.
13. Johanning, E.; Landsbergis, P.; Gareis, M.; Yang, C.S.; Olmsted, E. Clinical experience and results of a sentinel health investigation related to indoor fungal exposure. Environ. Health Perspect. **1999**, *107* (3), 489–494.
14. Hansen, K. Biological discolouration of wood finishes. Paint Ink Int. Sept. **1996**, 12–14.
15. North, N.A.; Davis, J.S. Airborne algae from north–central Florida. Florida Sci. **1988**, *51* (2), 92–99.
16. Brown, R.M.; 1971. Studies of Hawaiian freshwater and soil algae. I. The atmospheric dispersal of algae and fern spores across the island of Oahu, Hawaii, In *Contributions in Phycology*; Parker, B.C., Brown, R.M. Jr., Eds.; Allen Press: Lawrence, KS, 1964.
17. Hill, D.O.; April, G.C. J. Paint Technol. **1972**, *44* (571), 43.
18. O'Neill, T.B. Succession and interrelationships of microorganisms on painted surfaces. J. Coatings technol. **1986**, *58*, 51–56.
19. Becker, R.; Guterman, M.; Laks, J. *The Effect of Porosity of Emulsion, Paints on Mould Growth*. Durability of Building Materials Vol. 3, Elsevier Science: Amsterdam, 1986.

20. Opperman, R.A.; Goll, M. J. Coatings Technol. **1984**, *56*, 712.
21. Neely, W. Action of formaldehyde on micro-organism, I. Correlation of activity with formaldehyde metabolism. J. Bacteriol. *85*, 1028–1031.
22. Neely, W. Action of formaldehyde on micro-organism, II. Formation of 1,3-thiazane-carboxylic acid in *Aerobacter aerogenes* treated with formaldehyde. J. Bacteriol. **1963**, *85*, 1420–1422.
23. Jacobs, W.A.; Heidelberger, M.; Bull, C.G. The bacterial properties of the quaternary salts of hexamethylenetetramine. III. The relation between constitution and bactericidal action in the quaternary salts obtained from halogen acetyl compounds. J. Exp. Med. **1916**, *23*, 577–99.
24. Riha, V.F.; Sondossi, M.; Rossmoore, H.W. The Potentiation of industrial biocide activity with $Cu^{2+}$. II. Synergistic effects with 5-chloro-2-methyl-4-isothiazalin-3-one. International Biodeterioration. **1990**, *26*, 303–313.
25. Miller, G.A.; Lovegrove, T. Isothiazolone, a new class of antifoulant toxicant. J. Coatings Technol. **1980**, *52* (661), 69–72.
26. Kappock, P.S.; Flaherty, P. Discoloration prevention in pyrithione-containing Coating Compositions. US Patent 5,939,203, 1999.
27. Kappock, P.S.; Waldron, C. In-can and dry film antimicrobial. US Patent 5,518,774, 1996.
28. Kempson, A.K. The microbiological deterioration of paints. Austr. OCCA Proc. News November, 1976; 1976; 5–14.
29. Jakubowski, J.A.; Gyuris, J.; Simpson, S.L. Microbiology of modern coatings. J. Coatings Technol. **1983**, *55* (705), 49–53.
30. Cornish, A.; Hodge, D.; Sianawati, E. Chemistry is the key to microbiology for coatings. Paint Coatings Ind. June **2000**, 76–78.
31. Kappock, P.S. Fungicide concentration gradient: A formulation variable. Mod. Paint Coatings March **1997**, 35–38.