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Saving the Paints from Constant Threat of Microbial Attack

Paint has become the most essential item in modern times, whether it is meant for residential purposes, or industrial applications. Decoration and protection are two main purposes of all paints. Therefore, 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 formulating paints, newer and safer pigments, and innovative formulation as also application technology of paints for their usage. These efforts are oriented to achieve better chemical properties of formulated paints, so that paint films would give extended life to the satisfaction of the ultimate customers. A new parameter added to these technical developments, is to probe the microbial stability of paints, since any such growth on painted surface is known to deteriorate the functional usage of paints. This property has assumed prime importance in modern times, last two decades, in paints used in homes. Paint applied in residential complexes, for exterior or interior use, can be grouped into two general categories, waterborne and solvent borne, and it typically has two basic functions, protection and decoration. Contamination of paint, by microbial growth in it, in either the wet state or on dried film can destroy these functions, leading to both aesthetic and physical degradation of the painted surface. For this reason, millions are spent annually by the paint industry on chemicals to protect their paint from microbial damage. These chemicals are called as Paint Preservatives.

The protection of paint from attack by microorganisms is an area of the coatings formulation that is often misunderstood. This note provides an understanding of microbial contamination and can assist coatings manufacturers in preparing to do battle with the problems created by microbiological organisms.

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, as do algae, which are unicellular or filamentous organisms that require light. <u>While 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</u>. (Unfortunately, in solvent-borne coatings, hardly anyone adds film protecting preservative, but film's deterioration in talked about from every other angle and lot of experimental work goes in to seek improvements, except towards microbial probing.)

To control these troublesome organisms, coatings formulators use microbiocides, or paint preservatives, that fall primarily into categories: bactericides, fungicides and algaecides. Bactericides come under the general identification of in-can preservatives and are designed to prevent microbial deterioration that results in spoilage of waterborne paint. <u>Fungicides and algaecides are to be predominantly included in a formulation to inhibit the growth of fungi and algae on the dry film of both water- and solvent borne paint.</u> This combination offered in a formulated form, but with certain well-defined technology behind, is called as Paint Preservatives in general.

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Wet-state contamination

A can of waterborne paint is an ideal environment for microorganisms (bacteria/fungi) to grow in due to the available nutrient sources (surfactants, thickeners, de-foamers, minerals etc.), available water supply, adequate oxygen supply, and suitable pH (most bacteria prefer 3.0–10.0). Bacterial contamination, especially of products “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.

Aqueous raw materials, notably surfactants, wetting agents, de-foamers, polymer emulsions, pigment dispersions and china clay slurries, are themselves susceptible to microbial degradation. Unless these materials are manufactured under relatively clean conditions and with biocidal protection, they can become contaminated, thereby introducing that contamination into the finished product. The largest agency for carrying the contamination further is water, particularly recycled water, or stored water. DM water is not free of micro-organisms, contrary to general belief.

Powdered raw materials, including fillers/extenders (minerals), starches, pigments and others, particularly those originating from natural sources, are most frequently heavily contaminated with spores of bacteria and fungi. They add further to problems of Paints.

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, it cannot be. Storage and mixing tanks may be open to the air or subject to considerable condensation when closed.

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. Similarly, accumulated dried and semi-dried products in mixing vessels, storage tanks, pipe-work, and filling lines can also become contaminated and, in turn, infect new product with which they come into contact. Coatings manufacturers should be aware of and address all of these potential infection sources to minimize the risk of contamination, and simultaneously protect their paints from microbial attack.

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 smaller compounds that are no longer capable of functioning as a thickener. For example, cellulose used as the thickening agent in a majority of waterborne paints is attacked by cellulytic enzymes and is degraded to cellubiose. The cellubiose is then further degraded to glucose or other sugars those bacteria and fungi ferment, producing acids and carbon dioxide. The production of acid formed by the degradation can significantly lower the pH, possibly resulting in further stability problems. As the breakdown of the thickener continues, the paint separates and suspended solids drop to the bottom of the container. In addition to the loss of viscosity, other effects can also be seen in contaminated paint.

Since carbon dioxide is also produced, it is common for contaminated paint to have foul odors, bulging cans, and even lids that pop off the containers. Finally, the paint may become discolored and have a stringy appearance. Occasionally a coating displays gassing or a loss of viscosity that was not instigated by chemical causes, nor are any microorganisms present. The most common reason for this occurrence is that microorganisms were present but eventually died or were killed in the coating environment.

A second explanation is that an enzyme was introduced into the system with a raw material, and there was no bacterial contamination of the paint. Another potential reason is that a microorganism exists in the system but was not found by the normal test methods for aerobic bacteria, which uses specific food media and is carried out in the presence of air. Such microorganisms may have specific nutritional requirements or they may be anaerobic and thus are inhibited, or killed by atmospheric oxygen. This would explain why no bacteria would be found with traditional test methods.

Anaerobic microorganisms in the finished paint, raw materials or wash waters function differently than their air-loving cousins. Anaerobic bacteria oxidize organic matter using electron acceptors other than oxygen for nutrients. In carrying out their metabolic processes, they produce carbon dioxide, water, hydrogen sulfide, methane gas, nitrogen, ammonia, reduced organics and more bacteria. The degradation activities of anaerobic organisms are the result of a hydrolytic or simultaneous oxidation-reduction-type reaction, which most often leaves large acidic fragments in the paint. These acids could react in the paint with any calcium carbonate or a secondary pigment that is present as filler and produce carbon dioxide gas. Even though anaerobic organisms produce a series of compounds different from aerobic bacteria, in the end, as far as the paint manufacturer is concerned, the results are similar: loss of viscosity, production of offensive odors, color changes, and/or gassing.

The most common bacteria found in paint fall into two main categories: gram-negative and gram-positive. **Gram negative** means that during the accepted staining procedure the bacterial cells are stained red, where as for **gram-positive** bacteria, the cells are stained purple. Alone, the staining procedure tells very little, as it is simply a means of differentiating bacteria. However, the gram-negative organisms are prevalent in contaminating waterborne paint, and the few gram-positive organisms that do appear are considered to be just fellow travelers. Except for an occasional situation, gram-positive organisms are not considered the primary culprits in contamination.

The following gram-negative organisms are commonly found in contaminated waterborne paint: *Pseudomonas* sp., *Enterobacter* sp., *Proteus* sp., *Micrococcus* sp. and *Aerobacter* sp. Gram-positive organisms of the Bacillus sp. may also be found in contaminated paint.

The following anaerobic species have been isolated from contaminated waterborne paint: Bacteriodes and Desulfvobrio, which are gram-negative, and Clostridium and Lactobacillus, which are gram-positive.

Knowledge of why, where and when microbial contamination can occur would alleviate many problems that coatings manufacturers encounter. A common-sense approach should always prevail. The coating manufacturer should recognize that contamination can be introduced through the raw materials, and that the microbiocide should be added early in the production process. Keeping the plant as clean as possible, and paying special attention to the cleanliness of the mixing vessels, pipe-work, hoses, and storage tanks would stop or curtail any plant-related problems. Clean environments in conjunction with an in-can preservation program can minimize any loss due to contamination. In general, a statement can be made that **such preservatives should be used at the earliest stage during the manufacturing operations.**

Today, it is meaningless to talk about ‘In-can preservative’, the concept has gone further to ‘Wet state Preservation and preservatives’ and it holds many dimensions. We will be talking on them separately later.

The few of the Wet-state preservatives from Melzer range:

(i) **Microcheck MZ 36**

(ii) **Microcheck MZ 3H**

(iii) **Microcheck MZ 521**

(iv) **Microcheck MZ 408**

(v) **Microcheck MZ BT20, etc.,**

Melzer offers to clients, who are Paint Manufacturers, microbial status testing services for the paints formulated with Preservatives from this range. Thus it is possible to verify the optimum performance expected from such paints. However, such tests cannot lead anyone to predict the life of the paint; what would the best known is the profile of microbial resistance that a paint has achieved by addition of the respective dosage of paint preservative/s.

As an example, photograph below is a typical presentation of Microbial Analysis of a paint, in which Microcheck MZ 36 was used as "wet-state preservative", (which would not allow deterioration of paint in the sealed can by way of microbial growth in paint,) the dosage was 0.15% w/w. In the absence of preservative, the paint has shown the bacterial growth.

Dry Film Preservation

Surface growth of fungi and algae has been recognized for many years as the major cause of disfigurement and deterioration of the dry film of both water and solvent borne coatings. This defacement is a serious problem that requires expensive and sometimes extensive actions to repair; apart from that; such growth on paint films causes serious health problems too. This subject, of providing long life to the film of dry paints by avoiding the microbial growth on the film, has been in limelight. This is so, especially since some of the materials used in earlier decades for film protection, such as mercury salts, chlorinated phenols and phenates etc., have been banned throughout the World due to their very high toxicity to human, as also due to damage that they cause to environment by contamination. Thus newer materials to be used as Dry Film Preservatives need to be effective enough, but friendly to human and Nature. The control on the toxicity from usage of such DFP is a responsibility for both, paint manufacturer as also biocide supplier.

(a) Fungal growth on dry film of Paint

Fungal growth can be found in many areas in and around the home: bathrooms, basements, and garages, any location that is warm, damp, and in proximity of high humidity. On exterior surfaces, fungal growth is often heaviest in locations where shrubbery or shade trees restrict rapid surface drying and on north-facing walls. Paint surfaces protected from direct rainfall accumulate detritus (products of disintegration or wearing away) and fungi.

In general, fungi develop more commonly on paint coated over wood surfaces than on metal or masonry. It has been shown that wood substrates can provide nutrients from their water-soluble extractives that diffuse into the paint film and can be a significant moisture and food source. Certain species of wood are more fungal resistant than others (i.e., cedar), while most species of pine exhibit relatively little fungal resistance. Paint disfigurement results primarily from the growth of pigmented fungi and the development of spore clusters on the coated surface. The aesthetic properties of the paint film are often further reduced by the accumulations of dirt and airborne detritus that cling to the sticky exposed mycelia or spore clusters. Optimum fungal growth conditions include a humid environment and a neutral-to-acidic pH with an organic food source with less available sunlight.

The addition of an effective fungicide to the paint formulation during production provides protection during both storage and use.

A key variable in the susceptibility of a coating to fungal attack is the formulation itself. Once applied to a surface, emulsion paint loses water by evaporation, and the polymer particles coalesce to form a paint film that contains pigments plus residues of the various components and additives of the paint. The types and amounts of these residues will significantly influence microbial susceptibility of the film.

The organic nutrients required by fungi may also come from an accumulation of organic debris, such as airborne dirt. Given a suitable moist or humid condition, fungal spores present on the surface of the susceptible paint film will germinate to produce a fine network of filaments (hyphae) or colonial growth.

The most common fungal species found on contaminated dry paint film are *Aureobasidium*, *Alternaria*, *Aspergillus*, *Cladosporium* and *Penicillium*. However, the dominant fungal species will vary with the climate and condition of the paint film.

The addition of an effective fungicide to the paint formulation during production provides protection during both storage and use. Ideally, fungicides must be highly effective against fungi, nonvolatile, safe in handling and use, environmentally acceptable, compatible with other paint components, have limited solubility, and produce no color changes.

'Dry Film Preservatives' used in paints is quite a complex subject by itself. There is much to know, but the subject is often too simplified. At the same time, many questions that are related to dosage and performance of DFP had remained unanswered over more than two decades, where Melzer has done lot of contributions while attempting to provide the answers. It is not that the usage of such DFP in certain dosage solves the problems in paints in a magical manner; rather proper integration of paint formulation and choice as well as proper dosage of a DFP is very essential in order to give a good performing paint to customers, and such paint should be environmentally safe too. Often such requirements are overlooked, but that has already created an alarming situation..

A few of Dry film preservatives from Melzer range:

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(i) **Microcheck MZ 33**

(ii) **Microcheck MZ 90**

(iii) **Microcheck MZ 96**

(iv) **Microcheck MZ 27**

(v) **Microcheck MZ 123**

(vi) **Microcheck MZ P01**

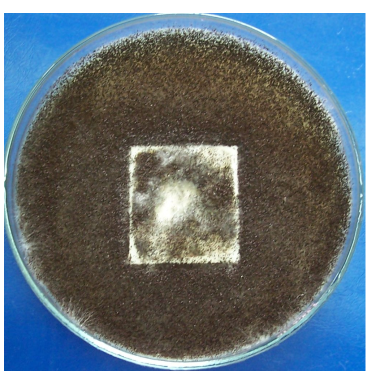
(vii) **Microcheck MZ 906**

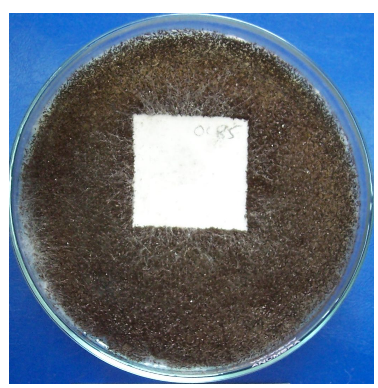
(viii) **Microcheck MZ 810, etc.,**

All these formulated products are very strictly handled on quality and performance expectations at Melzer. Ensuring the Human and Nature-safety from the usage of these preservatives are the most important criteria while formulating these preservatives. In fact, every DFP from above has been a speciality by itself, and it has been designed innovatively, but while doing so, it has been ensured that none is crossing the guidelines provided by Biocide Product Directives for the safe and continued usages. A few of these formulations are globally unique and are recognized today as Melzer's primary contributions to microbiocide technology.

Once again, Melzer offers the services of microbial performance evaluation of paints formulated with dry film preservatives, with respect to prevention of growth of fungi and algae on dried paint film.

As an example, photograph below is a typical presentation of Microbial analysis of a paint film. Microcheck MZ 33 was used as Dry film preservative in paint; the dosage was 1.2 % w/w. In the absence of preservative, the paint film (on left) has shown fungal growth.





(Well-protected paint film from fungal growth.)

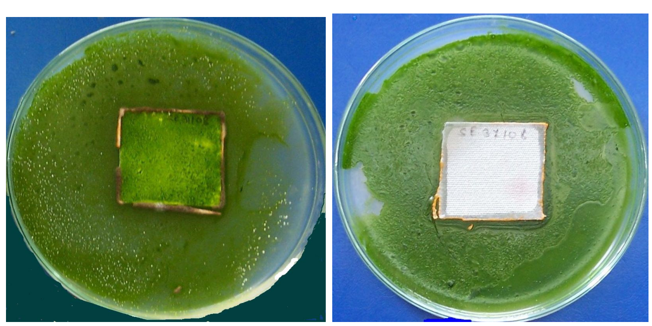
(b)Algal growth on dry film of Paint

In addition to fungi, algae are the other main organisms that disfigure dry paint films. Algae are sometimes confused with fungi, especially if the color of the algae is black, brown or orange instead of the more common green. Growth of algae is vegetation. Algal growth requires high humidity, a neutral-to-alkaline environment, and light to allow for photosynthetic processes. To facilitate growth, algae also need trace minerals, which they can find on masonry surfaces. Protection of the dry film from algal disfigurement has become almost compulsive trend in the paint industry, for water borne paints but it has to be the same story for solvent borne paints too.

For algae to grow on coated surfaces, the criteria previously stated must be met. The growth can be rapid and take place over a wide temperature range. Algal growth is mainly a problem of appearance, as it does not primarily cause damage. Direct deterioration by these organisms is not considered detrimental; however, their capacity to hold water may indirectly result in significant damage. With their chlorophyll and light use, algae can build up organic material from water and carbon dioxide, which can then serve as nutrient material for fungi and other microorganisms. Algal growth in temperate climates tends to be profuse but is much more prolific in the tropics. As with fungi, their initial disfigurement effects result in the discoloration of coatings applied to masonry, metal, timber and other substrates.

The following are representative algal species that have been isolated from contaminated paint surfaces: Chlorella, Chlorococcum, Oscillatoria and Trentepohilia. Since algae obtain their nutrients by photosynthesis, the addition of an algaecide that disrupts this process can prevent growth and development

As an example, photograph below is a typical presentation of Microbial analysis of a paint film. Microcheck MZ 33 was used as Dry film preservative in paint, the dosage was 1.2 % w/w. In the absence of preservative, the paint film has shown algal growth.



(Well-protected paint film from algal growth.)

Can one load excess of dry film preservative in a paint to get the best performance? What would happen if the dosage of a dry film preservative were kept too low to control the cost component of paint?

These two questions in fact define the best performing paint, apart from the right choice of preservative as the primary one, which is most responsible for it!

Empirical experiments have suggested the best range of optimum dosage for almost all dry film preservatives in paints at around 1.0 to 1.5% w/w, depending of course on paint formulations and applications. However, it is not uncommon to find a few paint manufacturers using far lower dosage in the paints. Often, the presence of preservatives in very low dosage is of no value to the performance of such paint in actual environment, and these paints fail.

Secondly, it is realized by now that loading the finishing paints with dry film preservatives with such dosage, and leaving the under coats, such as primers and surfacers without a dry film preservative in them, is expecting too much from too thin a build up on a wall! Thus, primers, surfacers and filling putties used on wall also need to be dosed with appropriate dry film preservative at right dosage, so as to get the best long duration performance from this entire system of paints.

Finally, the components or the active ingredients of dry film preservatives should not cause harm to Nature too. Of course, much depends on the way the paint is formulated, in order to avoid the ill effects that are often caused by such components of dry film preservative used in paints. The ill effects mainly occur due to rains received by the painted surface.

Leaching of the components of dry film preservative (that means wash off of such components) from the paint film due to excessive rains falling on painted surface, thereafter these components entering into soil below through the seeped water, their retention in soil thereafter for indefinite period due to their non-biodegradation, damaging the water reservoirs by their presence and thereby the worst-effect transferred on environments on many fronts from these components from ill-formulated paints have become serious issues today. Unfortunately, many microbiocide suppliers have not addressed them rightly. Most often, it is possible to formulate these kinds of preservatives with utmost care, so as to minimize the leaching property, but at the same time getting the best performance of paints; and once again, Melzer has carried out distinct work on these issues and have found almost the best possible solution to avoid such damage to the environment caused by the paints.

Typically, on-the-site photograph as below, is of a painted bungalow façade, which has very small size wall. The photograph shows the damage to the environment, which has been caused by the leached component of a dry film preservative used in the formulation of paints due to rainwater flowing down from the painted surface (wall). One can see, that in the band, which has received rainwater directly from the painted surface, the soil has been damaged by contamination to almost permanently non-fertile state, and grass failed to grow in this band, whereas it has shown reasonable growth elsewhere if not good growth which was expected. The only solution to this would be to replace the soil in that zone!!

What would happen to the environment if the wall receiving the paint were to be a multi-storied building? And many such buildings were to use this paint? It is a serious issue indeed.

Usage of a right dry film preservative in right dosage and well-controlled paint formulation can definitely avoid this ill effect.

Conclusion

Microorganisms are capable of the destruction and disfigurement of both water- and solvent borne coatings, costing the coatings manufacturer and consumer millions per year in contaminated material and damage claims. Under favorable conditions such as an ample supply of nutrients, moisture and proper temperature etc., microbial contamination of unprotected coatings is a virtual certainty. With a minimal amount of effort and some common sense formulating, coatings manufacturers can ensure that their coatings are protected in the can, in use, and on the dry film. Preventing microbial contamination is the most crucial element in the fight against microorganisms. The best line of defense is a regimen that entails the use of microbiocides, proper house cleaning, and knowledge of the factors that contribute to microbial attack.

It is equally important to note that most often corrosion is initiated and propagated by the growth of microbes on the surface of the dry film, and not by chemical attacks alone. Or, after initial chemical attack, microbes take over to deteriorate the dry films faster thereafter. It is hard to realize that most of the pipelines in open and unattended areas are damaged not merely by atmospheric corrosion, but by the corrosion set in by microbes. While Paint Companies pay lot of attention to create chemical resistant paint media as best as possible; neglect towards microbial attack on dry film under favourable conditions is often from a lack of awareness on microbial behaviour. Therefore, every application where corrosion control is the basic aim needs to have well-protected paints, which makes the use of dry film preservatives mandatory in all paints. The paints, which show chalking, are the subjects of microbial growth, and very rapid corrosion beneath the apparently good-looking (or continuous) film of paint sets in before it is noticeable. In such cases, it is too late to rectify the damage caused to the substrate by these microbes, including sulphate-reducing bacteria, by way of metal erosion**;** atmospheric exposure worsens the situation to higher state of corrosion, leading to compulsive replacement of metal. A paint technologist critically pays attention to the paint composition on experiencing such corrosion, rather than giving sufficient thought to the simultaneous basic need of preventing the microbial growth on such paints. We in Melzer in fact isolated the microbes involved in corrosion and could physically show microbe-induced-corrosion on NACE test panels. It has been a mis-concept that the solvent based paints, including epoxy and polyurethane, least to talk on latex, do not require any such extra protection due to the chemistry of such paints.

Of late in 2005, it is advised to use Dry Film Preservatives in Automobile Coatings as their performance is noticed to be better than before, which marks a beginning of a new revolution in Paint Industry; though Marine Coatings already make use of new generation tin-free DFP as anti-foulants.

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