AN EFFECTIVE AND HIGH PERFORMANCE NEW BIOCIDES BLEND FOR IN-CAN PRESERVATION OF PAINTS

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INTRODUCTION

Paints are susceptible to microbial contamination, which can result in malodors, changes in pH, discoloration, off-gassing that can cause packaging deformation, and loss of physical properties that provide product functionality. Microbial contaminants can be introduced from water, raw materials, processing equipment, or poor plant hygiene. Bacteria are the most common microbial contaminants that attack wet paints, but mold and yeast may also cause deterioration. To prevent microbial contamination, paints require the addition of an effective antimicrobial that can provide protection during the manufacturing process and also during an appropriately long shelf life period.

Preventing paint damage due to microbial contamination is important to manufacturers, as customers demand high quality products. Damaged products are usually returned to the production facilities to be reworked or disposed, causing important economic losses and damaging the manufacturer’s reputation. This is the reason manufacturers require a robust antimicrobial that is effective against a broad range of microorganisms, including isolates from industrial facilities that are usually more resilient. There is a broad range of antimicrobials with different chemical and biological properties available in the market, and one can be more appropriate than another depending on the paint formulation or manufacturing processes. (3)

One antimicrobial agent that has been traditionally used in the paint industry, particularly in low-cost products, is free formaldehyde. However, due to increasing regulatory restrictions and safety concerns regarding human exposure, the use of free formaldehyde as an in-can preservative for paints is decreasing worldwide. Alternative products that are competitive both in performance and cost-to-treat are needed. Combining two or more antimicrobial agents with different properties and modes of action in a synergistic way can establish better performance and much more efficient microbial control. This approach also allows the use of well established antimicrobials while also creating novel solutions for formulators concerned about bacterial contamination problems (3).

A new in-can antimicrobial product was developed to address the need for a cost effective antimicrobial that does not contain free formaldehyde. This product is based on isothiazolinones (IT) in combination with a controlled-release formaldehyde compound (FR) called BIOBAN™ 616 LA Antimicrobial. Some ITs have been known for years as quick-acting biocides that utilize a two-step mechanism that results in the quick disruption of metabolic pathways that regulate critical functions in microbes (6). ITs inhibit microbial growth, halt bacterial respiration, react with protein thiol groups, and produce free radicals; these mechanisms give them a broad spectrum of activity at low usage levels (6).

In contrast, the reaction of a FR, a protein denaturant with receptive proteins, occurs rapidly, causing loss of viability of the cell and, consequently, cell death. This action is pH-dependent, working better at alkaline pH (1). FRs have been used in paints and other industrial applications because they are economical and effective...
against a wide variety of microbial contaminants. However, there are many types of FRs in the market. To identify the best FR to form a synergistic blend with ITs, extensive tests were conducted. The identified FR is highly water soluble, compatible with most water based formulations. The combination of ITs with an appropriate FR can provide a fast-acting preservative with long lasting protection. BIOBAN™ 616 LA Antimicrobial is an effective preservative that can be used under a typical range of pHs and temperatures for the preservation of water based systems such as polymer latexes and emulsion systems, paints, coatings, and adhesives. In addition, unlike other commercial antimicrobials containing FR, BIOBAN™ 616 LA Antimicrobial has almost no odor.

**METHODOLOGY**

Extensive efficacy testing was conducted in different types of paints, ranging from economical to premium ecological (low-VOC) paints from different manufacturers from South, North and Caribbean areas of Latin America. Efficacy was evaluated by challenging the paints dosed with different concentrations of the biocide against a “pool” of laboratory strains of bacteria (at $5 \times 10^6$ CFU/mL) that are common microbial contaminants found in paints: *Pseudomonas aeruginosa* (ATCC #10145); *Staphylococcus aureus* (ATCC # 6538); *Enterobacter aerogenes* (ATCC # 13048). Four consecutive challenges (inoculations) against the pool of microbes were performed weekly. These challenges represent the different stages of the process of paint production during which a paint product can get contaminated with microorganisms. The first challenge represents bacterial introduction from incoming raw materials; the second from equipments used during the manufacturing process; the third is from canning process, and the fourth represents the microbial introduction by the end user. The bacterial challenge testing was conducted using Dow Microbial Control’s proprietary TAUNOVATE® High-Throughput Testing (HTP) system (shown in Figure 1A). This is an automated system that can provide multiple data points for multiple biocides in a very short time. The use of conventional methods for a similar study is more resource-intensive and requires much more consumable materials, space, and more time to complete (Figure 1B).

**Figure 1A.** The Taunovate High-Throughput Testing system. *Photo credit: Jamie Munda*

**Figure 1B.** Standard microbiological evaluation requires large number of plates and sample cups. *Photo credit: Jamie Munda*

**BIOCIDE EFFICACY**

The antimicrobial efficacy of BIOBAN™ 616 LA Antimicrobial in paints from four different LAA regions is summarized in Figure 2. Three out of four of the paints tested required only 666 ppm of BIOBAN™ 616 LA Antimicrobial to provide an effective protection from bacterial spoilage, while only one of them, a low-VOC premium product, required 2000 ppm for effective protection. It is very common for low VOC paint to require a higher biocide dosage for good preservation since this paint is much
more susceptible to microbial growth. Manufacturers are also reporting increased incidences of microbial contamination in their low-VOC products, so they demand robust preservation alternatives that usually involve higher doses of biocides.

**Effective of Bioban™ 616 LA Antimicrobial (ppm)**

![Bar chart showing effective dosages in different paints](image)

*Figure 2*- BIOBAN™ 616 LA Antimicrobial effective dosages in different paints

**BENCHMARKING**

The performance of the BIOBAN™ 616 LA Antimicrobial was also compared against other commercial antimicrobial used in the paint industry. The first group of commercial antimicrobials evaluated contained ITs and different FRs similar to BIOBAN™ 616 LA Antimicrobial. The second group was the previously leading antimicrobial that contains formaldehyde (FA), and, finally, the third group was antimicrobials without any FR or FA. The four consecutive challenge tests in economical paint against a variety of microorganisms were performed, and the results are summarized in *Figures 3A and 3B*. The effective dosage is determined using the criteria of no bacterial growth at maximum 24 hours contact time and after 4 cycles of repetitive challenges.

*Figure 3A* shows the efficacy results of BIOBAN™ 616 LA Antimicrobial compared with a variety of in-can preservatives available in the market against a pool of laboratory strains of bacteria that are common microbial contaminants found in paints: *Pseudomonas aeruginosa* (ATCC #10145), *Staphylococcus aureus* (ATCC # 6538), and *Enterobacter aerogenes* (ATCC # 13048) at 5 x 10⁶ CFU/mL. The paint tested required only 500 ppm of BIOBAN™ 616 LA Antimicrobial to provide effective antibacterial protection. BIOBAN™ 616 LA Antimicrobial performed at least as well as similar products in the market and outperformed all FA or FA-containing antimicrobials. BIOBAN™ 616 LA Antimicrobial also outperformed antimicrobials containing Benzisosothiazolinone (BIT, 1250 ppm), Methylisothiazolinone (MIT, 1000 ppm), and Chloro-methylisothiazolinone (CMIT, 750 ppm). BIOBAN™ 616 LA Antimicrobial is much more efficient than most common in-can preservatives in the market.
Currently, paint manufacturers demand efficient long-term preservation of their products not only against common laboratory microbes, but also against bacterial strains found in manufacturing facilities that are usually more resilient. The exceptional efficacy of BIOBAN™ 616 LA Antimicrobial was not limited to laboratory strains; the performance of the blend was also evaluated against bacteria recovered from contaminated paints. The results after four bacterial inoculations at $5 \times 10^6$ CFU/mL in an economical paint sample from a Brazilian manufacturer can be found in Figure 3B. As expected, higher dosage is needed against field isolated strains. However, only slightly higher dosages are needed for BIOBAN™ 616 LA Antimicrobial to achieve effective preservation. BIOBAN™ 616 LA Antimicrobial provided an effective level of protection at 750 ppm. In this study, BIOBAN™ 616 LA Antimicrobial’s performance is comparable to other IT+FR products. BIOBAN™ 616 LA Antimicrobial also showed similar activity trends to those previously described against other commercial products. From the performance data obtained against laboratory strains and microbes isolated from contaminated paints, we conclude that the effective dosage of BIOBAN™ 616 LA Antimicrobial is 750 ppm.

**Figure 3A.** Comparison of BIOBAN™ 616 LA Antimicrobial efficacy performance with other in-can preservatives in the market, against laboratory bacterial strains.
Figure 3B. Comparison of BIOBAN™ 616 LA Antimicrobial efficacy performance with other in-can preservatives in the market, against bacterial strains isolated from industrial facilities.

COMPATIBILITY

Antimicrobials used to preserve paints should not cause any adverse affects to the paint formulation. Compatibility of an antimicrobial with different paints is very important. Some physical properties, like pH, viscosity, color and gloss of paint may be affected when an antimicrobial is added. In order to obtain the maximum impact of BIOBAN™ 616 LA Antimicrobial on the physical properties of different commercial paint samples, the highest BIOBAN™ 616 LA Antimicrobial concentration, 2500 ppm, is used. An evaluation of BIOBAN™ 616 LA Antimicrobial's compatibility at this concentration was performed before and after 1 month of accelerated heat aging at 40°C. The pH and viscosity results can be found in Figures 4 and 5, and the color and gloss results are summarized in Table 1.
Figure 4. pH of various paints treated with BIOBAN™ 616 LA Antimicrobial at 2250 ppm before and after heat aging for 1 month at 40°C.

The results indicate that the variation of pH on the paint samples tested was minimal and did not change with heat aging; results presented a variation under 2% that is not considered significant. When the viscosity was evaluated, minimal differences were again observed; one sample varied 3.33%, while the others were close to or under 1% variation. These results indicate that BIOBAN™ 616 LA Antimicrobial does not significantly affect these physical properties of paints. Similar effects to the color and gloss of paints were observed. Based on color measurement using the CIEL a*b* method, neither whiteness (L) nor yellowing (b*) number showed a deviation of 0.25 unit compared to unpreserved paints. No variation was observed in
gloss of paint either. The results clearly show that there is practically no difference in color and gloss of the paint samples dosed with BIOBAN™ 616 LA Antimicrobial when compared with the samples without biocide. The overall results indicate that BIOBAN™ 616 LA Antimicrobial is highly compatible and can be used on different types of paints without affecting their physical properties in a significant way.

<table>
<thead>
<tr>
<th>Type of paint</th>
<th>Color (CIE La<em>b</em>)</th>
<th>Gloss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CIE L</td>
<td>CIE a*</td>
</tr>
<tr>
<td>Economical A</td>
<td>95.39</td>
<td>-0.19</td>
</tr>
<tr>
<td>Economical B</td>
<td>94.90</td>
<td>-0.02</td>
</tr>
<tr>
<td>Premium A</td>
<td>96.43</td>
<td>-0.36</td>
</tr>
<tr>
<td>Flat Paint</td>
<td>99.80</td>
<td>-0.11</td>
</tr>
</tbody>
</table>

*Table 1* Color and gloss of various paints treated with BIOBAN™ 616 LA Antimicrobial at 2250 ppm before and after heat aging for 1 month at 40°C.

**STABILITY**

Efficacy testing is critical to determine the proper biocide concentration to preserve paints effectively. To achieve a consistent preservation, good biocide product stability is required. Since generally biocide concentration used for in-can preservation is at ppm levels, a variation in the biocide product can affect the preservation effectiveness. Not knowing the stability of the biocide product used will make the shelf life of paints unpredictable. Paints will become more susceptible to microbial contamination, and eventually microbes will become more tolerant to biocide and higher biocide dosage will be required.

In order to test the stability of the formulation, BIOBAN™ 616 LA Antimicrobial was subjected to accelerated heat aging at a minimum of three months at 40°C. This accelerated aging represents 1 year of stability. After this period the active ingredients of the formula were evaluated using high performance liquid chromatography (HPLC). BIOBAN™ 616 LA Antimicrobial meets the stability required by the USA EPA requirements (< 5%). The result of this test is shown in *Table 2*.

**Heat aging during 3 month at 40°C**

*active ingredient % remaining*

<table>
<thead>
<tr>
<th>Isothiazolinones blend</th>
<th>FR</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIOBAN™ 616 LA Antimicrobial formulation</td>
<td>96.09 %</td>
</tr>
</tbody>
</table>

*Table 2: Stability of the active ingredients of BIOBAN™ 616 LA Antimicrobial after three months of accelerated heat aging at 40°C (representing 1 year of stability).*
CONCLUSIONS

Increasing safety concerns and regulatory restrictions for the use of free formaldehyde as a biocide for in-can preservation of paints has generated the need to create alternative products that are more competitive in antibacterial performance (particularly in cost-to-treat) and have better Environmental Health and Safety (EH&S) profiles than free formaldehyde antimicrobials. To respond to this challenge and to meet market needs, an extensive test of various biocide combinations was conducted and BIOBAN™ 616 LA Antimicrobial, a new alternative for in-can preservation of paints, based on a blend of isothiazolinones and a controlled release formaldehyde compound, was developed.

The strength of the new BIOBAN™ 616 LA Antimicrobial was assessed through challenge testing against bacteria typically present in contaminated paints, such as P. aeruginosa, S. aureus, E. aerogenes and, more importantly, against wild type strains isolated from contaminated paints. These challenge tests were designed to simulate repetitive microbial inoculations that may occur during the paint production process due to bacterial contaminants present in water, raw materials, from the equipment used in the production and canning processes, or finally from the end user.

The results demonstrated that the new BIOBAN™ 616 LA Antimicrobial product provides excellent in-can preservation at low doses (in the range from 750 to 2000 ppm) against both laboratory strains and those isolated from the field. This new BIOBAN™ 616 LA Antimicrobial product is effective in a variety of paint types and had no undesirable effects on the physical properties (pH, viscosity, color, gloss) of paints. When the new BIOBAN™ 616 LA Antimicrobial was benchmarked against other commercially available biocide products, the new formulation demonstrated superior performance and better efficiency, particularly when compared with traditional products based on free formaldehyde, BIT, MIT, and CMIT/MIT. BIOBAN™ 616 LA Antimicrobial is also very competitive to other FR products with the added benefit of presenting almost no odor.

REFERENCES


