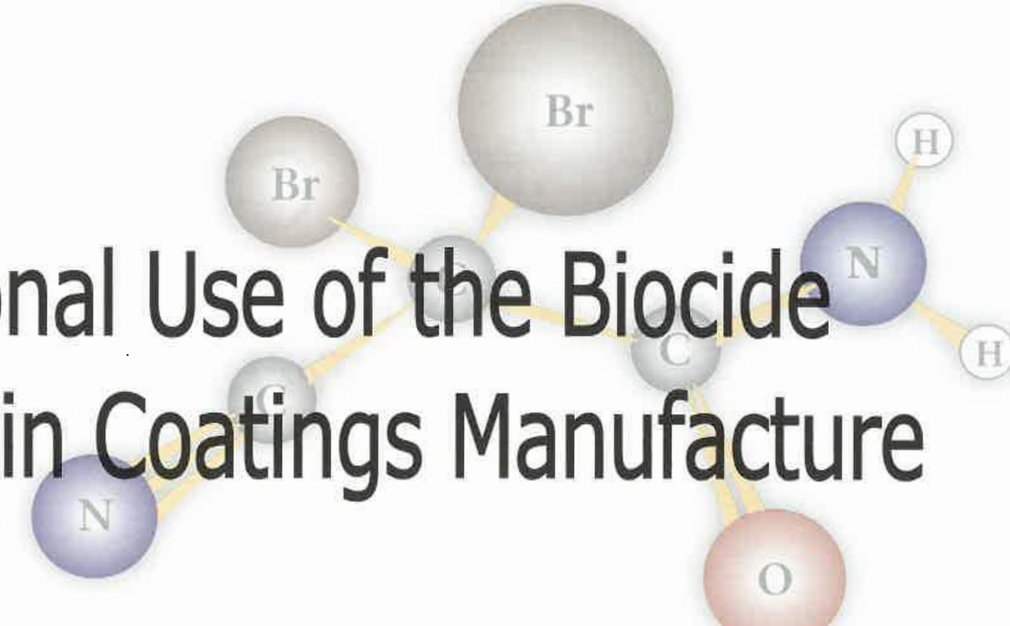

Nontraditional Use of the Biocide DBNPA in Coatings Manufacture

by Mary C. Chervenak, Gerald B. Konst, and William R. Schwingel

The Dow Chemical Company*

The synthesis and molecular structure of 2, 2-dibromo-3-nitrilopropionamide (DBNPA) was reported by Hesse in 1896,[1] but its antimicrobial properties were not discovered until nearly 50 years later. The DBNPA molecule was employed initially only as a seed fungicide,[2] but was later used as a slimicide in pulp and paper and in cooling water applications.[3] More recently, its use as an antimicrobial agent has expanded into enhanced oil recovery and into aqueous metalworking fluids.[4]

DBNPA is a powerful biocide with two unique properties: it kills microorganisms immediately upon addition and it degrades rapidly. Although DBNPA is compatible with many chemical classes, including oxidizing agents, it will react readily with nucleophilic agents and sulfur-containing reducing agents. The facile reaction of DBNPA with sulfur-containing nucleophiles common to microorganisms, such as glutathione or cysteine, is the basis of its mode of antimicrobial action. DBNPA is therefore not a typical oxidizing or halogen-releasing biocide. Unlike other thiol-reactive biocides, its action is such that thiol-based amino acids, like cysteine, are oxidized beyond the formation of disulfide species.[5] This reaction irreversibly disrupts the function of cell-surface components, interrupting transport across cell membranes, and inhibiting key biological functions. DBNPA degrades rapidly by both nucleophilic and hydrolytic pathways to relatively nontoxic products.[6] The rate of hydrolysis of DBNPA is strongly pH-dependent: at pH 6.0 and 25°C, the DBNPA molecule has a half-life of 155 hours (about 6.5 days), but at pH 8.0 and 25°C, its half-life is about two hours. The ultimate degradation products of DBNPA are ammonia, carbon dioxide, and bromide ion.

DBNPA, when formulated as a 20% solution in water and polyethylene glycol, is completely miscible with water and readily disperses upon introduction into a water-based system. The DBNPA molecule begins functioning as an antimicrobial agent immediately upon introduction into a system; the rate of this activity is not affected by pH and antimicrobial control is usually

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*1500 E. Lake Cook Rd., Buffalo Grove, IL 60089.

Figure 1A—Efficacy of a 20% DBNPA solution in contaminated paint wash water over seven days.

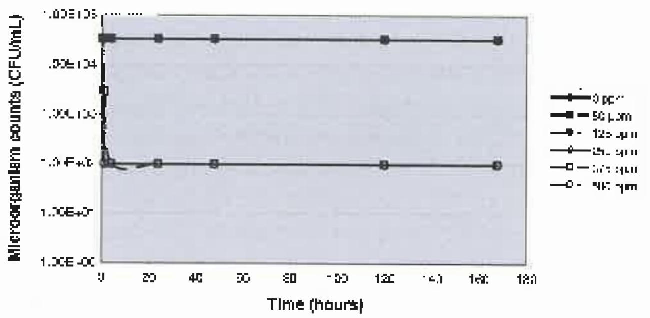
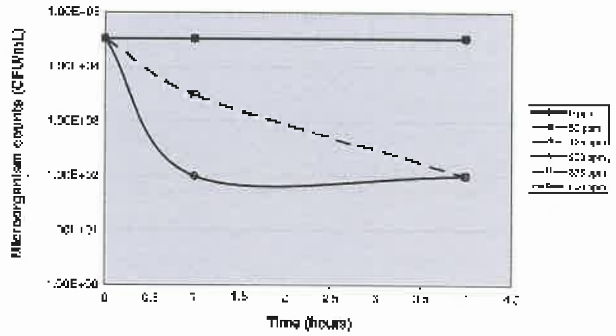


Figure 1B—Efficacy of a DBNPA solution in contaminated paint wash water during the first four hours after treatment.



achieved before complete degradation occurs. The combination of instantaneous antimicrobial activity and rapid chemical breakdown makes DBNPA a cost-effective biocide that swiftly degrades in the environment.

DBNPA AS A "QUICK-KILL" BIOCIDE AND SHORT-TERM PRESERVATIVE

These two complementary properties can be exploited when DBNPA is used as a quick-kill biocide and short-term preservative in water-containing systems that require microbial control. For example, a 20% DBNPA solution is ideally suited for treatment of waste water generated during the manufacture of paint. Paint manufacturers routinely recycle and store paint process/wash water to use as make-up water in future batches of paint. As paint companies become more conscious of their water use, they discard less and less during their manufacturing process. In the last 10 years, the National Paint & Coatings Association (NPCA) has recognized many paint manufacturers with Pollution Prevention Awards, honoring companies' outstanding efforts to protect the environment. The collection and reuse of all wash water used to rinse paint mixing vats have been emphasized as crucial to achieving environmentally responsible production. This wash water contains a high concentration of paint solids and is usually heavily contaminated with microorganisms; it must be decontaminated prior to its re-introduction into the paint-making process. DBNPA quickly and economically reduces microorganism counts in the wash water, preparing it for re-entry into the production cycle.

A seven-day study examining the effectiveness of a 20% solution of DBNPA in paint wash water determined that concentrations as low as 375 ppm (75 ppm as active DBNPA) controlled microorganism growth for the duration of the test. The process water samples arrived in the laboratory contaminated, with organism counts of 3.3×10^4. Fifty-gram samples were weighed into screw-cap jars and treated with a 20% solution of DBNPA (50, 125, 250, 375, or 500 ppm as product). An additional, untreated sample was used as a control. Samples were streaked on Tryptic Soy Agar (TSA) plates at the start of the study, and again after 4 hours, 24 hours, 48 hours, 4 days, and 7 days. DBNPA (as a 20% solution) concentrations of 50 and 125 ppm did not reduce the bacterial population over the course of the study. Concentrations of 250 and 375 ppm reduced the contamination to below the level of detection in 4 hr; a concentration of 500 ppm required only an hour for the same reduction. A minimum concentration of 375 ppm DBNPA (as a 20% solution) was required to maintain bacterial control for seven days (refer to *Figures* 1A and 1B).

DBNPA FOR TREATING CONTAMINATED RAW MATERIALS

Most water-based household and industrial products, ranging from laundry detergents to adhesives, are formulated with a preservative to maintain quality for the life of the product. The final formulation should be free of dangerous contamination upon packaging, and is ex-

Figure 2—Efficacy of a 20% DBNPA solution in a contaminated surfactant solution over seven days.

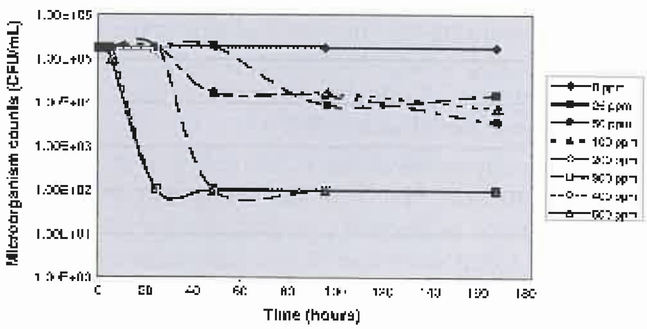


Figure 3A—Efficacy of a 20% DBNPA solution in contaminated latex over seven days.

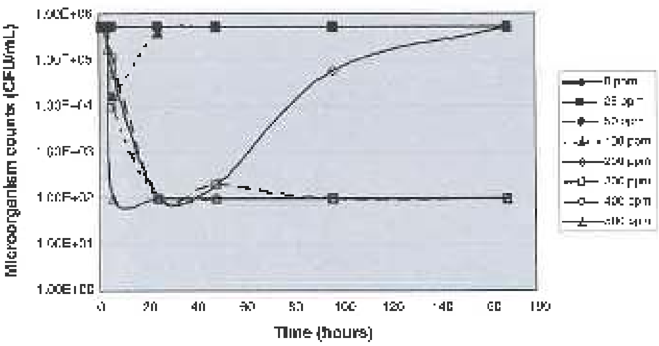
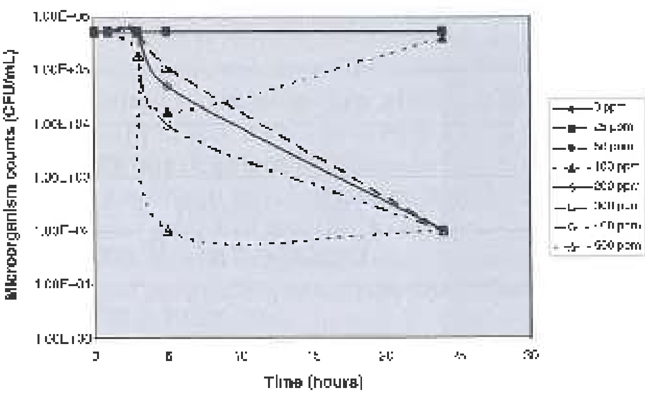


Figure 3B—Efficacy of a DBNPA solution in contaminated latex during the first 24 hours after treatment.



pected to remain preserved for a period of time despite repeated microbiological insults. However, contaminated raw materials, such as surfactants, latex, or mineral slurries, may stress the preservative system in the final formulation, resulting in spoiled or otherwise adulterated product. Mathematical models predict that DBNPA solutions will work effectively in systems where biocidal activity is required only briefly (hours rather than days or weeks).[7] Because the initial demand for DBNPA may be instantaneous and considerable, DBNPA provides only short-term biocidal activity in heavily contaminated systems. DBNPA therefore effectively decontaminates raw materials prior to their introduction into a formulation without disrupting the chemical balance of the final product. Longer-term preservation, however, may require the introduction of a slower acting preservative after treating the material with DBNPA.

A seven-day study where a 20% solution of DBNPA (25, 50, 100, 200, 300, 400, and 500 ppm [note: all concentrations as *product*) was used to treat an aqueous surfactant solution contaminated with microorganisms (1.8×10^5 CFU/mL) indicated that significant reductions in the organism population were observed with relatively low DBNPA concentrations. This study was conducted using the same protocol as that described for the study with the paint wash water samples. A 20% DBNPA solution, added at a concentration of 200 ppm (40 ppm active DBNPA) to the contaminated surfactant solution, dropped organism counts to below the detectable limit within 48 hours, and maintained the integrity of the solution for the entire seven day study. A slightly higher concentration, 300 ppm (60 ppm active DBNPA), reduced organism counts to below the detection limit within 24 hours, and controlled the organism population for the duration of the study (*Figure* 2). Similarly, treatment with a 20% solution of DBNPA reduced counts in contaminated latex (5.3×10^5 CFU/mL). A 20% solution, added at a concentration of 300 ppm, effectively killed most of the microorganisms after 24 hours, while 500 ppm achieved the same goal after only five hours (refer to *Figures* 3A and 3B).

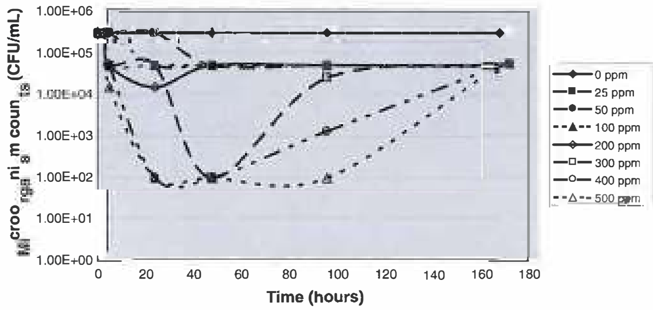
When lower concentrations of DBNPA are used in certain raw materials, like latex, microbial regrowth sometimes occurs. This regrowth is most likely the result of incomplete kill of the organisms already contaminating the material. An insufficient concentration of DBNPA will temporarily retard microbial growth, but rebound will occur as the molecule breaks down.

A 20% solution of DBNPA also worked well in two different mineral slurries. In a neutral titanium dioxide slurry, a DBNPA solution concentration of 500 ppm (100 ppm active DBNPA) reduced counts to below detection limits after 24 hours and a concentration of 1000 ppm (200 ppm active DBNPA) reduced counts to the same levels in less than two hours (*Table* 1). Although an alkaline calcium carbonate slurry proved more challenging to decontaminate, a concentration of 400 ppm (80 ppm active DBNPA) achieved greater than a three-log reduction within 24 hours. The speed and persistence of this reduction was improved as the concentration of DBNPA was increased. For example, a concentration of 500 ppm (100 ppm active DBNPA) reduced counts within 24 hours and maintained the reduced counts for at least 96 hours (*Figure* 4).

Table 1—Efficacy of a 20% DBNPA Solution in a Contaminated Titanium Dioxide Slurry

DBNPA Concentration (ppm as product)	Microorganism Counts (CFU/mL)	
	1.25 hr	24 hr
0	1700	4000
500	500	<100
1000	<100	<100
2000	<100	<100

Figure 4—Efficacy of a 20% DBNPA solution in a contaminated calcium carbonate slurry over seven days.



USE OF DBNPA TO RECOVER CONTAMINATED FINAL FORMULATIONS

Paint companies that manufacture interior and exterior water-based latex paint primarily for large commercial and government applications often formulate and package their products in sizable lots. Additionally, because some raw materials—particularly clay and calcium carbonate slurries—may be added directly to formulations with little clean up or antimicrobial pretreatment, the long-term preservative can, at times, be overwhelmed by existing bioburden. Periodic microbial problems are therefore not uncommon.

Paint formulations are typically preserved with a single preservative at a predetermined concentration. If an exceptionally large bioburden is present, insufficient preservation may lead to bacterial contamination in the paint. Bacterial contamination alters the character of the paint by causing viscosity loss and unpleasant odors; in addition, bacteria generate gas as a waste product which may result in bulging or exploding cans. Spoiled paint unsuitable for sale must either be reworked or discarded, which are expensive, time-consuming, and wasteful processes.

Routine pretreatment of raw materials with a solution of DBNPA decreases the demand on the long-term preservative system, resulting in a cleaner, less contaminated final product. The "clean" paint formulations can then remain adequately preserved with a suitable long-term preservative. Fewer contaminated paint batches reduces the need for product recall and rework.

Once DBNPA has been used to clean up a raw material or a formulation, the reduced bioburden may alleviate some of the stress placed on an in-can preservative, allowing the preservative to work longer and more effectively at lower concentrations. A preservation program that includes DBNPA may improve the quality of raw materials and final formulations, increase the shelf-life of paint formulations, and lower overall production costs.

USE OF DBNPA TO IMPROVE THE EFFICACY OF CONVENTIONAL LONG-TERM PRESERVATIVES

When used in combination with a DBNPA treatment (20% active), long-term in-can preservatives preserve paint longer and more effectively. A standard latex paint formulation was treated with one of several in-can preservatives, either alone or in combination with a 20% solution of DBNPA. The preservatives tested included 5-chloro-2-methyl-4-isothiazolin-3-one/ 2-methyl-4-isothiazolin-3-one or CMIT/MIT (1.5% active), 1, 2-benzoisothiazolin-3-one or BIT (19.3% active), and 4, 4-dimethyloxazolidine or DMO (78% active). After the addition of preservative, the paint formulation was inoculated with a concentrated bacterial cocktail (~1×10^9 CFU/mL). Samples of the contaminated paint were analyzed after 2, 4, 7, 24, and 48 hours and after 7, 14, 21, and 28 days.

The activity of CMIT/MIT, BIT, and DMO was enhanced when used together with DBNPA (note that all preservative concentrations are given as product and have not been adjusted to account for the concentra-

Figure 5A—Improved efficacy of CMIT/MIT in paint when used in combination with DBNPA over 28 days.

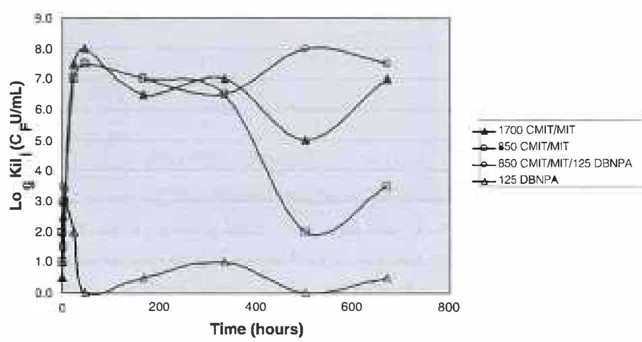


Figure 5B—Improved efficacy of CMIT/MIT in paint when used in combination with DBNPA for the first 48 hours after treatment.

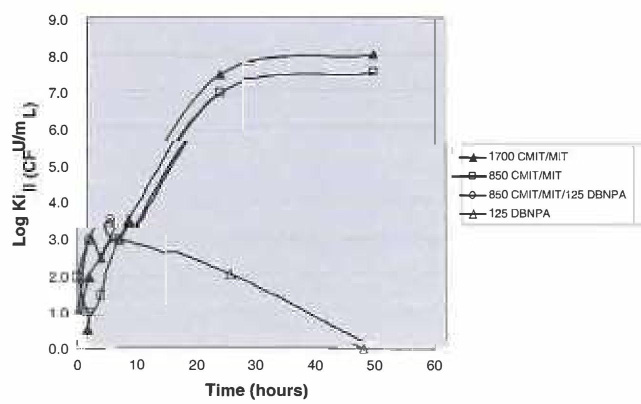


Figure 6A—Improved efficacy of BIT in paint when used in combination with DBNPA over 21 days.

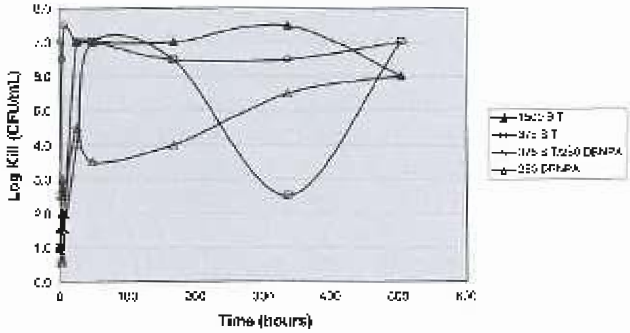


Figure 7A—Improved efficacy of DMO in paint when used in combination with DBNPA over 28 days.

Figure 6B—Improved efficacy of BIT in paint when used in combination with DBNPA for the first 48 hr after treatment.

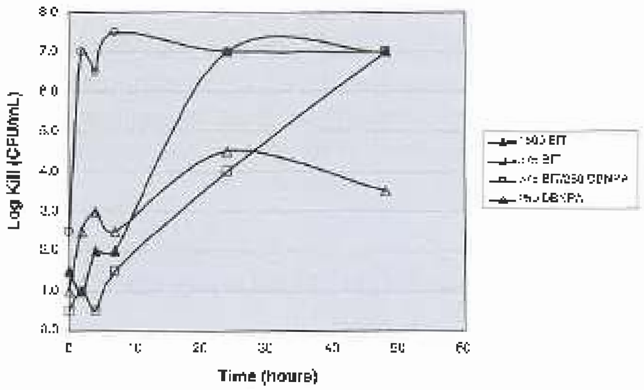
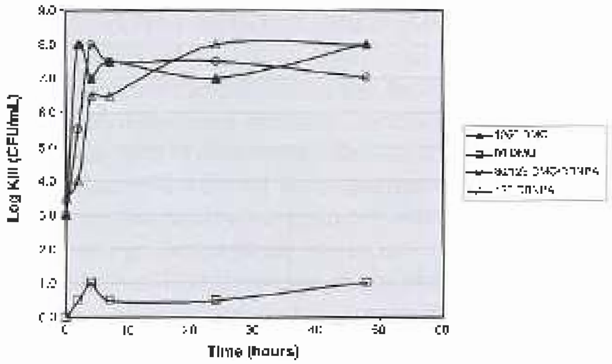


Figure 7B—Improved efficacy of DMO in paint when used in combination with DBNPA for the first 48 hr after treatment.



tion of the active). When 125 ppm DBNPA was used with CMIT/MIT, the required concentration of preservative dropped from 1700 ppm to 850 ppm (*Figures* 5A and 5B). Similarly, while 1500 ppm of BIT was needed for preservation when the product was used independently, only 375 ppm was required to maintain the 5.5 log kill for 21 days when used with 250 ppm of DBNPA (*Figures* 6A and 6B). DMO was effective at a minimum concentration of 1250 ppm, but when combined with 125 ppm of DBNPA, only 80 ppm was required to maintain the 7 log kill for 28 days (*Figures* 7A and 7B). In all three cases, DBNPA as a co-preservative resulted in comparable efficacy with considerably lower concentrations of the primary preservative.

CONCLUSION

Economic Benefits

Treatment of paint raw materials or formulations may reduce microbiological treatment costs by as much as 30 or 40%. When confronted with microbial contamination, manufacturers often employ the product used for long-term in-can preservation. Because a long-term preservative is not designed to act quickly, unusually high concentrations may be required to control the contamination; use of a long-term preservative in this manner can become expensive. Because the DBNPA molecule works quickly and at low concentrations—achieving complete kill long before a conventional preservative—it is far less expensive to use.

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