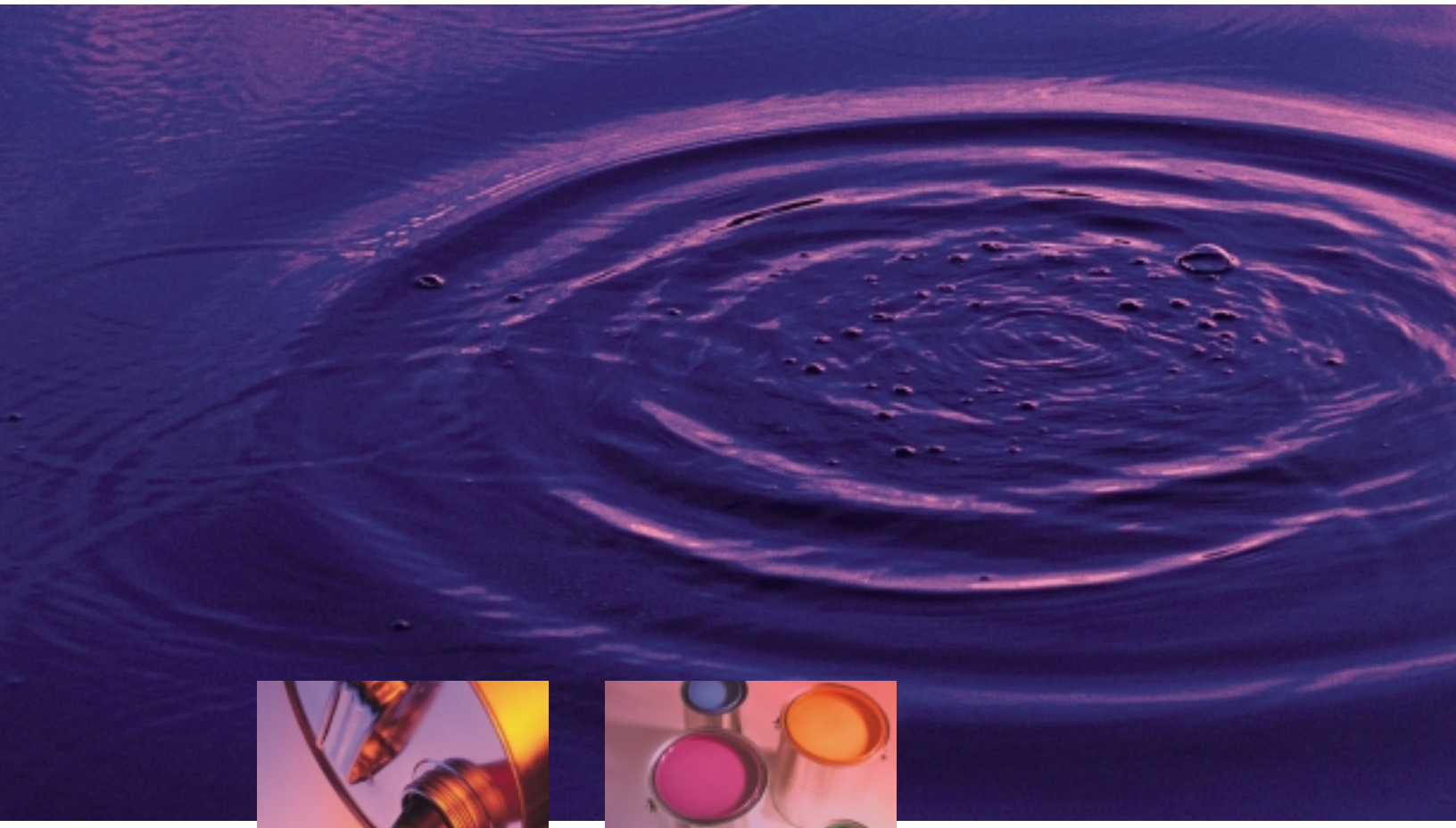
DOWICIL QK-20 Antimicrobial

A fast-acting, broad-spectrum biocide for treating raw materials, processing water, and contaminated products



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A fast-acting, broad-spectrum biocide for treating raw materials, processing water, and contaminated products

DOWICIL* QK-20 Antimicrobial is a fast-acting, broad-spectrum biocide that is ideal for reducing microbiological contamination in raw materials or products such as aqueous paints and coatings, polymers, slurries, adhesives, latex and resin emulsions, sizing, caulk, process water and specialty industrial products including inks, polishes, waxes, detergents, and cleansers.

Many manufacturers who use biocides for in-can preservation of finished products use the same biocide to treat stored raw materials, wash water, recycle water, and contaminated finished product. Although long-term preservatives may eventually get the job done, they may take too long to work—resulting in costly production delays. In addition, the cost of long-term preservatives can be quite high.

Now, Dow offers a targeted, customized biocide that is faster acting and less expensive in these applications.

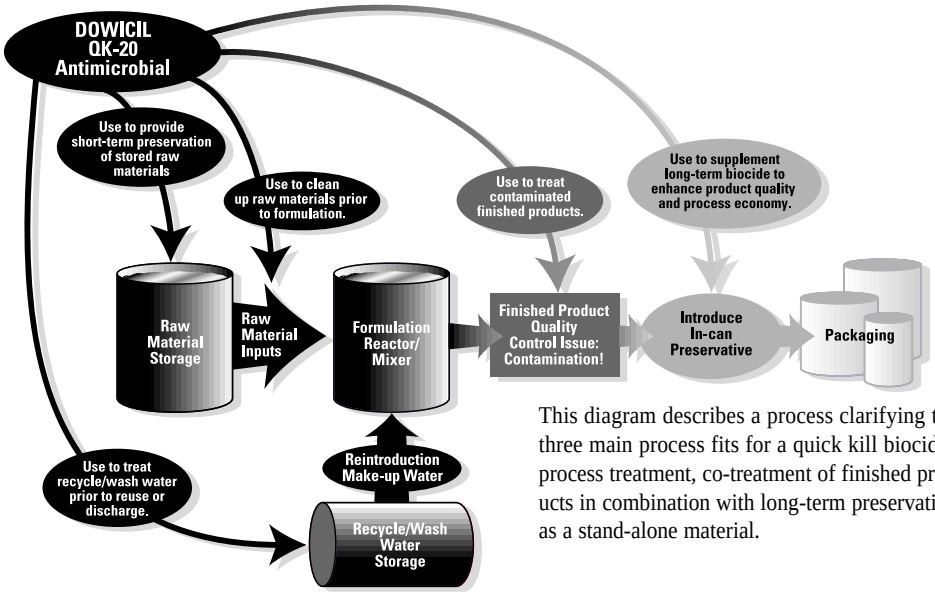
DOWICIL QK-20 Antimicrobial quickly and economically cleans up these potential sources of contamination without requiring you to shut down or delay production.

In finished products, DOWICIL QK-20 can be used effectively in combination with long-term preservatives to reduce the bio-burden on the long-term preservative and minimize the likelihood of organism tolerance. This can lower the chances for field failure, product recall, product rework, and downtime. In some cases overall preservative costs may also be reduced.

DOWICIL QK-20 also serves as a fast-acting, low cost preservative for aqueous formulations such as adhesives where short-term protection ranging from several days to several weeks is desired. When liquid raw materials such as latex and slurries are stored in bulk tanks, sometimes a heel of material can remain in the tank and become a source of contamination. DOWICIL QK-20 offers a fast, economical way to clean up these stored materials and provide short-term protection.

Figure 1 gives an overview of these typical uses for DOWICIL QK-20 Antimicrobial.

Figure 1: Treatment approach in a typical aqueous-based formulation



This diagram describes a process clarifying the three main process fits for a quick kill biocide: In-process treatment, co-treatment of finished products in combination with long-term preservatives or as a stand-alone material.

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Fast, economical antimicrobial performance in an array of applications

In-process "housekeeping" applications

- Incoming raw materials
- Process water/make-up recycle water

Combination or supplemental short-term preservative for finished products

- Aqueous paints and coatings
- Caulks
- Waxes and polishes
- Detergents and cleaners
- Resin emulsions
- Polymers
- Latex
- Sizing
- Adhesives
- Slurries
- Inks
- Surfactants

Fast, broad-spectrum antimicrobial action

DOWICIL QK-20 Antimicrobial is a formulation containing 20% of the active ingredient 2,2-dibromo-3-nitrilopropionamide, commonly referred to as DBNPA. Effective at low concentrations, DOWICIL QK-20 provides broad-spectrum control of bacteria, fungi, and yeast. DOWICIL QK-20 is completely miscible with water and easily dispersed upon introduction into your system. Effective control is often achieved within minutes (See "Field Test Results," page 3).

Decomposition

In aqueous environments, DOWICIL QK-20 decomposes quickly. Ultimately, only carbon dioxide, ammonia, and bromide ion remain as end products. The entire process may take place with a half-life of less than one-half hour, depending on system conditions.

The instantaneous antimicrobial activity of DOWICIL QK-20, combined with rapid chemical breakdown, presents one of the most cost-effective ways of eliminating microbiological contamination with diminished environmental concern and effect on the final product. DOWICIL QK-20 typically yields a 99.999 percent kill before it degrades sufficiently to lose effectiveness.

Excellent compatibility with formulation components and other preservatives

DOWICIL QK-20 Antimicrobial is compatible with formulation components and both oxidizing and non-oxidizing preservatives except for tetrahydro-3,5, dimethyl-2H-1,3,5-thiadiazine-2-thione. Contact Dow for a complete list of tested compatible compounds. Excellent formulation compatibility means that you can solve or prevent contamination problems without shutting down or delaying production and without undesirable effects on your finished product. DOWICIL QK-20 is also formaldehyde-free.

Please note that the active ingredient in DOWICIL QK-20 Antimicrobial will react with and may be inactivated by strong reducing agents and/or nucleophilic reagents.

Compatibility studies should be conducted on your specific application. Questions concerning compatibility of DOWICIL QK-20 Antimicrobial with specific chemicals should be addressed to The Dow Chemical Company.

Conveniently packaged and easy to use

DOWICIL QK-20 Antimicrobial is available in 5-gallon pails, 55 gallon drums, and <275-gallon one-way tote bins. The 5-gallon pails and 55-gallon drums are all polyethylene, providing the advantages of low weight, durability, and easy disposal. They are also equipped with vented bungs, which vent the small amount of carbon dioxide formed during storage and make pouring more convenient by allowing incoming air to displace outgoing liquid. DOWICIL QK-20 Antimicrobial is completely miscible with water and easily dispersed upon introduction into your system.

DOWICIL QK-20 is a skin irritant and workers should always use safe handling procedures and appropriate protective equipment. Complete safe use and handling information as well as material safety data sheets are available through your Dow representative.

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Field Test Results

Figures 2-7 show the results of field performance tests of DOWICIL QK-20 in a variety of real-life applications. In these tests, DOWICIL QK-20 was added directly to contaminated material.

Figure 2: Typical organism reduction in paint wash water by DOWICIL QK-20 Antimicrobial

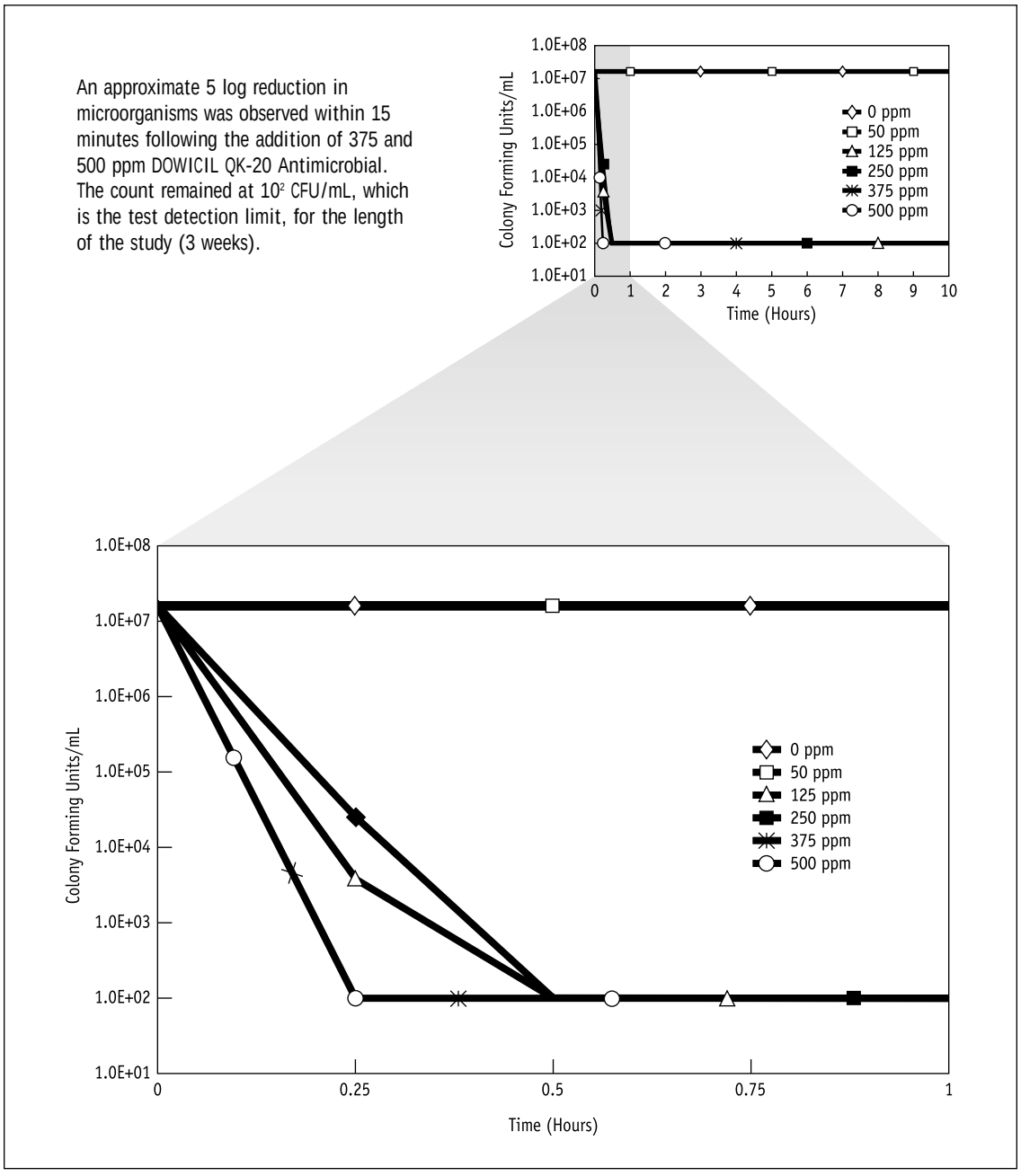
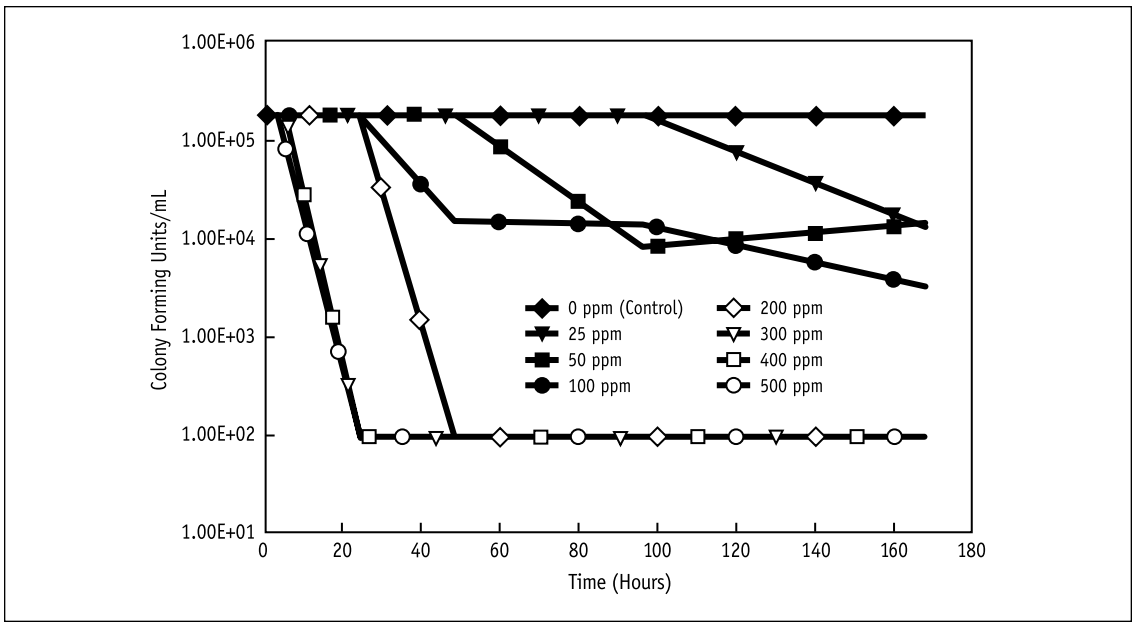
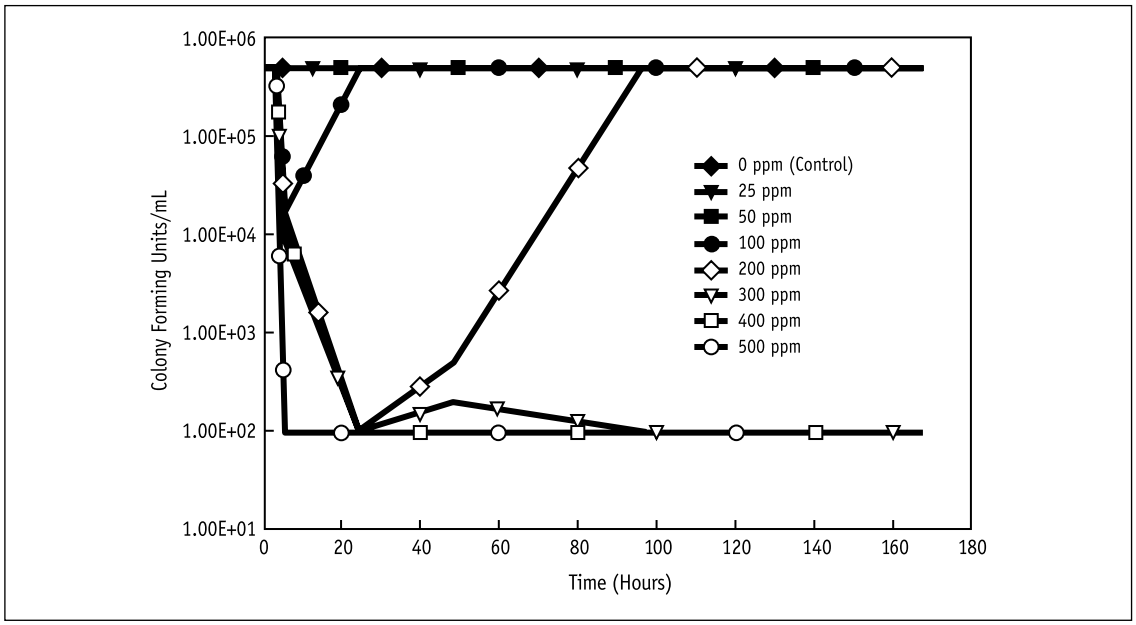


Figure 3: Typical organism reduction in an anionic surfactant by DOWICIL QK-20



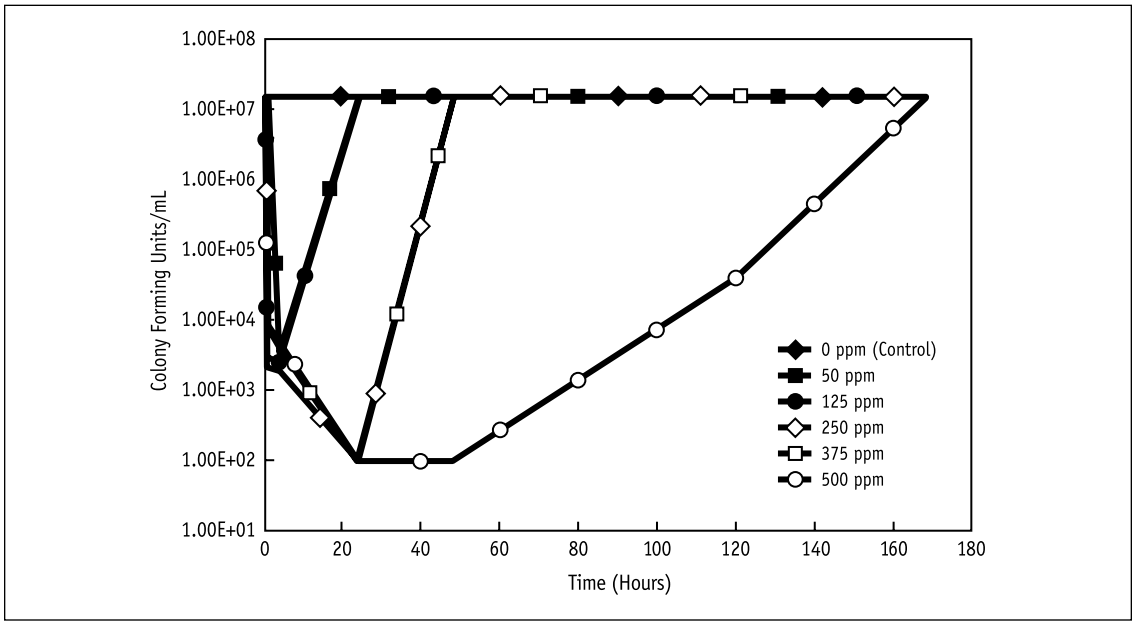
Greater than a 3 log reduction in microorganisms occurred within 48 hours following the addition of 200 ppm DOWICIL QK-20 Antimicrobial. This same approximated reduction in microorganism counts occurred within 24 hours following the addition of 300, 400, and 500 ppm DOWICIL QK-20 Antimicrobial. The counts remained at 10^2 CFU/mL, which is the test detection limit, for the length of the study (1 week).

Figure 4: Typical organism reduction in latex by DOWICIL QK-20 Antimicrobial



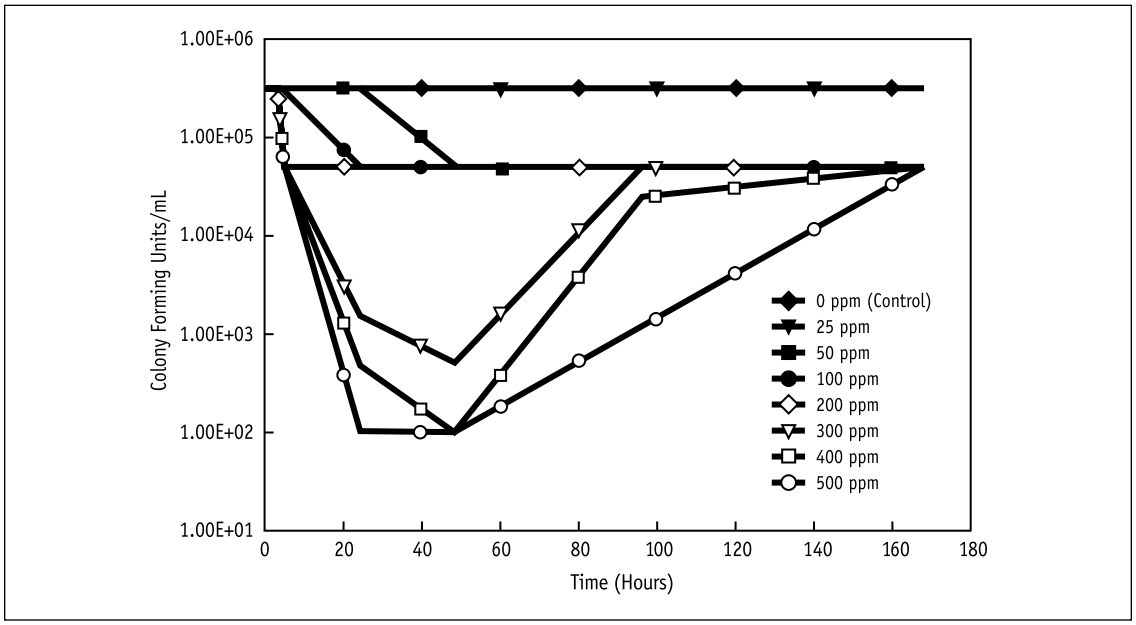
Greater than a 3 log reduction in microorganisms was observed within 24 hours following the addition of 300, 400, and 500 ppm DOWICIL QK-20 Antimicrobial. This same reduction in organisms occurred more quickly, within 5 hours, following the addition of 500 ppm DOWICIL QK-20 Antimicrobial. The counts remained at 10^2 CFU/mL, which is the test detection limit, for the length of the study (1 week).

Figure 5: Typical organism reduction in contaminated paint by DOWICIL QK-20



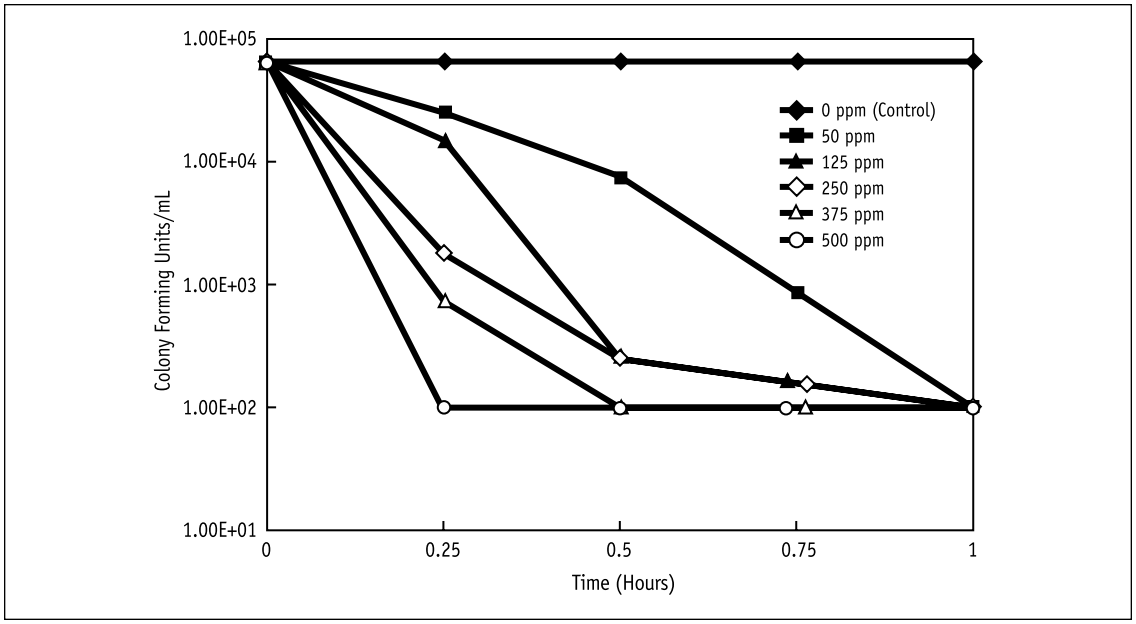
Greater than a 3 log reduction in microorganisms occurred within 1 hour following the addition of 125, 250, 375 and 500 ppm DOWICIL QK-20 Antimicrobial. An approximate 5 log reduction was observed for 250, 375 and 500 within 24 hours.

Figure 6: Typical organism reduction in calcium carbonate slurry by DOWICIL QK-20



Greater than a 3 log reduction in microorganisms occurred within 24 hours following the addition of 400 and 500 ppm DOWICIL QK-20 Antimicrobial. A slightly faster reduction in organisms and slower regrowth occurred at 500 ppm.

Figure 7: Typical organism reduction in kaolin clay slurry by DOWICIL QK-20



An approximate 3 log reduction in microorganisms occurred at 15 minutes following the addition of 500 ppm DOWICIL QK-20 Antimicrobial. This same reduction in microorganisms occurred at 30 minutes for 375 ppm DOWICIL QK-20 Antimicrobial. The count remained at 10^2 CFU/ml, which is the test detection limit for the length of the test (6 days).

DOWICIL QK-20 time kill test procedure

1. Weigh 10 grams of contaminated material into sterile test tubes. Fifty gram samples may be required if material is viscous. This volume allows for improved mixing. All samples arrived at the Dow Antimicrobials Laboratory contaminated with field organisms.
2. Material is acclimated to room temperature prior to beginning the test.
3. Add varying levels of DOWICIL QK-20 Antimicrobial to the samples.
4. Vortex (or stir) and streak each sample immediately on Tryptic soy agar after the addition of biocide and typically at the following time intervals thereafter: 10 min., 20 min., 30 min., 1 hour, 3 hours, 5 hours, 24 hours, 48 hours, 4 days and 7 days. Samples are stored in a 30°C room constant temperature between streaks. (Streak times were modified.)
5. Allow all plates to incubate 48 hours at 30°C.
6. Count the number of colonies per streak and record. Report data as Colony Forming Units per milliliter (CFU/mL).
7. A serial dilution of the contaminated starting matrices is plated as well to determine the number of organisms present before the addition of any biocide. The dilutions are 1/10 in 0.85% sterile saline. 0.1 mL of each dilution is plated on Tryptic Soy Agar using a sterile glass spreader. From this test, an accurate estimate of beginning microorganism counts is obtained.

Data interpretation

Assume a streak is 10µl or 1/100 of a milliliter. For determination of CFU/mL: The number of colonies counted x 100 = CFU/mL. Method detection limit based on this volume is 99 CFU/mL. Any sample with no colonies observable on the streak is recorded as 9.9×10^1 CFU/mL. Example: An observed streak resulted in 15 colonies. Therefore, $15 \times 100 = 1.5 \times 10^3$ CFU/mL.

Laboratory Test Results

Table 1: Minimum inhibitory concentrations for DOWICIL QK-20 Antimicrobial

Organism	ATCC#	Solution ppm pH 6.8
FUNGI		
Aspergillus niger	16404	1250
Fusarium oxysporum	48112	1250
Penicillium chrysogenum	9480	1250
Pullularia pullulans	16622	1250
Trichoderma viride	8678	1250
YEAST		
Candida albicans	10231	1250
Saccharomyces cerevisiae	4105	500

Organism	ATCC#	Solution ppm pH 6.8
BACTERIA		
Bacillus subtilus	8473	125
Enterobacter aerogenes	13048	125
Escherichia coli	11229	125
Klebsiella pneumoniae	8308	125
Proteus vulgaris	881	125
Pseudomonas aeruginosa	10145	125
Pseudomonas aeruginosa PRD10	15442	125
Salmonella choleraesuis	10708	125
Staphylococcus aureus	6538	125

Why MIC tests give misleading data for DOWICIL QK-20 Antimicrobial

It's important to understand that standard minimum inhibitory concentration (MIC) tests—designed to simulate actual system-operating conditions—do not actually do so with DOWICIL QK-20 Antimicrobial. During MIC tests, microorganism innoculants are added to nutrient agar plates already containing biocides. The time lag between preparation of the testing medium and the addition of the innoculant is sufficient to cause degradation of DOWICIL QK-20 Antimicrobial and greatly reduce its apparent microbial action.

Under normal conditions, DOWICIL QK-20 Antimicrobial is added to systems already containing microorganisms, so killing is extremely rapid and effective. In contrast, slower-acting biocides may take ten to twelve hours to achieve the antimicrobial results attained by DOWICIL QK-20 Antimicrobial within thirty minutes of treatment.

Minimum inhibitory concentration test method

MIC test results are determined by incorporating the test compound in either nutrient agar at pH 6.8, or malt yeast agar at 5.5. The agar is then poured into plates and inoculated with nine bacteria or seven fungi/yeast, respectively.

Nutrient agar at pH 6.8 was prepared by adding 23 g of Difco nutrient agar to each liter of deionized water. Malt yeast agar (MYA) was prepared by adding 3 g of Difco yeast extract and 43 g of Difco malt agar to each liter of deionized (DI) water. Thirty mL aliquots of the agar were then dispensed into 25 X 200 mm test tubes, capped and autoclaved for 15 minutes at 121°C. The tubes were cooled to 48°C in a water bath.

Stock 1% active solution of DBNPA was prepared using DI water. Appropriate amounts of the stock solutions were added to the 30 ml of agar in the test tubes to achieve final concentrations of solution 50, 125, 250, 500, 1250 and 2500 ppm of DOWICIL QK-20 Antimicrobial. The agar was mixed and poured into plastic disposable petri plates. After drying and aging at room temperature for 24 hours, the plates were inoculated with microorganisms.

Bacteria used in these tests and their ATCC numbers are listed in Table 1. Stock cultures of the bacteria are maintained in cryovials stored at -78°C. Nutrient broth cultures are prepared from the cryovials weekly, transferred daily, and stored at 30°C on an Eberbach shaker set at low speed.

Dilutions of the 24-hour bacterial cultures were made in sterile 0.85% saline to achieve suspensions containing 10^8 colony forming units (CFU) of each organism (determined through plate counts). Three 0.3 ml aliquots of each bacterial suspension were placed in a Steer's Replicator. Using this inoculating technique, 0.005 mL of each of the nine bacteria are placed in triplicate on agar plates containing different concentrations of DBNPA. Nutrient agar control plates at pH 6.8 were also inoculated in this manner. Each inoculated spot contained approximately 5 x 10^5 CFU. The plates were incubated at 30°C and read after 48 hours to determine if the biocide incorporated into the agar prevented the growth of this inoculum. The plates were rated with a (+) for growth, a (R) for resistant growth, and a (-) for no growth. The MIC was defined as the lowest concentration that prevented growth.

Fungal and yeast cultures were maintained on malt yeast agar slants and stored at 4°C. Spore forming cultures were harvested by washing the slant with a solution of 10 µl of Triton X100 surfactant in 9.9 mL of 0.85% sterile saline. Non-spore forming cultures were harvested by washing the slant with 9.9 mL of 0.85% sterile saline. To aid in the loosening of the organisms, the slants were rubbed gently with a sterile cotton swab. The resulting suspensions were diluted 1/10 into 0.85% sterile saline. These dilutions were placed into the wells of the Steer's Replicator. The malt yeast agar plates containing the test compounds and the malt yeast agar control plates were inoculated. The plates were incubated at room temperature for 72 hours, read and rated with the (+), (R), and (-) system described. Again, the MIC was defined as the lowest concentration which prevented growth.

Physical and Chemical Properties

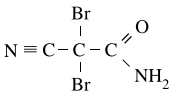
Active ingredient:

The compound 2,2-dibromo-3-nitrilopropionamide (DBNPA) is the active ingredient in DOWICIL QK-20 Antimicrobial.

Chemical name:

2,2-dibromo-3-nitrilopropionamide

Structural formula:



MW = 242

Table 2: Physical properties of DOWICIL QK-20 Antimicrobial

Active Ingredient	**2,2-dibromo-3-nitrilopropionamide**
CAS Number of DBNPA	1022-01-2
Percent Active Ingredient	20%
Inert Ingredients	Polyethylene glycol/water
Color	Clear to amber
Appearance	Liquid
Odor	Low, mildly antiseptic
Freezing Point	About -50°C (per ASTM D97)
Pour Point	About -45°C (per ASTM D97)
Free Flowing	About -30°C (per ASTM D97)
Freeze-Thaw Stability	Passed 7 cycles at -15° to +20°C
Boiling Point	>120°C for solution, but active ingredient decomposes
Specific Gravity	1.24-1.27 g/mL @ 23°C
Miscibility	Miscible with water in all proportions
Vapor Pressure (DBNPA)	2 x 10-5 mmHg @ 25°C
Flash Point	None detected (COC)
Partition Coefficient	P=0.1 for mineral oil/water
Storage Stability	Analysis shows that 95% of the original concentration of the active ingredient in DOWICIL QK-20 is maintained when stored in appropriate containers after 9 months.

Decomposition Pathways

DOWICIL QK-20 Antimicrobial possesses two characteristics that make it unique among nonoxidizing biocides: extremely fast antimicrobial action and rapid degradation to relatively non-toxic end products. The dominant degradation pathway under use conditions involves reaction with nucleophilic substances or organic material invariably found in water. Additional degradation reactions include pH-dependent hydrolysis, reaction with soil, and breakdown via exposure to ultraviolet radiation. Figure 8 shows the typical degradation pathways for DOWICIL QK-20.

Rate of hydrolysis of DOWICIL QK-20 Antimicrobial

The uncatalyzed hydrolysis of DOWICIL QK-20 has been studied in dilute solutions at various pH levels. The reaction proceeds via decarboxylation to dibromoacetonitrile. The rate of hydrolysis is a function of pH and temperature, and increasing either or both will increase the decomposition rate. Hydrolysis is relatively rapid at neutral to slightly alkaline pH.

The pH profile for the hydrolysis of DOWICIL QK-20 at 10°, 30°, and 50°C is shown in Figure 9.

Kill rate outpaces degradation rate

DOWICIL QK-20 typically yields a 99.999% microbial kill before it degrades sufficiently to lose effectiveness. At neutral pH and normal system operating temperatures, DOWICIL QK-20 exhibits a half-life of about nine hours. As pH increases, the rate of degradation of DOWICIL QK-20 increases, but virtually complete microbial kill is achieved well before significant degradation occurs.

Figure 8: Decomposition pathways of DOW DBNPA

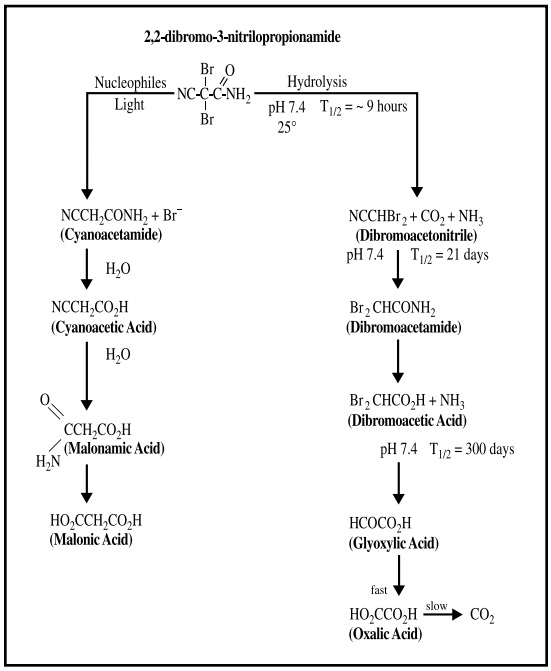
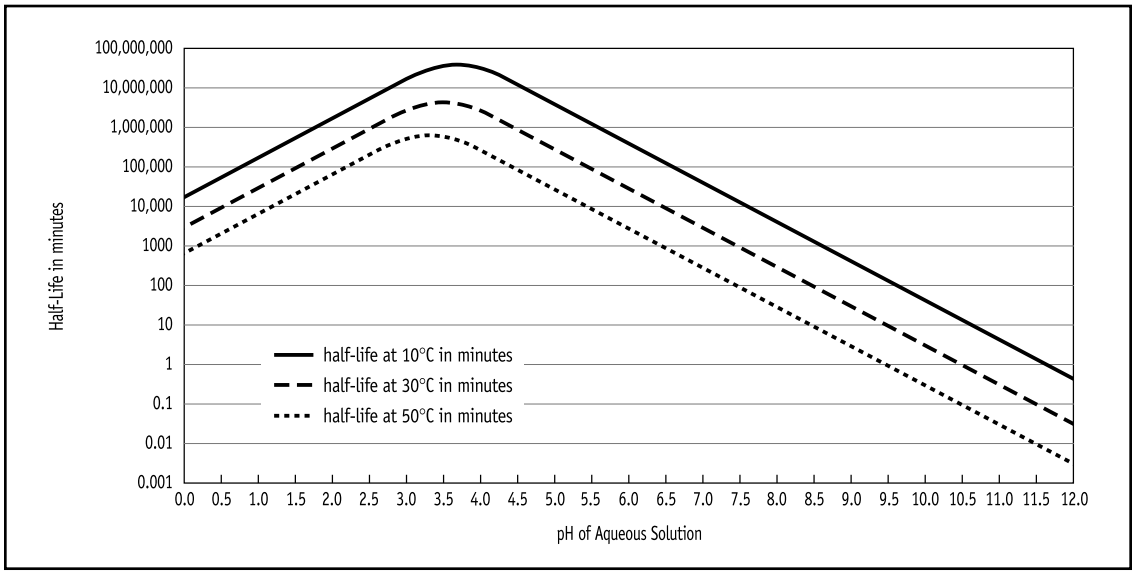


Figure 9: Half-life of DBNPA at three temperatures versus pH (minutes)



Safe Use and Handling

Routine Handling and Protective Equipment

As with all chemicals, handle DOWICIL QK-20 Antimicrobial only after hazards are thoroughly understood. Always use safe chemical handling procedures and appropriate protective equipment.

Please read the Material Safety Data Sheet for this product and understand the potential hazards before using DOWICIL QK-20 Antimicrobial.

Personnel should avoid eating, drinking, and smoking while handling DOWICIL QK-20 Antimicrobial.

Eye protection – Chemical workers' goggles must be worn to minimize the possibility of eye exposure. The most significant handling concern with DOWICIL QK-20 Antimicrobial is eye contact. Laboratory studies show the potential for very serious eye damage, including the possibility of permanent impairment or loss of vision, should DOWICIL QK-20 Antimicrobial contact the eyes.

Protective clothing – Short-term contact, even with concentrated solutions, is not likely to cause injury to the skin. However, even accidental short-term contact should be avoided if possible. Prolonged contact or contact with abraded skin may result in a chemical burn. For these reasons, clean, long-sleeved and long-legged clothing should be worn at all times when handling concentrated solutions. If there is a chance of repeated or extended exposure to DOWICIL QK-20 Antimicrobial, impervious gloves and foot protection should also be worn.

Ventilation – To minimize the possibility of exposure to vapors in the container headspace, drums should be opened and stored in an area with adequate general ventilation. If DOWICIL QK-20 Antimicrobial is stored in large tanks, the headspace should be vented or scrubbed in accordance with local air regulatory requirements.

Bulk handling

DOWICIL QK-20 Antimicrobial is temperature sensitive. Therefore, all external sources of heat or energy must be eliminated or controlled to ensure product stability and safety. The following are potential sources of heat or energy: sunlight, radiation, warehouse lights and heaters, agitators and pumps, and steam used to thaw a frozen line or drum. Remember that the storage temperature has a direct effect on the rate of product decomposition. Customers should examine their operations carefully and consider these points.

Screening tests have established suitable materials of construction for handling DOWICIL QK-20 Antimicrobial. The formulation contains DBNPA, water and polyethylene glycol. Polyethylene glycol is essentially noncorrosive; therefore, the corrosion potential of the two formulated products is a function of increasing DBNPA concentration.

Container labeling – All containers of DOWICIL QK-20 Antimicrobial, including dilutions and formulations, must be clearly labeled in accordance with the standards set by the U.S. Environmental Protection Agency (EPA).

Temperature/decomposition rates

DOWICIL QK-20 Antimicrobial is effective and environmentally safe as a biocide when properly administered. However, the active component, dibromonitrilopropionamide (DBNPA), is temperature sensitive and will decompose exothermically (liberate heat) at elevated temperatures. In addition, its decomposition rate increases with increasing temperature once the exothermic reaction begins.

If DOWICIL QK-20 Antimicrobial is stored under adiabatic conditions, that is, where the heat cannot be removed or dissipated rapidly enough, the liquid temperature in the container will increase with decomposition, and this in turn will increase the decomposition rate.

To ensure safe handling and product quality, it is important to determine which storage systems are nearly adiabatic, and once identified, to monitor the temperature within those storage containers. In relation to tank size, heat transfer from a bulk liquid decreases as its total volume increases. When volume increases relative to a surface area, there is a "self-insulating" effect, allowing temperature to build up within the storage facility.

It is for this reason that adiabatic conditions exist most commonly in large storage tanks and tank trucks. Also, adiabatic conditions can be found in large pumps or pumps made of (or coated with) Teflon Resins, such as those used to unload tank trucks.

Field experience indicates that DOWICIL QK-20 Antimicrobial can be stored safely and shipped in uninsulated tanks and tank trucks with maximum capacities up to 4,000 gallons (15,000 liters). Contact your Dow representative for information on bulk handling of DOWICIL QK-20 Antimicrobial.

- When filling bulk containers, keep the loading temperature of the DOWICIL QK-20 product at 30°C (86°F) or less. Use a side-arm heat exchanger if necessary to maintain this temperature.
- Do not store DOWICIL QK-20 products in tank trucks for more than 6 days from the time of filling because of potential temperature rise and subsequent decomposition.
- Use gravity flow or air pressure transfer wherever possible.
- If pumping is necessary, be certain there are interlocks to prevent operation of the pump when valves are closed or when a line is plugged. This can be accomplished by installing a temperature probe in the pump. A high temperature alarm should be set at 50°C (122°F) to indicate any malfunction.
- Avoid the use of pumps lined with Teflon Resins for large volume transfer. These pumps are unacceptable for large volume transfer because the lining tends to separate over time, and there is the potential for overheating of the entrapped DBNPA product. Small pumps lined with Teflon Resins or pumps with solid Kynar resin, and used for metering the product into a storage handling system, are acceptable.
- Do not recirculate DOWICIL QK-20 Antimicrobial in bulk storage tanks unless a source of cooling is provided. The mechanical energy is transformed into heat and the tank may increase in temperature because of the adiabatic conditions within.
- Install pressure-relief devices in all pumps and vessels handling DOWICIL QK-20 Antimicrobial.

Storage and materials compatibility

As a class of materials, non-metallics such as polypropylene, polyethylene, Kynar resin, Teflon resins, and fiberglass reinforced plastic (FRP) are superior to metallic materials. Hastelloy C-276 alloy, titanium, and 316 SS (short-term storage or shipping), however, are satisfactory metallic materials for storage and shipment containers. In general, mild steel, aluminum, 304 SS, and nickel 200 are unsatisfactory primarily because of excessive corrosion or pitting.

Prolonged storage of the formulations of DOWICIL QK-20 Antimicrobial in 316 SS, especially at elevated temperatures, can discolor the product and cause pitting of the metal. This can be prevented by keeping the residence time in the tank or vessel to a minimum, and then thoroughly flushing with water after usage. If flushing is not possible, a protective coating should be applied to the stainless steel, especially if longer term storage is necessary. There are two acceptable coatings for the manufacture and storage of formulations of DOWICIL QK-20 Antimicrobial:

Heresite P-403 high bake phenol-formaldehyde resin

Plasite 4005 protective coating

These coatings provide excellent protection when properly applied, but should be inspected periodically for damage.

If an FRP tank or tank lining is required for product storage or transfer, check with Dow to be sure that the resin being used is acceptable. Resins that have performed well are DERAKANE* 411-45 vinyl ester resin and DERAKANE 470-45 resin. Rubber-lined vessels are not acceptable because the rubber swells excessively and discolors the product. Glass-lined vessels are generally acceptable.

Table 3: Summary of Materials Acceptable for Bulk Handling and Shipping of DOWICIL QK-20 Antimicrobial

Storage Tank and Tank Truck	Pipe Linings and Hosing
Titanium Hastelloy C-276 alloy Glass-lined steel 316 stainless steel, preferably with a protective coating such as Heresite P-403 or Plasite 4005 DERAKANE FRP 411-45 resin or DERAKANE FRP 470-45 resin (coated fiberglass) Polyethylene Polypropylene	Polypropylene Kynar resin Teflon resin Braided reinforced hosing of Teflon (stainless steel on outside)
Pumps	**Gasket Materials**
Titanium 316 SS Solid Kynar resin Solid Teflon resin	Chlorinated polyethylene (CPE) Viton resin Teflon resin

Transfer

The most preferred method of transfer is by pressure transfer or gravity feed.

The preferred construction materials for pumps used to transfer DOWICIL QK-20 Antimicrobial from a truck to storage are titanium, solid Kynar resin, solid Teflon Resins, or 316 SS. Pumps lined with Teflon are unacceptable for large volume transfer because there is the tendency for the lining to separate over time. However, small pumps lined with Teflon — used for metering the product into a system — are acceptable because of the lower volume displacement and the resulting reduction in equipment stress.

Gasket materials

We recommend gasket materials made of Viton resin, Teflon, chlorinated polyethylene (CPE), and asbestos. Other materials tend to discolor the product. We also recommend that any elastomer be checked for discoloration and swelling in a sample of the antimicrobial before using it in gaskets.

Pipes and hosing

Materials of construction acceptable for lined piping used with DOWICIL QK-20 Antimicrobial are polypropylene, Kynar, and Teflon. Braided reinforced hosing of Teflon (stainless steel on the outside) is a very suitable hosing material.

Corrosivity

In concentrated form, DOWICIL QK-20 Antimicrobial is corrosive to most metals. Mild steel, 304 SS, nickel 200, and aluminum rapidly corrode or pit and may cause degradation of DOWICIL QK-20 Antimicrobial. Although it is less susceptible, 316 SS will corrode if prolonged contact is expected. If 316 SS is used for short-term storage of DOW* antimicrobials containing DBNPA, it should be thoroughly flushed with water following use.

Titanium and Hastelloy C-276 alloy are acceptable for use with DOWICIL QK-20 Antimicrobial. Glass-lined metal vessels are also acceptable providing that the lining is intact. Metals that are normally unacceptable may be

*Trademark of The Dow Chemical Company

used if they are coated properly in advance. These coatings include Heresite P-403 high bake phenolformaldehyde resin 23 ambient cure vinyl resin, and Plasite 4005 protective coating. Rubber-lined vessels are not acceptable for use with concentrated solutions of DOWICIL QK-20 Antimicrobial because the rubber swells unacceptably and may fail as a liner.

Most non-metallic materials exhibit good long-term resistance to corrosion from concentrated solutions of DOW antimicrobials containing DOWICIL QK-20 Antimicrobial, including:

Polyethylene

DERAKANE 411-45 resin

Polypropylene

DERAKANE 470-45 resin

Kynar resin

Teflon resin

Viton resin

Disposal

The DOWICIL QK-20 Antimicrobial products described in this document must be disposed of in accordance with applicable federal, state, and local regulations. If residual product cannot be disposed of by use according to label instructions, contact your state Pesticide or Environmental Control Agency, or the Hazardous Waste representative at the nearest EPA Regional Office for guidance.

Empty drums should be properly discarded as per recommendations on the label.

Products containing DOWICIL QK-20 Antimicrobial may also be disposed of by appropriate industrial incineration, provided that all federal, state, and local regulations for disposal are met.

For assistance in emergencies, human exposure, or disposal of degraded material, call The Dow Chemical Company, (517) 636-4400.

Mammalian Toxicology

Table 4: Mammalian summary toxicologic profile of DOWICIL QK-20 Antimicrobial

Test	Species	Results
Acute Oral	Rat	LD_{50}, 20% DBNPA material = approximately 400-600 mg/kg LD_{50}, 5% DBNPA material = greater than 3000 mg/kg
Eye Irritation	Rabbit	Corneal injury, iritis, and severe conjuctival irritation; severity greatest with 20% DBNPA material. Injuries did not heal within 15 days. Chemical workers' goggles must be worn while handling and using these products.
Skin Irritation	Rabbit	DBNPA has been shown to have moderate skin irritation potential on contact with abraded skin. A marked irritation could result from prolonged or frequently repeated exposure.
Skin Absorption	Rabbit	LD_{50} is greater than 2000 mg/kg for the active ingredient.
Skin Sensitization	Guinea Pig	Moderate skin sensitization after induction with 5% - 20% aqueous solution, followed by challenge with 2.1% - 5% aqueous solution. Negative for skin sensitization after induction with aqueous solution, followed by challenge 0.5% aqueous solution.
Skin Sensitization	Human	Out of 26 subjects, there was no sensitization reaction to an aqueous solution containing 1250 ppm active DBNPA.
Inhalation	Rat	No adverse effect noted after a six-hour exposure to vapors generated by bubbling air through an aqueous solution of 2000 ppm DBNPA.
Mutagenicity	Varies	Negative when tested by the Ames Test, Rat Hepatocyte Unscheduled DNA Assay, Mouse Bone Marrow Micronucleus Test, and Chinese Hamster Ovary Cell/Hypoxanthine (Guanine) Phosphoribosyl Transferase (CHO/HGPRT) Forward Mutation Assay. Negative for sister chromotid exchange in Chinese hamster ovary cells when tested with/without microsomal activation, respectively.
Developmental Toxicity (Birth defects)	Rabbit	No teratogenic effects, even when given at higher doses that were toxic to the pregnant rabbits.
Reproductive Toxicity	Rat	Found not to be a reproductive toxicant when studied in a multi-generation reproductive study that included examination of multiple male and female reproductive parameters (including detailed examination of testes and ovaries).
Subchronic Toxicity	Rat	Subchronic toxicity studies conducted via dermal route of exposure indicated a no-observed-adverse-effect-level (NOAEL) of 1031 mg DBNPA/kg body weight/day. This dose level represented the maximal dose that could be retained on the dermal application sites on the rat. Subchronic toxicity studies conducted with DBNPA (or breakdown products) ingested via drinking water inducted a NOAEL of 10-17 mg/kg/day in rats.

Fish and wildlife toxicity

Table 5 provides information about the toxicity of DOWICIL QK-20 Antimicrobial to aquatic, marine, and avian wildlife.

Based on the several degradation pathways of DOWICIL QK-20 and its intermediate degradates, the proper use of DOWICIL QK-20 in industrial water systems results only in traces of the compound in discharge water. Chemical and biological decomposition, and dilution of the effluent water, result in rapid disappearance of these traces. Therefore, DOWICIL QK-20 does not present a serious fish toxicity hazard when used properly. However, all discharges of DOWICIL QK-20 into lakes, streams, ponds, or public waters must be in accordance with a National Pollutant Discharge Elimination System (NPDES) permit. The current data indicate that DOWICIL QK-20 has the potential for localized fish kill only if a large amount of biocide is discharged into a lake or river. For further guidance, contact your local environmental regulatory office.

Table 5: Evaluation of hazard of 2,2-dibromo-3-nitrilopropionamide (DBNPA) to wildlife

Aquatic Life	
Bluegill sunfish, 96-hour LC_{50}	1.3[1] (1.0-1.6)[2] mg/L
Rainbow trout, 96-hour LC_{50}	1.0 (0.6-1.5) mg/L
Fathead minnow, 96-hour LC_{50}	1.36 (1.24-1.48) mg/L
Daphnids, 48-hour LC_{50}	1.24 (1.06-1.94) mg/L
Largemouth bass finerlings, 96-hour LC_{50}	1.63 (1.54-1.73) mg/L
Marine Life	
Eastern oyster[3] (larvae), 48-hour LC_{50}	>0.56, <1.0 mg/L
Fiddler crab, 96-hour LC_{50}	14 (5.3-36) mg/L
Pink shrimp, 96-hour LC_{50}	>1.8, <3.2 mg/L
Glass shrimp, 96-hour LC_{50}	11.5 (8.69-15.22) mg/L
Asiatic clam, 96-hour LC_{50}	>80 mg/L
Brackish water clam, 24-hour LC_{50}	20 mg/L
Sheepshead minnow, 96-hour LC_{50}	1.4 (1.0-2.0) mg/L
Avian Life	
Mallard duck, oral LD_{50}	
Male	205 mg/kg
Female	216 mg/kg
Bob White quail, oral LD_{50}	
Male	166 mg/kg
Female	150 mg/kg

[1] All values based on active DBNPA
[2] 95% confidence interval
[3] Percentage of abnormally developed larvae (not mortality)

Degradation of DOWICIL QK-20 Antimicrobial in the presence of soil

DOWICIL QK-20 is also degraded by a number of nucleophiles such as sulfite, bisulfite, thiosulfate, and sulfide. These compounds debrominate DOWICIL QK-20 instantaneously to form cyanoacetamide. Soil, which is a source of a number of nucleophiles, also accelerates the degradation of DOWICIL QK-20. This has been demonstrated in a number of experiments in which DOWICIL QK-20 was added to aqueous suspension of a number of different types of soil at a final concentration of 50 ppm. Typically, half-lives of 4 hours were observed at neutral pH, and 15 hours at pH 5. Lower concentrations of DOWICIL QK-20 would be expected to degrade even faster.

The disappearance of solutions of DOWICIL QK-20 in the presence of soil (Table 6) could be due to absorption, chemical degradation, microbial degradation, or hydrolysis. Microbial degradation of DOWICIL QK-20 has been demonstrated by the use of tracer techniques. Rapid reaction in the soil occurs with a variety of nucleophilic reagents to form cyanoacetamide, a compound that is biodegradable and which can hydrolyze further to biodegradable materials such as malonic acid.

Microbial degradation of DOWICIL QK-20

In addition to degradation by hydrolysis, photodegradation, and reaction with nucleophiles, low concentrations of DOWICIL QK-20 also degrade to carbon dioxide as a result of microbial attack (biodegradation). In a modified OECD ready biodegradation test, radiolabeled DOWICIL QK-20 (<0.1 ppm) degraded to 78% $14CO_2$ in 28 days. Mineralization of 58% of the [14C] DBNPA to $14CO_2$ occurred within 10 days of the start of biodegradation, just below the 60% for a “ready biodegradation” classification. The degradation products of DOWICIL QK-20 will further hydrolyze and biodegrade

Reaction of DOWICIL QK-20 with sunlight

Decomposition tests show that DOWICIL QK-20 is degraded by sunlight with the formation of inorganic bromide ion. In one experiment, dilute aqueous DOWICIL QK-20 was maintained in a sealed tube in an outdoor environment for 28 days (pH 4). Less than 1% of the DOWICIL QK-20 remained and more than 95% of the theoretical amount of bromide was formed. The half-life was thus estimated to be 7 days under ambient climatic conditions. Exposure of a dilute solution of DOWICIL QK-20 to a sunlamp in a laboratory resulted in a half-life of less than 1 day.

The amount of DOWICIL QK-20 remaining after exposure to sunlight for 28 days is less than 1% of an original test concentration of 4000 ppm. The percent of DOWICIL QK-20 from the same solution after 28 days in darkness is 91%. Thus, photolytic degradation of DOWICIL QK-20 is rapid, and in fact, is significantly fast relative to hydrolysis at pH less than 5.

Table 6: Half-life of DOW DBNPA in various soil types

Description	% Sand	% Silt	% Clay	% Organic Carbon	pH of Aqueous Slurry	T1/2hr
Sandy Loam	72.4	23.2	4.4	0.46	~7.5	4
Loam	38.0	41.0	21.0	2.37	4.8	12
Silty Loam	13.6	64.0	22.4	2.26	5.8	15
Sandy Loam	59.0	28.0	13.0	1.16	6.5	15
Loamy Sand	83.0	11.6	5.4	5.70	5.8	6
Silty Clay Loam	10.0	62.0	28.0	1.68	5.1	25
Loam	28.6	47.0	24.4	1.86	4.8	15

Regulatory Information

Indirect food contact status

United States

The active ingredient of DOWICIL QK-20 Antimicrobial (DBNPA) is approved by the Food and Drug Administration (FDA) for use as a slimicide in the manufacture of paper and paperboard intended to contact food at a maximum level of 0.1 lb DBNPA/ton of dry weight fiber (21 CFR 176.300).

U.S. FDA approval is pending for use as a component of adhesives (21 CFR 175.105) and coatings (21 CFR 176.170) of paper and paperboard in contact with food.

Important Note: DOWICIL QK-20 Antimicrobial is NOT acceptable for use in the formulation process or material clean-up for personal care and pharmaceutical products.

Germany

BgVV (Bundinstitut fuer gesundheitlichen Verbrachershutz und Veterinaermedizin) is the German Federal Institute for Consumer Health and Protection and Veterinary Medicine. It is a scientific institution and is the highest ranking German Federal agency in the field of health-related consumer protection.

Chemicals used in the manufacture of paper products intended to be in contact with foodstuffs are covered in the category “BgVV 36.” Chemicals used in plastic dispersions, such as paints and coatings intended to be used for food contact applications must fulfill restrictions listed in “BgVV 14.”

DBNPA is listed under BgVV recommendation 36 at a maximum concentration of 0.0045% based on dry fiber. DBNPA must not be detectable in the finished product (method of detection still unpublished). Approval for BgVV 14 is currently in progress.

High performance liquid chromatography (HPLC) QC method for DOWICIL QK-20 Antimicrobial

Dow Test Method

Date: 03 March 99

1. Scope

This method is applicable for the assay of 2,2-dibromo-3-nitrilopropionamide (DBNPA) over the range of 1.02 to 40.82 wt. % in DBNPA formulations.

2. Safety

Each analyst should be acquainted with the potential hazards of the equipment, reagents, products, solvents, and procedures before beginning laboratory work. Sources of information include operation manuals, material safety data sheets, literature, and other related data. Safety information for non-Dow products should be requested from the supplier. Disposal of waste materials, reagents, reactants, and solvents must be in compliance with laws and regulations from all applicable governmental agencies.

3. Principle

The sample is diluted for analysis in a mixture of n-heptane/2-propanol. The resulting solution is injected into a liquid chromatograph, and the components are separated on a normal-phase silica column and are monitored with an ultraviolet detector at 214 nm. Quantitation is by external standard using a computing integrator or data system.

4. Apparatus

(a) Detector: variable wavelength ultraviolet spectrophotometer capable of monitoring at 214 nm, Programmable Absorbance Detector, Model 785A, available from The Perkin-Elmer Corp., 761 Main Avenue, Norwalk, CT 06859, or equivalent.

(b) Pump: capable of 2.0 mL/min. and 3000 psig pressure, Model 307 Drive Module, available from Gilson, Inc., 3000 W. Beltline Hwy., PO Box 620027, Middleton, WI 53562-0027, or equivalent.

(c) Autosampler: equipped with injection value, Alcott Chromatography; 708 Series, available from Alcott Chromatography, 1770 Corporate Drive, Suite 550, Norcross, GA 30093-2928.

(d) Column Heater: capable of holding 35 ± 0.5°C, available from Jones Chromatography, PO Box 280329, Lakewood, CO 80228-0329, or equivalent.

(e) Integrator: ChromJet, available from Thermo Separation Products, 355 River Oaks Parkway, San Jose, CA 95134, or equivalent.

(f) Liquid chromatographic column: Zorbax Silica, 5 μm, 25 cm x 4.6 mm i.d., available from DuPont Company, Instrument Products Division, Concord Plaza, Wilmington, DE 19898, or equivalent.

5. Reagents

(a) n-Heptane and 2-propanol: HPLC grade, available from Fisher Scientific, or equivalent.

(b) DBNPA (2,2-dibromo-3-nitrilopropionamide): 99% pure or better (Note 12a).

(c) Ortho-Phosphoric acid: 99% crystals, available from Aldrich Chemical Co., Inc., 940 W. St. Paul Ave., Milwaukee, WI 53233, or equivalent.

(d) Diluent solution: 80% n-heptane / 20% 2-propanol by volume with 0.1 g phosphoric acid per 2 liters. The diluent solution is prepared by adding 1600 mL of n-heptane, 400 mL of 2-propanol, and 0.1 g phosphoric acid to a 2-L bottle. The resulting solution is capped and mixed well.

(e) Mobile phase: 90% n-heptane / 10% 2-propanol by volume with 0.1 g phosphoric acid per 2 liters. The mobile phase is prepared by adding 1800 mL of n-heptane, 200 mL of 2-propanol, and 0.1 g phosphoric acid to a 2-L bottle. The resulting solution is capped and mixed well. The mobile phase is degased by sparging with an inert gas such as helium before usage.

6. Analysis Conditions

Column:	Zorbax silica, 5 µm, 4.6 mm x 250 mm @ 35°C
Detector Wavelength:	214 nm
Sensitivity:	1.00 AUFS
Rise Time:	0.5 second
Eluent:	90% n-Heptane/10% 2-propanol (v/v)/0.1g H_3PO_4/2L
Flow Rate:	2.0 mL/minute
Injection Volume:	10 mL
Run Time:	21 min.
DBNPA Retention Time:	5.6 minutes (approximate)

See Figure 9 for a typical chromatogram.

7. Calibration

(a) DBNPA standard stock solution: Weigh (and record to the nearest 0.1 mg) 100 ±10 mg of DBNPA standard into a 100-mLvolumetric flask. Add about 80 mL of the diluent solution, a small spatula of phosphoric acid crystals, and sonicate to dissolve. Allow to cool to room temperature before diluting to volume with the diluent solution.

(b) DBNPA working standard solution: Pipet 20 mL (class A volumetric pipet) of the DBNPA stock solution into a 50-mL volumetric flask and dilute to volume with diluent.

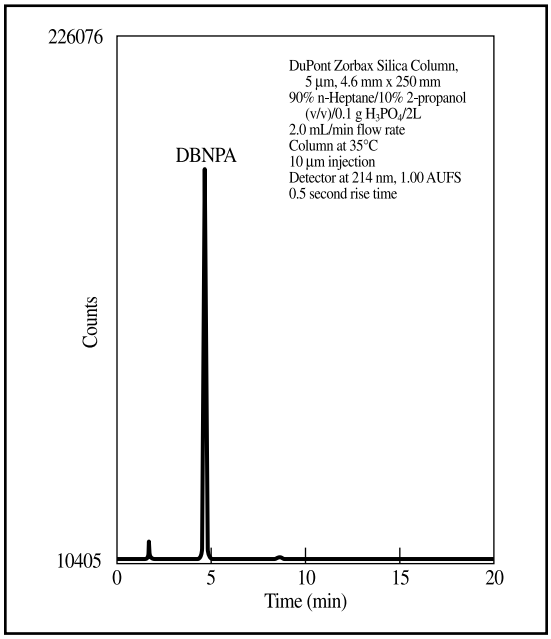
(c) Analyze the DBNPA working standard solution in duplicate using the instrumental conditions provided in Section 6. The corresponding peak areas are used to calculate response factors using the equation in Section 9. Once reproducible response factors are obtained based on the precision of the method, calculate an average response factor, and proceed to analyze the sample.

8. Procedure

(a) Weigh 100 ± 10 mg of sample into a 50-mL volumetric flask. Record the weight to the nearest 0.1 mg. Add approximately 40 mL of the diluent solution and shake vigorously several times. Place the flask in a sonication bath (about 10 seconds) until dissolution is complete. Dilute to volume with the diluent solution.

(b) Analyze the sample solution in duplicate using the instrumental conditions provided in Section 6. A representative chromatogram is shown in Figure 10. Report the average result from the analyses.

Figure 10: A representative sample chromatogram obtained using this method



9. Calculations

(a) Calculate a DBNPA response factor for each calibration standard injection as follows:

$$RF = \frac{Area}{C * 0.2}$$

where:

RF = response factor, peak area/mg in 50 mL solution

Area = peak area of DBNPA

C = DBNPA weight in calibration standard stock solution corrected for purity (in mg)

0.2 = dilution factor (20 mL of 100 mL stock solution transferred to working standard solution; expresses wt. per 50 mL of solution)

(b) Calculate the amount of DBNPA present as follows:

$$\% \text{ DBNPA} = \frac{\text{Area} \times 100}{\text{RF} \times \text{W}}$$

where:

RF = average response factor for DBNPA calculated above

Area = peak area for DBNPA in sample

W = sample weight in mg

100 = Converts mg component/sample weight to weight percent

10. Precision

Precision data determined by this procedure with multiple analyses [n = 10] of a single sample of DBNPA conducted over a 2-day period indicate a standard deviation of 0.19% wt. % determined at an average concentration of 16.16 wt. % DBNPA. The calculated value for the 95% confidence interval for the mean

$$[t_{(n-1)} \times \frac{s}{\sqrt{n}}]$$

where s = standard deviation, n = 10, and t(n-1) = 2.262] was 0.14 wt. % and the expected value for the 95% confidence interval for a single value [$t_{(n-1)}$ x s] was ± 0.43 wt.%. This assumes a normal distribution of results and equal variability between laboratories. (Note 12b)

11. Accuracy

A series of synthetic mixtures were prepared and analyzed to obtain linearity and recovery data. These mixtures were prepared by varying the amount of DBNPA added to the volumetric flask affording sample mixtures equivalent to 1.02 to 40.82% in DBNPA (20% is nominal in DOWICIL QK-20 Antimicrobial). These mixtures yielded recoveries over a range of 98.9 to 103.3% that averaged to 100.8% and with a standard deviation of 1.1%. Detector response was found to be linear over above concentration range. (Note 12b)

12. Notes

(a) The purity of the DBNPA used to prepare the calibration standard stock solution must be determined before use. An analytical standard of DBNPA may be prepared by drying and re-crystallizing technical material as follows: Place technical DBNPA in sufficient boiling methyl t-butyl ether to dissolve most of the solid. Add 0.5 g magnesium sulfate and 0.25 g decolorizing charcoal per g of DBNPA. Stir the mixture for 5-10 minutes, and rapidly filter using a warm funnel and filter paper into a well-dried container. Add 20% warm hexane by volume, and allow the solution to stand covered in the dark until crystallization is complete. Collect the crystals on a Buchner funnel, wash with several small portions of cold 80/20 methyl t-butyl ether/ hexane, and dry in an oven at 80°C for four hours. The purified DBNPA should be protected from moisture and light as much as possible. The material is sufficiently pure for differential scanning calorimetry (DSC) analysis if liquid chromatography indicates that the DBNPA peak comprises >99.8% of the total peak area (excluding the solvent peak). Samples with lower purity should be recrystallized. Final purity is determined by DSC (melting point 124.3°C).

(b) This method was validated using automated injections but could also be performed using manual injections. In either case, in accordance with good laboratory practices, it is strongly suggested that the precision, accuracy, linearity, limit of detection, and limit of quantitation of the method be re-determined if another set of equipment is to be used or the method is to be used in another laboratory.

Titrimetric QC method for DOWICIL QK-20 Antimicrobial

Dow Test Method, DOWM 101342-ME93A

Date: 05 January 93

1. Scope

This method is applicable to the determination of 2-40% (w/w) 2,2 dibromonitrilopropionamide (DBNPA) in liquid formulations (DOWICIL QK-20 Antimicrobial).

2. Safety

Each analyst should be acquainted with potential hazards of the reagents, products, and solvents before beginning laboratory work. Sources of information include material safety data sheets, literature, and other related data. Safety information on non-Dow products should be requested from the supplier. Disposal of reagents, reactants, and solvents must be in compliance with local, state, and federal laws and regulations.

3. Principle

The 2,2-dibromo-3-nitrilopropionamide in an acidic iodide solution will oxidize the iodide to yield two equivalents of iodine per bromine atom. The iodine is then titrated with standard sodium thiosulfate solution.

4. Interferences

This method is a nonspecific titration. Any brominated co-products or decomposition products present in the sample will contribute to the reported % DBNPA values.

5. Apparatus

(a) Autotitrator: e.g., Metrohm model 682 Titroprocessor, available from Brinkmann Instruments, Inc., 1 Cantiague Road, PO Box 1019, Westbury, NY 11590-0207.

(b) Autoburet: e.g., Metrohm model 665 Dosimat fitted with 20-ml buret, available from Brinkmann Instruments, Inc.

(c) Platinum combination electrode: or equivalent, available from Brinkmann Instruments, Inc.

(d) Analytical balance: capable of measuring to 0.0001 g, e.g. Mettler model AE163, available from Mettler Instrument Corp., PO Box 71, Hightstown, NJ 08520.

6. Reagents

(a) Potassium iodide: ACS certified grade.

(b) Acetonitrile: HPLC grade.

(c) Hydrochloric acid 12 N solution (concentrated).

(d) Sodium thiosulfate, standard, 0.1 N solution.

Dissolve 25 g of sodium thiosulfate pentahydrate in water and dilute to 1 liter. Add 0.5 ml chloroform as a preservative. Standardize at least weekly. The prepared solution is available from Fisher Scientific, 2000 Park Lane, Pittsburgh, PA 15275.

(e) Water: 18.2 megaohm, e.g., obtained by passing deionized water through a Milli-Q UV Plus filtration system, available from Millipore Corp., 80 Ashby Road, Bedford, MA 01730.

(f) Hydrochloric acid 6 N solution. Mix equal volumes of concentrated hydrochloric acid and HPLC grade water.

(g) Diluent: combine equal volumes of water and acetonitrile.

(h) Potassium iodate, available from Fisher Scientific.

7. Analysis Conditions

Set the following parameters on the Titroprocessor:

Titration rate:	3.0 mL/minute
Anticipation:	30
Stop potential:	0-50 mV (the value may vary slightly depending on the actual endpoint)
Equivalence point criterion:	3
Start volume:	10 mL for 20% DBNPA formulations

8. Standardization

(a) Weigh (and record to the nearest 0.0001 g) 0.10 g +/- 0.05 g of potassium iodate into a tared 150-mL beaker. Add a magnetic stir bar.

(b) Add approximately 2 g of potassium iodide crystals to the beaker.

(c) Add approximately 30 mL of the diluent to the beaker.

(d) Place the beaker on the titrator and start the magnetic stirrer. Stir to dissolve the potassium iodide crystals.

(e) Once the potassium iodide crystals have dissolved, add 2 mL of 6 N hydrochloric acid to the beaker.

(f) Start the autotitrator, and record the volume of sodium thiosulfate titrant required to reach the endpoint during the titration of the potassium iodate.

(g) Determine the normality (meq/mL) of the sodium thiosulfate titrant as follows:

$$N = \frac{W \times 28.04}{V}$$

where:

W = g potassium iodate titrated during the

V = standardization volume (mL) of sodium thiosulfate titrant used to reach the end point of the standardization titration [Section 8(f)]

9. Procedure

(a) Weigh (and record to the nearest 0.0001g) 0.50g +/- 0.05g of the sample into a tared 150-mL beaker. Add a magnetic stir bar.

(b) Add approximately 2 g of potassium iodide crystals to the beaker.

(c) Add approximately 30 mL of the diluent to the beaker.

(d) Place the beaker on the titrator, and start the magnetic stirrer. Stir to dissolve the potassium iodide crystals.

(e) Once the potassium iodide crystals have dissolved, add 2 mL of 6 N hydrochloric acid to the beaker.

(f) Start the autotitrator, and record the volume of sodium thiosulfate titrant required to reach the endpoint during the titration of the sample.

(g) Tare a clean, dry, 150-mL beaker and add a magnetic stir bar (this will serve as a blank). Repeat Sections (b) - (f) and record the volume of sodium thiosulfate titrant required to reach the endpoint during the titration of the blank.

10. Calculation

Determine the level (%) of DBNPA in the sample as follows:

$$\% \text{ DPNPA} = \frac{(V_s - V_b) \times N \times 6.048}{S}$$

where:

Vs = the volume (mL) of sodium thiosulfate titrant used to reach the endpoint of the sample titration [Section 9(f)]

Vb = the volume (mL) of sodium thiosulfate titrant used to reach the endpoint of the blank titration [Section 9(g)]

S = g sample titrated during the sample titration [Section 9(a)]

N = normality (meq/mL) of the sodium thiosulfate [Section 8(g)]

11. Precision

(a) Data obtained by this procedure at an average level of 5.13 weight % DBNPA indicate a relative standard deviation of 1.24% for ten sample analyses. The values obtained may be expected to vary from the average by not more than +/- 2.8% relative at the 95% confidence level.

(b) Data obtained by this procedure at an average level of 20.2 weight % DBNPA indicate a relative standard deviation of 0.38 % for ten sample analyses. The values obtained may be expected to vary from the average by not more than +/- 0.86 % relative at the 95% confidence level.

12. Accuracy

Analysis of ten synthetic samples containing from 2 to 40 weight % DBNPA resulted in recoveries that ranged from 91.5% to 99.1% with an average of 96.5% and a standard deviation of 2.4%.

Determination of DBNPA at use concentrations

DOWICIL QK-20 Antimicrobial may be used in a variety of sample matricies, and the concentration of DBNPA at use levels may be desired. Analytical procedures utilized for a specific matrix should be evaluated for precision, accuracy, linearity, limit of detection, and limit of quantitation prior to commencing analyses. Results may be matrix dependent. Two procedures for determining DBNPA at use concentrations in water samples are provided as references for developing analytical procedures. Modifications may be required so the procedures are appropriate for the matrix of interest. Update equipment and apparatus as necessary to obtain optimum method performance. Contact The Dow Chemical Company if additional assistance is needed for a particular matrix.

HPLC method for determining DBNPA at use concentrations

Dow Test Method, ML-AM-78-22

Date: 11 May 78

1. Scope

This method is applicable to the determination of 2,2-dibromonitrilopropionamide (DBNPA) in water samples in the range of 1-5 ppm.

2. Safety

Each analyst should be acquainted with the potential hazards of the equipment, reagents, products, solvents, and procedures before beginning laboratory work. Sources of information include operation manuals, material safety data sheets, literature, and other related data. Safety information for non-Dow products should be requested from the supplier. Disposal of waste materials, reagents, reactants, and solvents must be in compliance with laws and regulations from all applicable governmental agencies.

3. Principle

Dibromonitrilopropionamide is separated by reverse phase liquid chromatography on a Corasil/C_{18} column with 10% methanol/90% deionized water as mobile phase. Detection is by ultraviolet spectrometry at 210 nm. Concentration is measured by peak height using external standardization.

4. Apparatus and reagents

(a) Liquid chromatographic UV detector capable of operating at 210 nm., e.g., Perkin Elmer LC-55. Available from Perkin Elmer Corp., Norwalk, CT.

(b) Chromatographic columns and fittings, available from Anspec Co., Box 44, Ann Arbor, Ml 48107.

(c) Bondapak C_{18}/Corasil column packing, available from Waters Associates, Inc., Milford, MA 01757.

(d) Methanol, distilled, spectroscopic grade, available from Burdick and Jackson Laboratories, Inc., Muskegon, MI 49442.

(e) Dibromonitrilopropionamide, 99% pure or better. Available from The Dow Chemical Company, Midland, Ml 48674.

(f) Ammonium phosphate, ACS grade, available from Mallinckrodt, Inc., Hazelwood, MO 63042.

(g) Phosphoric acid, ACS grade (85%). Available from Mallinckrodt, Inc.

5. Liquid chromatographic conditions

(a) Column: 500 x 2.8 mm I.D.stainless steel or glass

(b) Packing: Bondapak C_{18}/Corasil

(c) Eluent[1]: 10% methanol in deionized water, adjusted to pH 4.6 with $(NH_4)_3PO_4$

(d) Flow rate: 1.0 mL/min

(e) Injection: 50 microliters

(f) Detector: UV @ 210 nm

(g) Sensitivity: 0.02 AUFS (absorption units full scale)

6. Calibration

(a) Prepare a stock solution of DOW DBNPA by weighing 10.0 ± 0.001 mg and diluting to 1 liter in a volumetric flask with methanol. This solution contains 10 ppm DOW DBNPA. Take aliquots of 4, 2, 1 and 0.5 mL and dilute each to 10 mL with methanol. These solutions result in concentration of 4, 2, 1, and 0.5 ppm, respectively. Chromatograph these four solutions to obtain an absorption peak height for each solution concentration.

(b) Plot the four obtained absorption peak heights versus concentration in ppm. With proper experimental technique, equipment in good working order, and proper reagents, this plot should be linear like the example shown in Figure 11.

7. Procedure

(a) Fifty microliters of sample are injected as received into the chromatographic column. Obtain chromatogram according to conditions outlined in 5 (a-g).

8. Calculations

Measure peak heights of analyzed sample and reference. Figure 12 provides an example. Calculate ppm DOW DBNPA in the sample using the equation below.

$$\text{ppm DOW DBNPA} = \frac{\text{peak height sample (mm)}}{\text{peak height standard}} \times \text{ppm std.}$$

Figure 11: Linearity study of calibration solutions of dibromonitrilopropionamide (DBNPA)

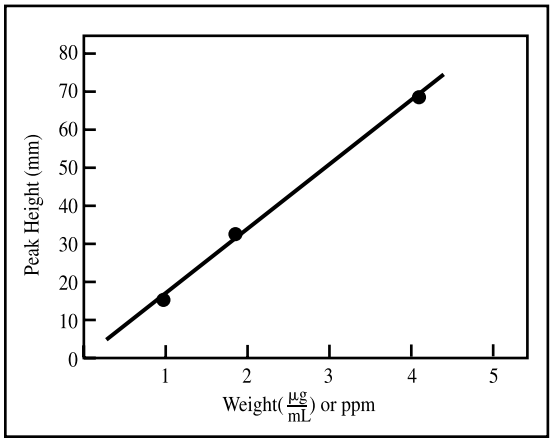
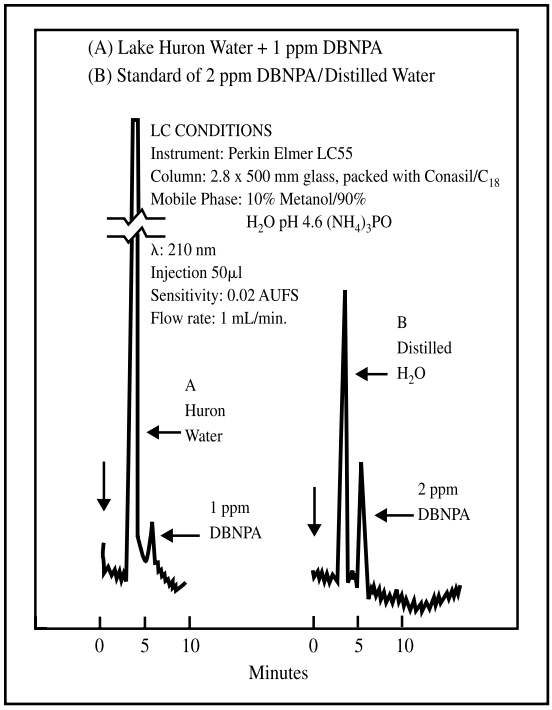


Figure 12: Liquid chromatograms of DOW DBNPA solutions



9. Precision

Data obtained by this method indicates a relative standard deviation of 5.58% at the 1 ppm level. Any single determination may be expected to differ from the average by not more than ±11.2% at the 95% confidence level.

10. Note

Because water samples may vary in composition, this method should be evaluated for each source of water samples.

The analytical procedures given herein have been adapted from literature sources or developed upon the basis of experimental data believed to be reliable. In the hands of a qualified analyst, they are expected to yield results of sufficient accuracy for their intended purposes but recipients are cautioned to confirm the suitability of the methods by appropriate tests. Recipients are also cautioned that The Dow Chemical Company makes no representation or warranty that the practice of the method described herein does not infringe third party patents. Anyone wishing to reproduce or publish the materials in whole or in part should request written permission from The Dow Chemical Company.

Spectrophotoiodometric method for determining DBNPA at use concentrations

1. Scope

The proper use of DOWICIL QK-20 Antimicrobial containing 20% 2,2-dibromo-3-nitrilopropionamide (DBNPA) often requires an analytical technique for determining the concentration of DOWICIL QK-20 Antimicrobial or DBNPA in water at use levels. In addition, it is sometimes desirable to determine low levels of DBNPA in water.

The spectrophotoiodometric analysis technique described satisfies both requirements, enabling the determination of DBNPA from about 20 ppm down to about 1.0 ppm. Since this procedure determines DBNPA, the concentration of DOWICIL QK-20 Antimicrobial in a water sample is calculated by multiplying the DBNPA concentration by five (accounts for 20% DBNPA in DOWICIL QK-20 Antimicrobial).

2. Safety

Each analyst should be acquainted with potential hazards of the reagents, products, and solvents before beginning laboratory work. Sources of information include material safety data sheets, literature and other related data. Safety information on non-Dow products should be requested from the supplier. Disposal of reagents, reactants, and solvents must be in compliance with local, state, and federal laws and regulations.

3. Principle

Potassium iodide in solution with 2,2-dibromo-3-nitrilopropionamide (DBNPA) produces a triiodide complex ion (I_3) with absorption peaks at 352 and 289 nm (Figure 13). The peak at 352 nm was chosen for this technique because it is in the visible—near ultraviolet—region of the spectrum; therefore, a portable spectrophotometer may be employed.

The absorbance due to the concentration of the I_3 complex liberated from the DBNPA solution agrees with the general formula: ppm DBNPA = 10 x absorption I_3 complex (Figures 14 and 15). This approximation holds true up to 10 ppm. The absorption readings were made using a Spectronic 20 Spectrophotometer set at 350 nm. These absorption readings were compared to those obtained from a Perkin Elmer Double Beam Spectrophotometer Coleman 124 set at 352 nm (Figures 14 and 15). The absorbance cell path length was one centimeter.

A calibration standard should be used to verify that the above approximation is acceptable for the instrument used for the analysis.

4. Procedure

Remove a sample of the water to be tested for DBNPA and measure a 500 mL aliquot into a volumetric flask. Add 1 mL of 1 N HCl and mix thoroughly. Add 1-2 g of solid analytical grade potassium iodide. Wait 5-10 minutes and read the absorbance at 350-352 nm in a 1-cm path length cell. Concentration may then be estimated using the absorbance vs. concentration graphs (Figures14 and 15).

This technique is most accurate if the absorbance is in the 0.1-1.0 range where absorbance vs. concentration of DBNPA is linear. If DBNPA concentrations >10 ppm are expected for a solution containing DOWICIL QK-20 Antimicrobial, a known dilution of the sample with distilled water to bring the estimated concentration below 10 ppm should be made prior to following the above steps.

Figure 13: Absorption spectrum of triiodide in 5% KI in water

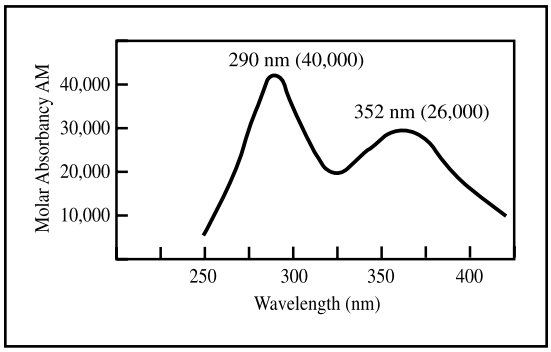


Figure 14: Absorbance I_3^- vs. DBNPA concentration, 0-2 ppm DBNPA

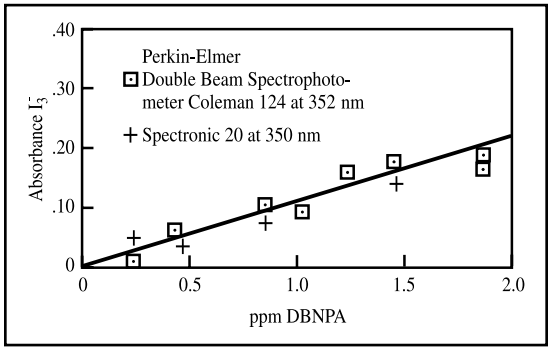
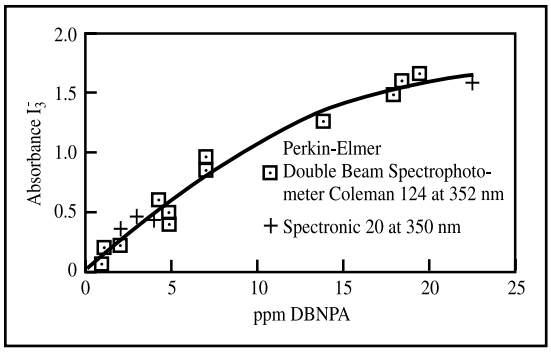


Figure 15: Absorbance I_3^- vs. DBNPA concentration, 0-25 ppm DBNPA



5. Apparatus

Spectronic 20 Spectrophotometer instrument or equivalent. Reagent: Potassium iodide, ACS grade.

6. Troubleshooting

If the solution being tested is cloudy or if extraneous material or suspended solids are present, a background absorption should be determined and subtracted from the original absorption at 350 nm. This can be done by adding a drop of 0.1 N sodium thiosulfate to the absorption cell contents and reading the absorption again without the I_3- species present.

Interference resulting from the presence of manganese, iron, or nitrite may be minimized by buffering to pH 4.0 before the addition of potassium iodide.

The CrO_3- ion, or other species that will oxidize the iodide ion, will give a high, incorrect reading. If incorrect values are suspected, the analysis should be checked with a more specific technique. Water blanks without DBNPA should be analyzed whenever possible to detect species that will oxidize the iodide ion. A correction to the sample absorbance may need to be made to correct for background effects.

Should concentrations of DBNPA below 1 ppm need to be determined, contact The Dow Chemical Company for assistance.

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