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# Protectol® and Myacide® Bronopol Products

**Protectol BN**  
**Protectol BN 18**  
**Protectol BN 30**

## Products for North America

**Myacide AS Plus**  
**Myacide AS Technical**  
**Myacide S2**  
**Myacide S15**  
**Myacide S30**

Biocidal products with the active ingredient bronopol (2-bromo-2-nitro-propane-1,3-diol) for the preservation of industrial and consumer products, odour control and sanitation as well as for the treatment of industrial and process water.

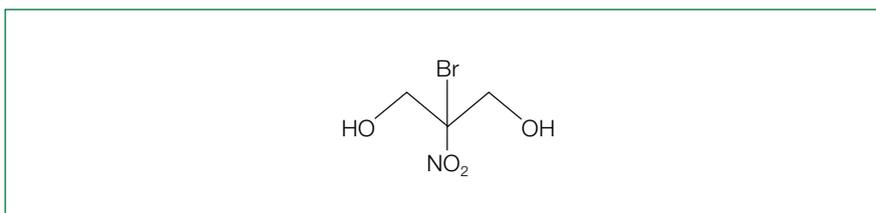
## Properties

### Chemical nature

<b>INCI Name</b>	2-Bromo-2-nitropropane-1,3-diol	
	2-Bromo-2-nitro-1,3-propanediol	
<b>Synonym</b>	Bronopol	
<b>PRD-Nos.*</b>	Protectol BN	30212030
	Protectol BN 18	30231920
	Protectol BN 30	30231923
	Products for North America	
	Myacide AS Plus	30171569
	Myacide AS Technical	30171567
	Myacide S 2	30063161
	Myacide S 15	30063160
	Myacide S 30	30063162

\*BASF's commercial product numbers.

### Structural Formula



<b>Molecular formula</b>	C <sub>3</sub> H <sub>6</sub> BrNO <sub>4</sub>
<b>Molar Mass</b>	200 g/mol
<b>CAS-No.</b>	52-51-7
<b>EINECS-No.</b>	200-143-0

Product name	Description	Approx. composition %	pH*	Density**
Protectol BN Myacide AS Plus Myacide AS Technical	White, or almost white crystals	Bronopol 99.0	min 5 - 7	1.08 - 1.1 (bulk)
Protectol BN 18	Clear colourless to pale yellow liquid	Bronopol 18.0 w/w Dipropylene glycol monomethyl ether 22.0 w/w Water 60.0 w/w	Max. 4.5	1.10
Protectol BN 30 Myacide S 30	Clear, colourless to pale yellow liquid	Bronopol 30.0 w/w Propylene glycol 60.0 w/w Water 10.0 w/w	2.5 - 4.5	1.20
Myacide S2	Clear, colourless to pale yellow liquid	Bronopol 40.0 w/w Dipropylene glycol monomethyl ether 45.0 w/w Water 15.0 w/w	Max. 4.5	1.23
Myacide S15	Clear colourless to pale yellow liquid	Bronopol 10.0 w/w Propylene glycol 10.0 w/w Water 80.0 w/w	Max. 6.0	1.06

\* 1% aqueous solution at 20°C

\*\* g/ml at 20°C

The above information does not necessarily form part of the product specification. A detailed specification is available from your local sales office.

## Solubility and Miscibility

Bronopol can be incorporated readily into aqueous formulation systems. Concentrated aqueous solutions may show a tendency to crystallise at low temperatures. Bronopol is poorly soluble in non-polar solvents but shows a high affinity for polar organic solvents. The solubility profile of bronopol at room temperature is shown below.

<b>Solvents</b>	<b>% w/v</b>
Water	28
Methanol	89
Ethanol	56
Isopropanol	41
Ethylene glycol	61
Propylene glycol	52
Dipropylene glycol	48
Propylene glycol methyl ether	61
Dipropylene glycol methyl ether	54
Propylene carbonate	42
Methyl carbitol	54
N-methylpyrrolidone	102
Diethyl sebacate	10
Isopropyl myristate	< 0.5
Arachis oil	< 0.5
Castor oil	< 0.5
Cottonseed oil	< 0.5
Olive oil	< 0.5
Liquid paraffin	< 0.5

In non-aqueous systems, it is possible to achieve effective levels of bronopol by careful choice of raw materials or by using a suitable carrier solvent.

## Storage Stability

When stored in sealed containers at ambient temperature, the crystalline grades of bronopol are stable for at least 5 years, the liquid formulations for at least 2 years. When aqueous solutions of crystalline material are prepared, bronopol is most stable when the pH of the system is acidic.

In the absence of buffers, solution concentrates of bronopol tend to self stabilise. The optimum pH for stability is around pH 4 and data from studies on dilute solutions of bronopol suggests that the half-life at room temperature and pH 4 is in excess of 5 years.

As the pH and temperature increases aqueous Protectol BN solutions become less stable as shown below:

<b>Temperature</b>	<b>pH 4</b>	<b>pH 6</b>	<b>pH 8</b>
5°C	> 5 Years	> 5 Years	6 Months
25°C	> 5 Years	> 5 Years	4 Months
40°C	2 Years	4 Months	8 Days
60°C	2 Weeks	< 2 Days	< 1 Day

These half-lives are derived from HPLC assays on the dilute solutions (300 ppm a.i.). Due to its mode of action bronopol can keep its biological activity even at low half-lives.

## Compatibility

Studies have shown that concentrated aqueous Protectol BN solutions (18% w/w) are compatible with Stainless Steel (321 Grade), Rigid PVC, Polythene (XDG33), Plasticised PVC (flexible), Silicone Rubber, Nylon and Polypropylene. A dilute aqueous bronopol solution representative of in-use levels (0.02%) has been shown to be compatible with Stainless Steel (321 Grade), Aluminium, Brass, Copper, Rigid PVC, Polythene (WJG11) and Polythene (XDG33).

## Trace metal Content

Analysis of a representative number of batches of crystalline BASF bronopol grades for trace metal content has shown that the manufacturing process is such that it is unlikely to give rise to trace metal contamination and that in total this is likely to be less than 10 ppm in the delivered product. This would result in less than 2 ppb of trace metals in a product preserved with 200 ppm bronopol.

## Antimicrobial Activity

Bronopol has a complex mode of antimicrobial action. Bronopol has a broad spectrum of activity against all groups of bacteria including the anaerobic sulphate reducing bacteria (SRB). The majority of bacteria are inhibited at between 6.25 and 50 ppm.

The activity of bronopol against fungi is more variable and generally higher doses are required to inhibit growth. For most yeasts and moulds, between 400 and 1600 ppm is needed for inhibition, however spoilage fungi can require in excess of 6400 ppm, and thus cannot always be controlled at economic dosage rates by bronopol alone. In such situations, combinations with other actives are recommended.

## Mode of Action

Evidence from several published and unpublished studies indicate that bronopol has a complex mode of action, involving electrophilic and radical reactions with thiol containing enzymes, resulting in inhibition of respiration and metabolism. Additionally, bronopol damages components of the electron transport chain, which leads to the generation of peroxides and oxidising radicals. Repair mechanisms within the microbial cell are also disabled.

Studies have proven that the activity of bronopol is not due to formaldehyde release. For more details please contact your local sales office.

## MIC Values for bronopol

The Minimum Inhibitory Concentrations (M.I.C.) for bronopol (ppm active ingredient) against a range of test organisms are shown below. M.I.C. data was generated using in-house methodology:

Gram positive bacteria	<i>Micrococcus flavus</i>	(Industrial isolate)	25.0
	<i>Staphylococcus aureus</i>	NCIB 9518	25.0
	<i>Staphylococcus epidermis</i>	NCTC 7291	25.0
	<i>Streptococcus faecalis</i>	NCTC 8213	25.0
Gram negative bacteria	<i>Escherichia coli</i>	NCIB 9517	25.0
	<i>Klebsiella aerogenes</i>	NCTC 418	25.0
	<i>Legionella pneumophila</i>	NCTC 11192	50.0
	<i>Proteus vulgaris</i>	NCTC 4635	25.0
	<i>Pseudomonas aeruginosa</i>	NTCT 6750	25.0
	<i>Burkholderia cepacia</i>	NCIB 9085	25.0
	<i>Pseudomonas fluorescens</i>	NCIB 9046	25.0
	<i>Salmonella typhimurium</i>	NCTC 74	12.5
	<i>Serratia marcescens</i>	(Industrial isolate)	12.5
Sulphate reducing bacteria	<i>Desulphovibrio desulphuricans</i>	NCIB 8301	12.5
	<i>Desulphovibrio vulgaris</i>	NCIB 8303	12.5
Fungi	Bronopol has moderate antifungal activity with a MIC > 400 ppm active ingredient against a range of organisms		

## Algae

Bronopol can also be effective in controlling algal growth. Mixed populations can be inhibited by 50 ppm of active ingredient and single strains require levels as low as 6.25 ppm.

## Bactericidal vs. bacteriostatic activity

Bronopol shows bactericidal activity, as measured by kill tests, at concentrations of only 2 to 4 times higher than bacteriostatic levels. For contact periods of less than 24 hours, higher concentrations are required. Bronopol can also be used in combination with other active ingredients to enhance its antimicrobial spectrum and speed of kill.

## Application areas and case studies

Bronopol and its solutions are suitable for use in a wide variety of application areas. These are described below, together with the recommended grade of bronopol to use.

Further information concerning the use of bronopol in these and other application areas is available on request from BASF.

### Industrial Product Preservation

Preservation of technical products e. g. polymer emulsions adhesives, industrial additives

Bronopol is especially useful when used in combination with isothiazolinones (IT). They have been used effectively and extensively in many product preservation applications, however it is known that a build up of IT tolerant "house" organism can become problematical. Combinations of IT with bronopol have proven especially effective in combating this potential threat, giving the necessary peace of mind to plant operators.

### Case study

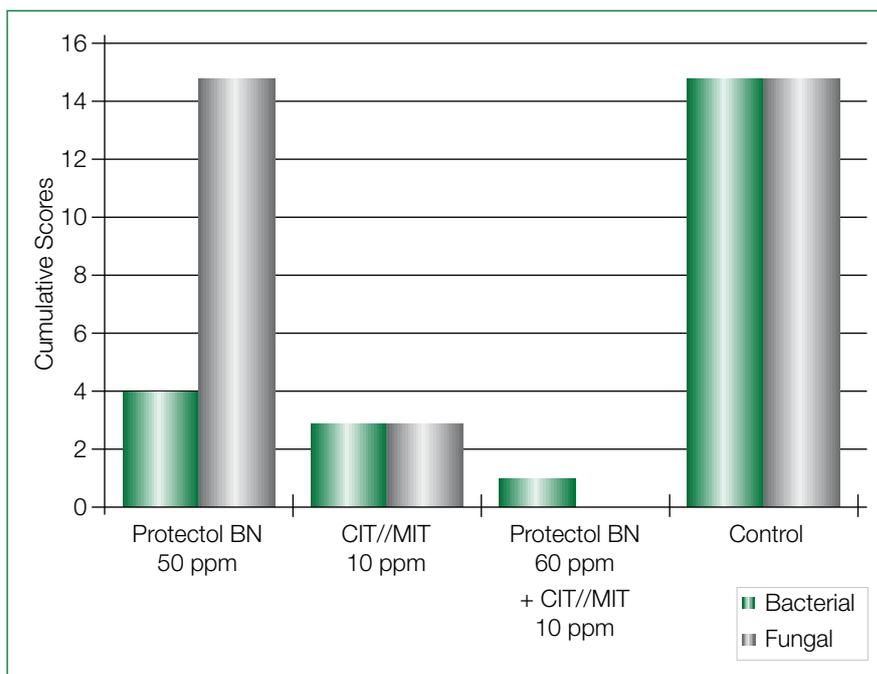
A laboratory study was initiated to assess the ability of Protectol BN to control microbial contamination in a water-based emulsion paint.

Protectol BN was dosed at 200 ppm into an unpreserved emulsion paint and its performance was assessed by three different methods – the ASTM: D2574-94 test method, the International Biodeterioration Research Group (IBRG) test method and the UK Paint Research Association method. Protectol BN successfully passed all three tests.

In further trials, paint samples dosed with Protectol BN were contaminated with a mixed bacterial inoculum and stored at 32°C for 14 days. The number of surviving organisms was determined at suitable time intervals over the storage period. All treatment levels down to 10 ppm controlled the bacterial challenge. The test was repeated on further paint samples that were stored at ambient and challenged at regular intervals up to 12 months. At the twelve-month sampling point Protectol BN at 100 and 200 ppm successfully controlled the challenge within 7 days after inoculation.

In a separate study where additional antifungal activity was required it was shown that a ratio of 6 parts Protectol BN to 1 part CIT/MIT (a. i.) can be successfully employed in polymer dispersions.

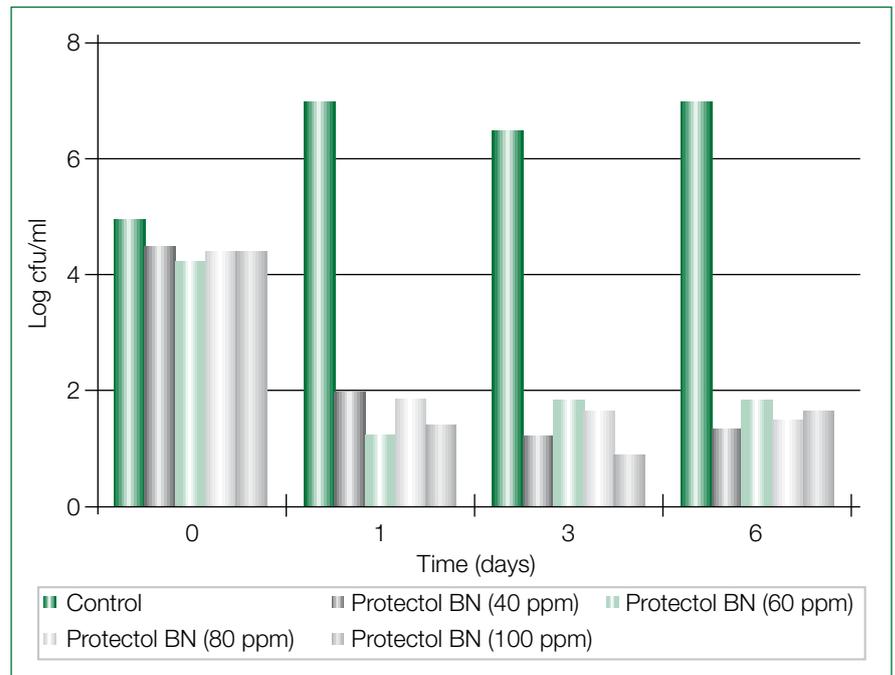
*Activity of Protectol BN and CIT/MIT in an acrylate dispersion*



## Case study

A laboratory study was initiated to assess the ability of Protectol BN to control microbial contamination in drilling muds. A typical starch/bentonite mud was formulated at pH 9.5 and inoculated with a mixture of common aerobic water-borne and cellulolytic bacteria including *Pseudomonas sp.*, *Klebsiella pneumoniae*, *Escherichia coli* and *Cellulomonas flavigena*. The initial inoculum level was  $10^4$  cfu/ml. Aliquots were dosed with Protectol BN at 40, 60, 80 and 100 ppm and monitored over a 6-day period at 25°C. The results are shown in the next figure and confirm that Protectol BN was able to clear the contamination at all levels tested. The untreated control showed significant growth over the same period.

*Efficacy of Protectol BN in a starch/bentonite drilling mud*



## Consumer Product Preservation

Preservation of cosmetics, toiletries and household products and their raw materials

In accordance with the European Cosmetics Directive, BASF does not test bronopol on animals for cosmetic and toiletry purposes, animal tests are also not arranged through third parties. Bronopol was last tested for cosmetic purposes in 1975.

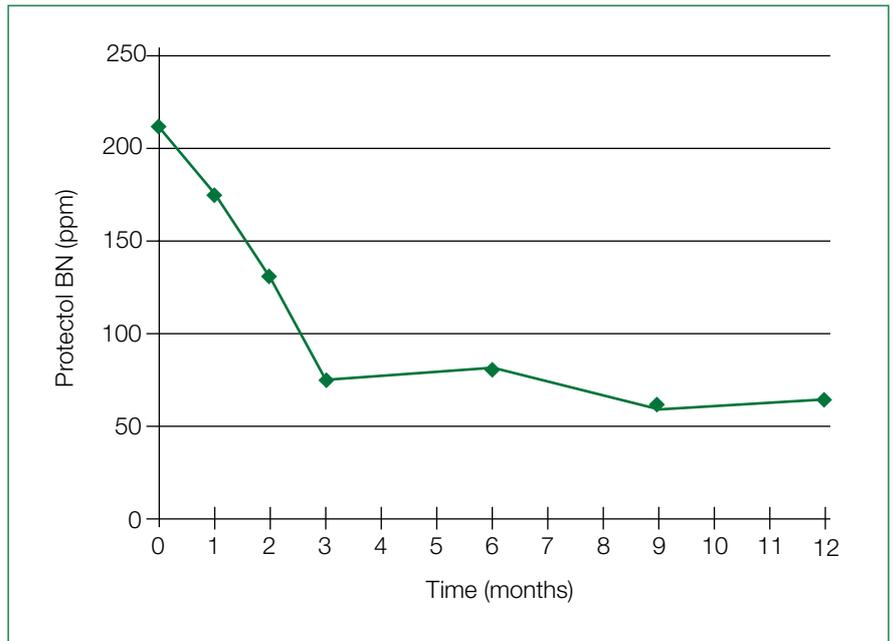
## Case study

Although Protectol BN is potent enough to perform at very low levels in a diverse range of household products, it is also sufficiently stable to give long term protection. A simple household formulation is shown below, Protectol BN passes the BP (British Pharmacopoeia) preservation test at the initial and the 12 months stage.

### Fabric Softener

Ingredient	% by weight
Quaternium-27	6.67
Protectol BN	0.02
Perfume	q.s.
Water	to 100

*Protectol BN in a fabric softener*



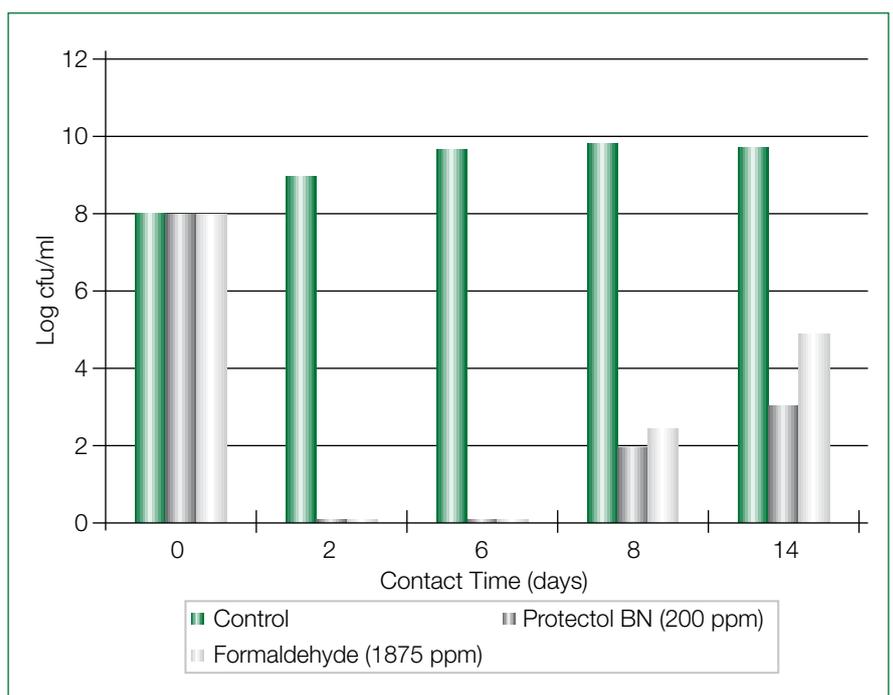
**Odour Control and Sanitisation**

For incorporation into chemical toilet formulations and for odour control in cat litter preparations

**Case study**

Deodorant concentrates were prepared based on nonionic surfactant, fragrance, buffer, dye and water. Biocides were added at appropriate levels to provide two formulations, one containing Protectol BN and the other formaldehyde – a common toilet fluid biocide. These products were then diluted to achieve in-use concentrations of 200 ppm (Protectol BN) and 1875 ppm (formaldehyde) respectively. The dilutions were challenged initially with *Escherichia coli* at  $10^9$  cfu/ml. Thereafter, daily challenges were continued at  $10^5$  cfu/ml. At each challenge, tryptic soy broth was added as a simulated organic loading. All samples were stored at 37°C throughout the 2-week test. At suitable intervals, samples were removed and assessed using a standard plate count method.

*Efficacy of Protectol BN in a simulated chemical toilet fluid*



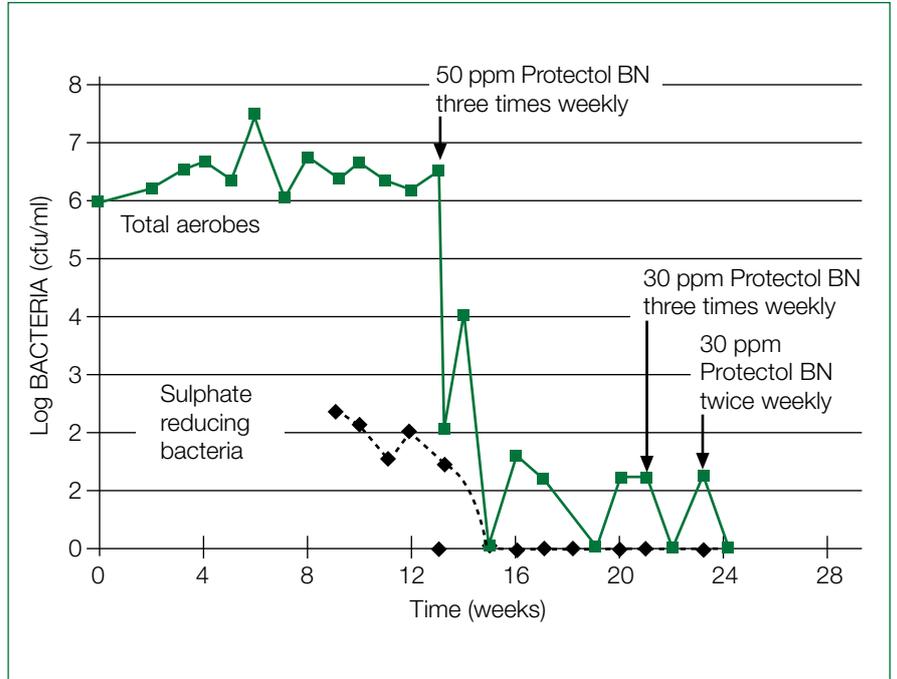
**Water Biocides**

Treatment of industrial recirculating water systems.

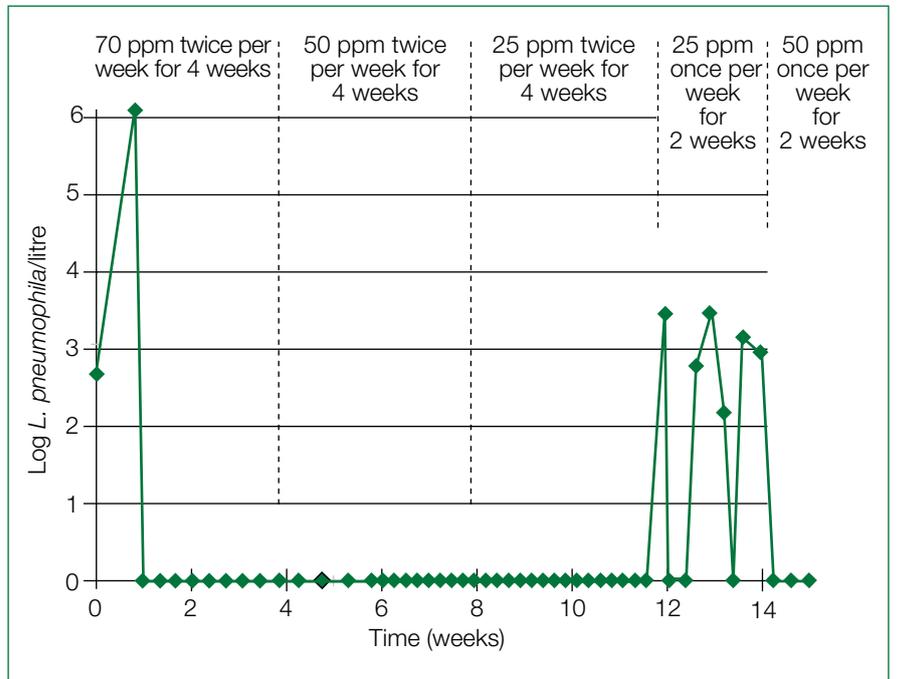
**Case study**

Protectol BN was successfully tested under field conditions in a cooling tower versus aerobic and anaerobic bacteria. The microorganisms can be effectively controlled with the right combination of dosing rate and frequency as shown below:

*Use of Protectol BN in a cooling tower*



*Protectol BN versus Legionella pneumophila*

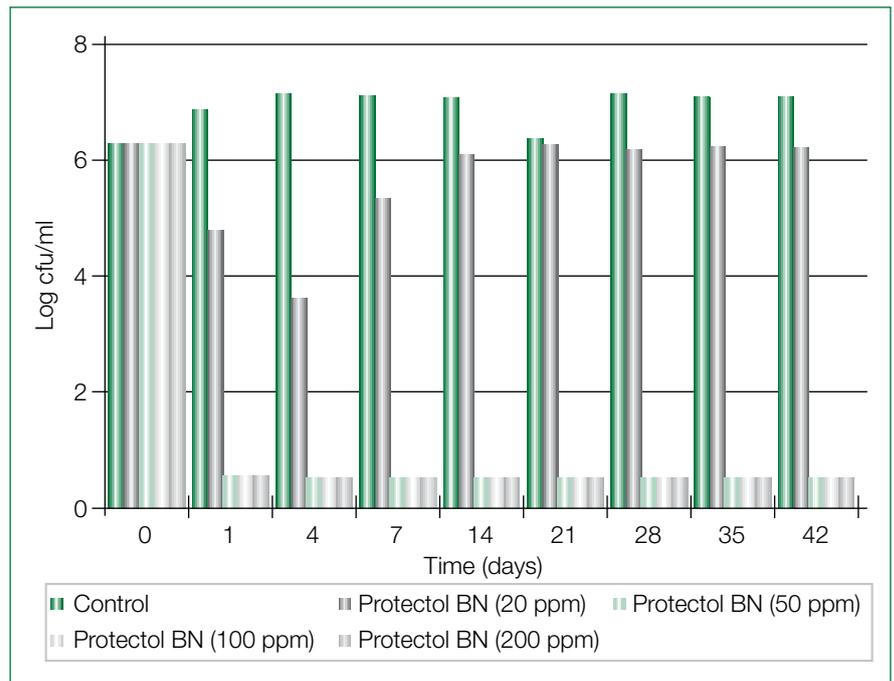


**Paper Industry Biocides**

Treatment of process water and preservation of mill additives

**Case Study**

The following example demonstrates the efficacy of Protectol BN in preserving a typical paper mill additive based on calcium carbonate. The procedure used was ASTM E 723-91 at pH 9.5 with a mixed inoculum of *Pseudomonas aeruginosa*, *Enterobacter cloacae* and *Klebsiella aerogenes*. Protectol BN at a level of >20 ppm was able to control this mixed inoculum for a period of six weeks following a single initial challenge of 10<sup>6</sup> cfu/ml and a reinoculation at 21 days.

*Efficacy of Protectol BN in a calcium carbonate slurry.***Quantitative determination of bronopol in formulations**

Information relating to the analysis of bronopol in some typical formulations can be obtained from your local sales office.

**Registrations and Approvals**

Bronopol is registered and approved in many countries throughout the world for use in a wide range of application areas.

*Europe*

Listed in Annex VI of the EU Cosmetics Directive 76/768/EEC as an approved preservative for use up to 0.1% except where there is a risk of nitrosamine formation.

BASF has submitted dossiers on bronopol as a biocidal active ingredient under the European Biocidal Products Directive (BPD) 98/8/EEC, for product types 2, 6, 11 and 12.

Bronopol solid and liquid formulations have been notified in those countries implementing national product registers under the BPD.

*Belgium*

Protectol BN 18 is approved for various industrial applications.

*Denmark*

Protectol BN and Protectol BN 18 are registered by the Danish EPA for use as paper slimicides.

*Finland*

Protectol BN 18 is registered as a paper slimicide by the Finnish Environmental Institute (FEI).

*France*

Approved for food contact applications as a paper slimicide by the Ministère de la Consommation (Brochure No. 1227) and as a preservative under the Répression des Fraudes.

*Germany*

Approved by the BgVV for food contact uses in latex preservation (No. 14) and paper slimicides (No. 36). More recently the use of bronopol in the manufacture of cooking and hot filter papers (No. 36/1) has been approved.

Class 2 for danger to the aquatic environment (German WGK, "Wassergefährdungsklasse").

*Netherlands*

Protectol BN and Protectol BN 18 are registered for use in recirculating cooling water systems and the paper and cardboard industry. Bronopol is included in the Dutch Warenwet under 2.2.1 g for the preservation of coatings.

*Spain*

Protectol BN is registered as an active substance for biocidal uses.

*Sweden*

Protectol BN 18 is registered for use as a paper slimicide.

Switzerland	Approved as a preservative at up to 0.05% in skin care formulations and up to 0.1% in rinse off products.
United Kingdom	Protectol BN is approved for use in the offshore chemical notification scheme (OCNS).

## North America

<i>Canada</i>	<p>Bronopol products are registered by Health Canada under the Pest Control Products Act.</p> <p>Health Canada have granted letters of “no objection” for the use of bronopol as a slimicide used for manufacturing paper and for use in paper coatings intended for food contact.</p> <p>Bronopol is listed on the Domestic Substances List.</p>
<i>USA</i>	<p>The Environmental Protection Agency (EPA) has registered the following products:</p> <p>Manufacturing uses: Myacide AS Technical (33753-3).</p> <p>Application uses: Myacide AS Plus (33753-5), Myacide S2 (33753-7), Myacide S15 (33753-17), 2K7 Bugstick (33753-18) and Myacide S30 (33753-20).</p> <p>These products are approved for one or more of the following uses:</p> <p>Industrial recirculating water in cooling towers and evaporative condensers, air conditioners, air washers and humidifier systems, consumer products, household products, institutional products, surfactants, oil, gas and industrial process water, metal working fluids, adhesives, paper mill pulp and process water, starch, pigment and extender slurries, paints, latex and antifoam emulsions, absorbent clays, water based printing inks and print solutions, water based pesticides and chemical toilet solutions.</p> <p>FDA approval for indirect food contact use in adhesives (21 CFR 175.105), paper slimicides at a maximum level of 0.6 lb/ton of dry weight fibre (21 CFR 176.300) and paper components in contact with aqueous and fatty foods at a level not to exceed 0.01% by weight of those components (21 CFR 176.170).</p> <p>Bronopol is listed under TSCA.</p> <p>CTFA's Cosmetic Ingredient Review stated in 1980 that bronopol is safe as a cosmetic ingredient at concentrations up to 0.1% except where there is a risk of nitrosamine or nitrosamide formation.</p>

## Other regions

Brazil	Bronopol is approved by the Ministry of Health as a preservative and antiseptic for use in cosmetics and toiletry applications.
Japan	The Existing and New Chemical Substances (ENCS or MITI) registration number is 2-325.

## Safety

### Toxicological data

Bronopol has been used as a cosmetic preservative in a wide range of products for over 30 years and more recently as an industrial biocide. During this time, extensive safety data has been generated. At normal in-use concentrations, bronopol is non-irritant to human skin.

Acute oral toxicity studies (rat LD50 254-342 mg/kg) indicate that bronopol is moderately toxic by ingestion, while acute dermal studies have shown it to be harmful in contact with the skin (rat LD50 1600 mg/kg). Acute inhalation studies, however, have shown that bronopol is not harmful. Safety studies have given no indication of mutagenicity, carcinogenicity or reproductive toxicity.

In the E.U., under the Dangerous Substances Directive, bronopol is officially classified as harmful and irritant (R21/22, R37/38, R41).

**Environmental data**

Bronopol does not accumulate in the environment and has been shown to be biodegradable. Bronopol is toxic to algae (0.4–2.8 mg/l) and daphnia (1.4 mg/l) but less toxic to fish (41.2 mg/l). The log  $P_{ow}$  is low, indicating that bronopol does not bioaccumulate. In the E.U. member states, bronopol is classified as dangerous for the environment (R 50). However, under normal use conditions, bronopol is not expected to cause adverse effects on either effluent treatment plants or to the environment following discharge into wastewater.

**Safety Note**

According to the experience gained over many years and to other information at our disposal, the bronopol products supplied by BASF's Care Chemicals should not exert any harmful effects on health. This is provided that they are used properly, that due attention is given to safety and industrial hygiene precautions necessary for handling chemicals and that the information and advice given in our Safety Data Sheets are observed.

**Handling and Storage**

Contact with eyes and skin should be avoided. Safety goggles must be worn when handling the concentrated product. Bronopol should be stored at ambient temperature in sealed containers as supplied, in cool, dry conditions. Containers should be kept clear of sources of ignition, oxidising agents, alkalis and metals.

**Requirement for the European Directive 98/8/EC**

Use biocides safely. Always read the label and product information before use.

**Labelling**

Refer to the latest Safety data Sheet for detailed information on product safety.

**Classification according to UN criteria**

Bronopol is listed as Class 4.1, packing group III with the UN number 3241. Bronopol is not a flammable solid but is listed as Class 4.1. as a substance related to a self-reactive substance.

**Europe**

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June 2009