

Controlling Microbial Contamination in Metal Working Fluids

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abstract

Mounting concerns over operational and waste management costs, as well as the quality and safety of the work environment have provided increased impetus for both formulators and end-users to strive to improve coolant life. There are a number of alternative approaches to achieving this objective. In this paper, the concepts of bioresistance and biostatic are defined and compared. A discussion of both chemical and non-chemical treatment technologies follows. Non-chemical technologies considered include pasteurization, irradiation, sonication, and filtration. Coolant formulation strategies and biocide use are explored as illustrative chemical technologies. The discussion of biocide use includes remarks on alternative dosing tactics and biocide selection criteria.

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INTRODUCTION

Despite increased focus on total quality management principles throughout the manufacturing industry, microbial contamination remains an insidious drain on the profitability of the metalworking industry. Fortunately, there is a continuing trend for chemical process operators and their managers at manufacturing plants to improve their understanding of the role of microbes in affecting the performance of their coolants. Moreover, coolant formulators have come to recognize that the longevity of fluid performance characteristics often determines their continued tenure at an account.

This heightened appreciation of microbial contamination problems has come at a time when people are becoming increasingly aware of their personal accountability for improving the quality of the work environment and for reducing the volume of industrial wastes. Formulators and coolant system managers are seeking a balance between costs and performance. Regulatory issues and safety concerns are being integrated with engineering and design strategies. This holistic approach to coolant system management is nothing less than revolutionary. It is imperative that personnel responsible for making decisions regarding coolant system operations be equipped with accurate and current information. That is why SME sponsors these annual clinics.

In this paper, I shall discuss a number of concepts which have been receiving increased attention in the coolant marketplace over the past several years. I shall discuss bioresistance, non-chemical treatments and the use of microbiocides. I will not reiterate the basic concepts of microbial contamination in metalworking fluids which have been presented at earlier SME clinics¹ and elsewhere^{2,3}.

TERMINOLOGY

"Bioresistant" versus "Biostatic"

In Europe, and more recently in the United States, so-called bioresistant metalworking fluids are becoming increasingly popular. The impetus for this trend is two-fold. On one hand, there is a demand for products with extended functional lives in order to minimize waste generation and its associated disposal costs. At the same time, customers want to eliminate "toxic" components from coolants used in their plants. Since perception is often a greater consideration than reality, additive suppliers may feel pressured into labeling their non-U.S. EPA registered **biostatic** additives as **bioresistant**. The distinction between these two terms is significant, and should be understood by both formulators and end-users.

A material is **bioresistant** if, in the presence of an active microbial community, its structure and properties tend to remain unchanged. For example, glass is bioresistant, as are many xenobiotic (synthetic) organic chemicals (for example: polychlorinated biphenols). Molecules which resist bioconversion are sometimes referred to as **recalcitrant** molecules. Bioresistance is often concentration-dependent. Thus, a coolant formulation which is stable for several years in drums may degrade after a few weeks after having been diluted to working concentration. Note that the concept of bioresistance makes no assumptions about the survivability of the contaminating microbes. Microbes in direct contact with bioresistant surfaces, such as steel and concrete pipe-walls, may thrive on nutrients which they assimilate from the surrounding air or fluid.

The relative bioresistance of materials, including dilute coolants, is a function of the environment as well as properties of the materials themselves. It is not unusual for a "non-bioresistant" coolant in a well managed coolant system to outlast a bioresistant coolant in a poorly managed system. I've discussed my ideas regarding coolant system management at previous Metalworking Coolant Clinics^{4,5}, and shall not reiterate them here. The point is that inhibition of microbial activity and/or proliferation is **not** a property of bioresistant materials.

In contrast, **biostatic** materials do inhibit either the growth or the proliferation of microbes. Understand the difference between growth and proliferation. **Growth** refers to the increase in the size or mass of an individual cell, whereas **proliferation** refers to the increase in the number of cells within a system. Growing cells produce enzymes and metabolites which may mediate significant biodeterioration even though the population density may not be

increasing. This is why process operators occasionally see indirect evidence of microbial activity (such as reduced pH, changes in emulsion stability, etc.) when dip-slide test results indicate that the coolant is "sterile"^a.

Since, by definition, biostatic chemicals inhibit microbes, they are subject to the same requirement for U.S. EPA registration as are other biocides⁶. A **biocide** is a product used to kill microorganisms. There is a tendency to differentiate between **preservatives** (products used to prevent proliferation or growth) and **biocides** (products used to bring rampant contamination under control). This distinction is artificial.

Generally, antimicrobial products are used as preservatives at one dose range, and as **disinfectants** (products which destroy microbes) at some higher dose range. Consequently, the distinction is often dose-dependent. Figure 1 illustrates the **oligodynamic** effect of dose on the impact of a registered biocide on proliferation of a microbial population. At low doses, the product actually **stimulates** population growth. At somewhat higher concentrations, the effect is biostatic. Population density does not increase in the test system. Once the biocide concentration exceeds 125 ppm, microbial proliferation is inhibited completely. Therefore, we understand **biostatic** chemicals to be toxic and apply them with the same care and good judgement with which we use all antimicrobials.

Potentiators

Some years ago, Prof. E. O. Bennett coined the term "biocide potentiator" to describe coolant additives which do not exhibit antimicrobial characteristics when used alone, but which improve the performance of biocides with which they might be used con-jointly.

Bennett uses persistence-of-effect as his criterion for evaluating potentiator-biocide blend performance. Arguably, speed-of-kill or spectrum-of-activity might be equally useful criteria for evaluating biocide potentiators. As with biocides, the performance of potentiators varies among coolant formulations.

^a**Sterile** is another often-misused term which refers to a product which is totally free of viable microbes. Zero counts on a dip-slide, or zero viable counts by any other culture method simply means that the sample did not have enough individuals of species capable of forming colonies on the solid medium (or cause turbidity in the liquid medium) which the person performing the test selected. A sample may have contained millions of microbes, which, for any of a number of reasons were unable to elaborate into colonies.

NON-CHEMICAL TREATMENT

There are several non-chemical technologies worth reviewing. These include irradiation, pasteurization, sonication and filtration. As a group, these technologies share a common disadvantage. All of them treat the target fluids^b at a single point in the system. There is no residual antimicrobial activity in the fluid recirculating through the rest of the system. Consequently, any microbes which survive treatment are able then to colonize on downstream surfaces, thereby neutralizing the benefits which might otherwise have been derived from point-source treatment. It is likely that microbes which have survived a non-chemical treatment are physiologically stressed and are therefore more susceptible to the effects of biocides. Whether this might lead to reduced biocide costs remains conjectural. Such savings would have to be balanced against the capital and operating expense associated with the non-chemical process.

Pasteurization

Adapted from the food disinfection process^c, pasteurization entails heating coolant to a temperature which will kill the microbial species instrumental in coolant biodeterioration, but which will not affect the coolant adversely. Pasteurization works well in liquid foods where the objective is to kill potentially pathogenic bacteria. Most of the potential pathogens die-off at temperatures significantly above that of the healthy human body (yet well below temperatures which would affect food quality adversely). Unfortunately, microbes participating in biodeterioration processes are often more robust. Some are **thermotolerant** or **thermoduric**, meaning that they are not inhibited by high temperature.

Pasteurization is energy-intensive. Coolant must be heated to $\geq 61^{\circ}\text{C}$ (142°F) and maintained at that temperature for 30 min. Elsmore and Hill⁷ obtained good results applying continuous heat (70°C), but noted that more diverse microbial populations developed in coolant treated by intermittent pasteurization. Consequently, the cost-effectiveness of this technology depends on the availability of cheap steam or electricity and the capacity to treat 100 percent of the recirculating coolant.

Irradiation

Four radiation technologies have been used, at least in prototype operations. Ultra-violet irradiation has been used to disinfect process water for several decades. In most UV

^b Although we are concerned with metalworking coolants in this discussion, these technologies have been applied to a variety of process fluid streams, including water & waste-water treatment, sludge disinfection, food processing and oilfield injection systems.

^c Pasteurization is the process of heating a fluid to $61 - 63^{\circ}\text{C}$ ($142 - 145^{\circ}\text{F}$ for 30 min).

systems, a thin film of water flows through an irradiation bank. Susceptible microorganisms undergo lethal mutations or are killed outright by the ionizing effect of UV energy. Two drawbacks to this type of equipment are: 1) UV light-energy is rapidly attenuated by water, so that unless the film is uniformly thin (<1 - 3 mm) performance will be inconsistent; 2) algal blooms tend to develop on the interior walls of UV irradiation devices, providing masking protection for the microbes in the process fluid. UV systems, therefore require a relatively high maintenance effort. Moreover, since UV rays do not penetrate opaque material very well, this technology is restricted to surface decontamination and clear fluids.

High-energy electron irradiation (HEI) has been used to treat domestic sewage sludge. It suffers some of the same limitations as UV irradiation. A beam of high-energy electrons forms a flux field through which a thin sheet of fluid passes. The killing mechanism is the same as that described for UV irradiation. However, HEI performs somewhat better with turbid fluids. As with pasteurization, HEI is an energy-intensive technology and is not likely to be a cost-effective solution in metalworking plants.

Gamma-irradiation represents a potentially beneficial use for spent nuclear fuel. As with the two aforementioned ionizing radiation technologies, fluid passes over the radiation source as a thin film. Gamma-rays have significantly greater penetrating power than either UV-rays or high-energy electrons. This technology is gaining some acceptance in the food industry, and may prove to have application in the metalworking industry⁸. Barriers which need to be overcome are mostly perceptual. Contrary to common belief, gamma-irradiated coolant does not become radioactive. However, personnel responsible for irradiation-unit operation and maintenance will need to be well-trained in radiation safety. Current estimates are that radioactive-source material should function for 5 - 10 years before needing replacement. Since ionizing radiation is known to stress cells, any of these systems may be expected to enhance the impact of chemical antimicrobials⁹.

Microwave irradiation does not appear to be a particularly useful disinfection technology for industrial process fluids, since the primary effect seems to be heat-related. However, at least one laboratory has reported some success¹⁰.

Sonication

The effectiveness of sonication is dependent on the frequency and intensity of the sonic pulse. Eucaryotic microbes, such as fungi and algae are substantially more labile to sonication than are bacteria. Although preliminary laboratory work has been promising¹¹, there have not been any sonication systems marketed to the metalworking industry.

Filtration

Filtration systems are designed to remove particulates from the recirculating coolant stream. Since microbial populations tend to flourish on surfaces, particle removal reduces the surface area available for colonization. Biocides tend to work more effectively in clean fluids. However, filter-media selection may also affect biocide performance. Some filtering agents may scavenge certain biocides from cutting fluids¹². Overburdened filters may become sources of microbial contamination.

All of the aforementioned non-chemical technologies may have a future role in preserving metalworking fluids. To date, except for filtration, the requisite investment, operating expense and performance limitations of non-chemical treatments are too great to be justified by the potential savings in disposal and chemical treatment costs. As disposal becomes a less viable option, there may be greater impetus for the industry to adopt one or more non-chemical treatment technologies.

CHEMICAL TREATMENT

At one time, the concept of chemical treatment would refer only to the use of antimicrobials. Now, both coolant formulators and end-users have a variety of chemical strategies from which to choose.

Synthetic versus emulsifiable oil formulations

One approach to building bioresistant coolants is to use defined components in the formulation. The development of synthetic coolants represents such a strategy. Distillate stocks from which naphthenic and paraffinic-based emulsifiable coolants are formulated are complex mixtures of hydrocarbons. Although a petroleum derivative base-stock may have certain nominal properties which characterize it as a naphthenic oil, the actual chemistry varies substantially among production lots. Vegetable- and animal-derived oil compositions are equally variable. These complex fluids are readily attacked by many microorganisms. Since emulsifiable oil formulations contain 70 - 90 percent base-oil, it is difficult to formulate bioresistant products without incorporating products with antimicrobial properties. Formulators of synthetic blends have greater flexibility in selecting recalcitrant molecules for each of the functional properties designed into the blend. Childers discussed the selection of bioresistant metalworking fluid components at the 1991 Society of Tribology and Lubrication Engineering annual meeting (unpublished). The guiding principle is to select combinations of molecules which tend not to serve as food sources for bacteria or fungi at end-use concentrations. This is balanced by treatability considerations.

All coolant systems are drained periodically. In systems where sludge build-up or coolant oxidation are not problems, there remains a need for periodic maintenance or engineering work. I have heard of systems which had run for five years before being drained, but at some point all metalworking fluid which has not been lost by other routes becomes a disposal problem. The importance of this issue is reflected in the attention that it is receiving at this clinic. Twelve of the twenty papers to be presented this week address the

waste-stream issue. Therefore, it is important to design metalworking fluids that have long functional lives, but which are also handled easily by waste treatment systems. Coolant concentrate should be readily separable from dilution water. Concentrate should be susceptible to reconditioning or bioremediation. The latter may seem paradoxical, but with recent advances in biologically-mediated waste treatment technologies, bioremediation may be more cost effective than alternative disposal strategies.

In Europe, boramides and boramines have become increasingly popular. Here's where the issue of **bioresistance** versus **biostatic** becomes relevant. Alkylamines are reacted with boric acid to yield boramides and boramines. The borate derivatives do not contribute to the amine functionality of the parent molecules. Rather, they contribute to its resistance to microbial attack. Consequently, boramides fit the definition of bioresistant molecules.

Several alkanolamine products have been introduced in the U.S. in the past decade. Most of the literature describing their application focuses on either their ability to suppress microbial growth or to potentiate antimicrobials. There are no published data referring to other functional properties, such as emulsion stability enhancement, buffering, corrosion inhibition, etc. It seems then, that these products are used primarily for their biostatic properties. One might argue over the semantics, but to this author that sounds very much like the function of a preservative.

Biocides

It is easier to suppress microbial growth than to disinfect heavily contaminated metalworking systems. This is one of the principal arguments for incorporating biocides into coolant formulations. The other primary reason for including biocides in formulations is that this practice reduces the need for handling biocides at the end-use site. However, this practice is not a panacea, for reasons which I shall now discuss.

There are nearly a hundred antimicrobial products registered by the U.S. EPA for use in metalworking fluids^{13,14}. Of these, approximately a dozen are used commonly by formulators and end-users (Table 1). No single biocide has proven to be universally effective. Consequently, several criteria must be considered in biocide selection. The following discussion assumes that all alternatives are U.S. EPA-approved for use in metalworking fluids, and, consequently, are safe when used in accordance with manufacturers' instructions. This is an important assumption. The health risk due to exposure to biocides is not significantly different from the risk due to exposure to other industrial chemicals.

Biocide selection criteria

Treatment objective: As discussed above, biocides may be used as preservatives or as disinfectants. Some antimicrobials which prevent the development of contamination do not serve well as disinfectants. In contrast, some excellent disinfectants may not persist sufficiently to function as long-term preservatives [ozone is an example of a disinfectant with a short chemical half-life (time required for 50% reduction in concentration) in fluids].

Biocide may be added to formulated concentrates only to prevent biodeterioration in the drum. Alternatively, biocide may be formulated into a concentrate at levels sufficient to preserve the diluted coolant in its working application.

The aforementioned application strategies suggest four different performance evaluation protocols. Unfortunately, neither ASTM D 3946¹⁵ nor ASTM E 686¹⁶ provide schemes for evaluating a biocide's ability to meet more than one of the possible treatment objectives. Shennan¹⁷ reviewed several strategies for predicting biocide performance in end-use applications. For biocides intended to be used as shock treatments, a modification of ASTM E 686 is appropriate. Instead of waiting 64 hours between treatment and microbiological testing, samples should be drawn and analyzed periodically over the first 24 hours (for example, at times 0, 0.5, 1, 2, 4, 8 and 24 hours). If a formulator expects significant antimicrobial activity from a biocide which has been built into a concentrate, comparative tests must be run between fresh and aged blends. Differences in performance may reflect chemical incompatibilities between candidate biocides and other coolant components. If the objective was only in-drum preservation, then tests on dilute coolant are superfluous. Thus, standard test methods provide a guide for evaluating biocide performance, but must often be modified to ensure that they are apropos of the application objective.

Mode of application: Biocides may either be formulated into coolant concentrates or added to coolant systems tank-side.

Each strategy has advantages and limitations.

Typically a biocide built into a metalworking fluid will function as an in-drum preservative in the concentrate, and will also provide some measure of contamination control at use-dilutions. This approach minimizes the requirement for handling concentrated biocide at the end-use site, and ensures that biocide is added to the system proportionately with the coolant concentrate. However, a variety of site-specific factors affect biocide performance^{18,19, 20}. Consequently, formulators must choose between potentially using excess biocide in concentrates or risking application failures. Moreover, individual coolant components are depleted at different rates. If fresh coolant is added to a heavily contaminated system, the biocide concentration may be depleted rapidly, leaving the remaining components unprotected against biodeterioration.

Microbial contamination can be controlled by adding biocide tank-side at the end-use site. Coupled with an appropriate monitoring program, tankside addition provides more immediate remediation of contamination problems. Biocide selection can be tailored to plant operating parameters such as water hardness, coolant residence-time (as affected by drag-out, misting, splashing, evaporation, etc.), personnel (responsibilities, training, etc.) and waste-treatment processes. Prophylactic treatment can be coupled to data from biocide concentration, biomass and/or microbial activity measurements. Treatment should always be initiated **before** significant adverse effects on coolant performance are noted.

There are several disadvantages to tankside treatment. End-users must maintain an inventory of the appropriate biocides. Tankside application is more labor intensive than is depending on biocide built-into coolant concentrate. Personnel responsible for biocide

application must be trained in proper handling procedures as well as the criteria for dosing. All personnel need to understand the precautions and benefits attendant to in-plant biocide use. Labor relations can become a pivotal issue because of the mystique associated with the appellation: "biocide."

Performance: We have already discussed performance in the context of treatment objectives and mode of application. Ability to prevent or suppress microbial growth is only one of several performance criteria. From a more holistic perspective, a biocide should have either a beneficial or neutral effect on other coolant properties such as:

- Corrosion Protection
- Emulsion Stability
- Filterability
- Foaming Tendency
- Lubricity
- Misting
- pH Stability
- Residue Buildup
- Swarf Removal
- Waste Treatability

Multifunctional performance increases the value of a biocide. A product which can eliminate or reduce the requirement for other fluid components generally translates into significant cost savings for both coolant formulators and end-users. Typically, formulators

will work cooperatively with both biocide manufacturers and end-users to evaluate biocide performance in this broader context.

Functional blends: There are two general classes of functional blends. Most common in the U.S. are blends of two or more active ingredients. These products typically are designed to extend the antimicrobial spectrum. For example, sodium pyridinethione oxide is selectively effective against fungi. Oxazolidines and triazines are selectively effective against bacteria. Commercial blends of anti-fungal and anti-bacterial agents reduce the number of products inventoried at the end-use site.

An alternative blending strategy entails combining one or more active ingredients with other additives which improve biocide performance. This approach is gaining favor in Europe, where regulations regarding blended formulations are less restrictive than they are in the U.S. An example of this type of blend is the combination of an isothiazolinone with an acidic formaldehyde condensate molecule. The isothiazolinone, when used alone, does not persist in coolant concentrates, whereas the blend does. It is likely that both types of blends will become increasingly prevalent in the U.S. over the next decade.

Performance expectations: Clearly, biocide selection is a complex task, comparable to the selection of other components of metalworking fluid formulations. However through the selection process, biocides are unlikely to function optimally in a neglected coolant system.

Biocides may be unable to penetrate thick slime-films accumulating on machine and conduit surfaces. As noted above, biocides do not act catalytically. Biocide demand may exceed the dose-rate in heavily contaminated systems. Filter-media may scavenge biocides from coolants, and other fluid components may neutralize biocides²¹. To derive maximum benefit from biocides, coolant systems should be well-maintained. Several of my fellow speakers will be elaborating on coolant system maintenance at this clinic. I strongly recommend that you consider chemical treatment as a component of these maintenance strategies rather than a substitute. Without good housekeeping, biocide performance is likely to be disappointing.

CONCLUSIONS

There are a variety of strategies for controlling microbial contamination in metalworking fluids. These include both chemical and non-chemical treatments as well as combinations thereof. Non-chemical treatments share the common disadvantage of providing disinfection at only a single point within a coolant system. Most non-chemical technologies also require considerable capital investment to install and high energy costs to operate.

There are two primary chemical strategies. One entails the use of bioresistant formulation constituents. The other involves the application of antimicrobials, either in-concentrate or tankside. Formulators using bioresistant additives are advised to ensure that these products are actually functional molecules which are recalcitrant to microbial attack, rather than unregistered preservatives sold as coolant "stabilizers." Biocides should be selected with a mind towards the specific application objective. There is no universally applicable biocide, nor is there a single best approach to biocide treatment. In practice, the most successful programs combine good coolant system management practices, high-quality coolants (often containing both bioresistant components and preservatives) and tankside biocide treatment. The ultimate goal is prolonged coolant life accompanied by low overall maintenance and waste treatment costs in a healthy work environment. This is achieved through the continuous cooperative efforts of end-users, formulators and additive suppliers.

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TABLE 1. COMMONLY USED PRODUCTS REGISTERED BY U.S. EPA FOR USE AS METALWORKING FLUID PRESERVATIVES

ALKANE DERIVATIVES	Tris(hydroxymethyl) nitromethane	TRIS NITRO ^o
	2-bromo-2-nitropropanediol	BIOBAN ^o BNPD
	2,2-dibromo-3-nitrilopropionamide	XD-8254 ^o , DBNPA
	1,2-dibromo-2,4-dicyanobutane	TEKTAMER 38 ^o
PHENOLIC DERIVATIVES	Sodium 2-phenylphenate	DOWICIDE A ^o
	Orthophenylphenol	DOWICIDE 1 ^o
TRIAZINES	Hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine	BIOBAN ^o GK GROTAN ^o ONYXIDE 200 ^o
	Hexahydro-1,3,5-triethyl-s-triazine	VANCIDE TH ^o
ORGANO SULFUR-NITROGEN COMPOUNDS	1,2-benzisothiazolin-3-one	PROXEL CRL ^o
	5-chloro-2-methyl-4-isothiazolin-3-one + 2-methyl-4-isothiazolin-3-one	KATHON ^o 886 MW
	Potassium dimethyldithiocarbamate	BUSAN 85 ^o
	Sodium pyridinethione oxide	SODIUM OMADINE ^o

MISCELLANEOUS

CIS 1-(3-chloroallyl)-3,5,7-triaza-1-
azoniaadamantane

DOWICIL 75°

4-(2-nitrobutyl)morpholine + 4,4,-(2-
ethyl-2-nitromethylene)dimorpholine

BIOBAN P-1487°

Glutaraldehyde (1,5-pentanedial)

UCONEX° 345

4,4-dimethyloxazolidine + 3,4,4-
trimethyloxazolidine

BIOBAN° CS-1135

5-hydroxymethyl; 5-
hydroxymethoxymethyl; 5-
hydroxypoly(methyleneoxy)methyl; 1-
aza-3,7-dioxabicyclo(3.3.0)octane
blend

BIOBAN° N-95

Poly[oxyethylene(dimethylimino)ethyl-
enedimethylimino ethylene dichloride]

BUSAN° 77

OLIGODYNAMIC EFFECT OF AN ORGANONITROGEN BIOCIDES

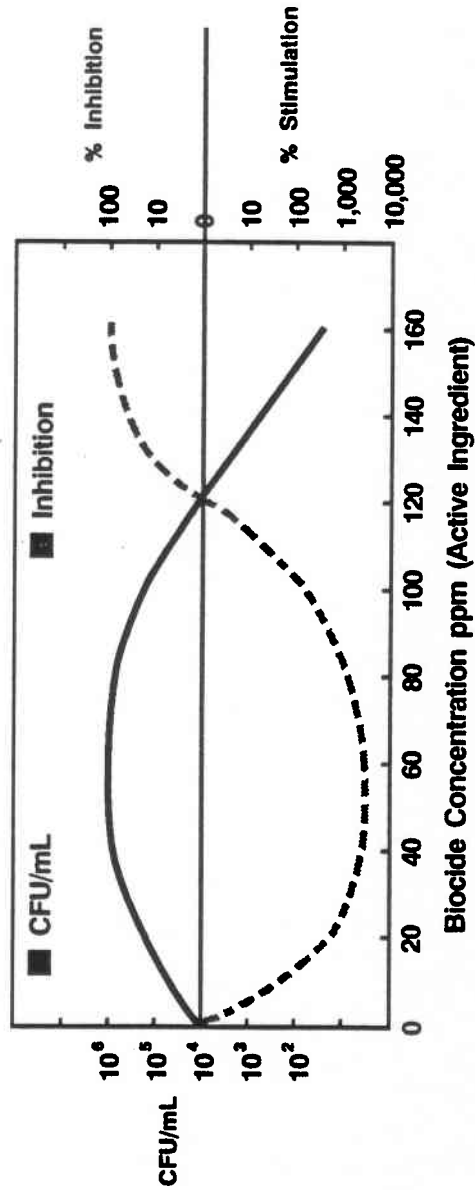


Figure 1