Biocides in Adhesives and Sealants

BY M. C. HUANG

CHEMICAL DIVISION
ABBOTT LABORATORIES
NORTH CHICAGO, ILLINOIS

Since the term "biocide" has not been used widely in the adhesive and sealants industry, its meaning may not be clearly understood. In its literal definition, biocide means a substance which kills life, both plant and animal! Obviously, this is not a good working definition because of its connotations concerning your life and mine. It is preferable to define biocide as a "chemical or system of chemicals which either kills *micro*organisms (microbes) or inhibits their normal growth."

For the adhesives and sealants industry, this means that a biocide should prevent the growth of microbes which might 1) hurt the adhesive properties of an adhesive or sealant product, 2) spoil its appearance, or 3) impart an offensive odor to it.

In an ADHESIVES AGE editorial ("On the Positive Side," February, 1973, page 6) B. J. Kotsher defined biocides, gave examples of types used, discussed Federal regulatory developments, and encouraged the adhesives and sealants industry "to become more familiar with all the facets of the (biocide selection) problem and with all the opportunities presented in finding solutions."

The purpose of this article is to expand on the editorial by providing more detail — hopefully by 1) giving the adhesives and sealants technical director a broader perspective on the problem and some guidelines for its solution, and 2) discussing related environmental issues.

The two most important questions concerning the spoilage problem are:

- Has the microbial attack occurred before the user opens a fresh container of your product, or does it occur after he has applied it?
- What is the nature of the offending microbe — is it bacterial or fungal, or both? Or is it an enzyme synthesized by the microbes, which may now be either living or dead?

"In-Can" Preservation

If the attack has occurred by the time the user opens his container, the organism was already in the adhesive or sealant when the container was filled. There are two possible sources of microbes leading to this condition. One is your manufacturing plant; a warm, humid environment creates ideal conditions for microbial growth and sporulation. The other possible source is the numerous raw materials which go into your formulations. Certain raw materials are particularly susceptible to microbial contamination.

As with larger organisms, microbes which present problems to the adhesives and sealants industry usually feed on organic matter — proteinaceous materials such as gelatin, casein, or zein — or cellulosic materials such as thickeners, starch, or dextrin. Beyond these obvious "foods," numerous other organic chemicals or binders can be metabolized by microbes. These include plasticizers, surfactants, certain synthetic latex systems, and so forth.

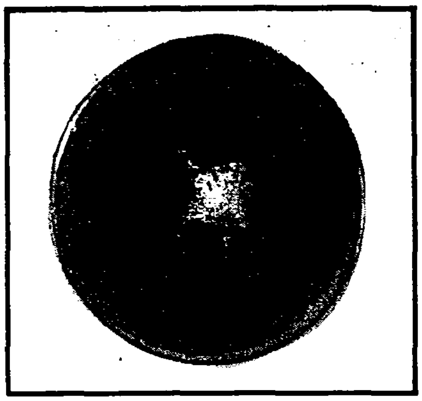
Usually, the only microbes which thrive in an air-tight container are bacteria; the so-called anaerobic bacteria do not require air for their source of oxygen. (Most fungi — the mold or mildew types of organisms — need air as their oxygen source.) In-can spoilage can usually be attributed either to bacteria or to the enzymes that certain bacteria secrete. These enzymes can hydrolyze organic materials, thereby rendering the adhesive ineffective. Separation of an animal glue or a starch paste into distinct water and solid phases is a familiar example of enzyme attack against emulsifiers.

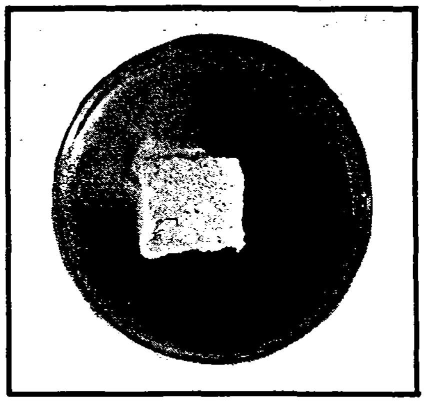
Enzymes, once formed, are not inhibited by many biocides. The modern approach to the enzyme problem is to prevent microbial growth by proper biocide selection to preclude the synthesis of enzymes.

"Post-Application" Preservation

In many cases, microbial attack occurs after application of the adhesive or sealant. Unlike in-can spoilage, the culprit in these cases is usually a fungus (mold), whose spores either are in the air or are dormant in the can until the presence of air and moisture enables their rapid growth. Examples of this include:

- The familiar blackening of bathtub chalk results from *Aspergillus niger* (a black mold), which feeds on the caulk or on the adhesive behind the tiles.
- Splotches of *Aspergillus niger* or *Aspergillus oryzae* (green mold) some-



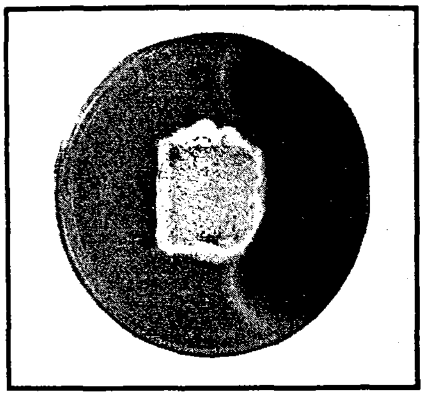


protection/100 gallons, blank.

protection/100 gallons, 12 oz.

protection/100 gallons, 14 oz.

protection/100 gallons, 16 oz.



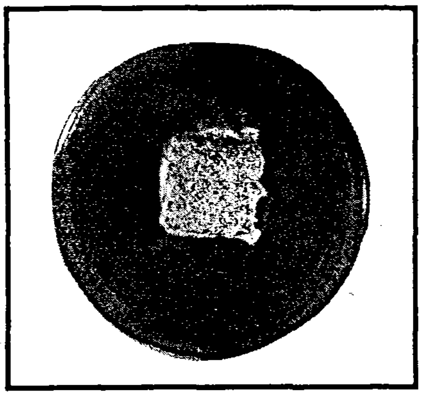
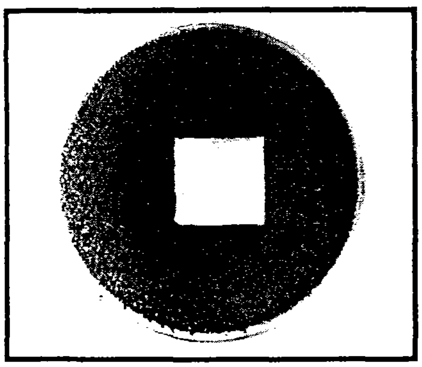
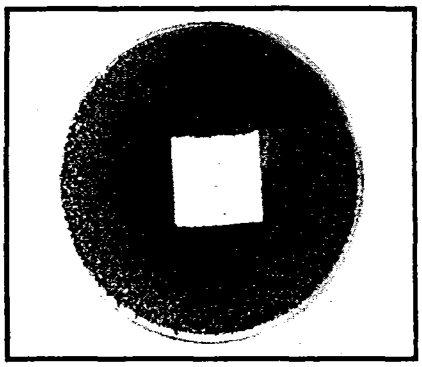


Figure 1 — Microbiological evaluations run with Amical mildewcides in adhesive and sealant formulations to determine optimum concentrations to use on a cost/use basis. Abbott-modified ANSI test; test organism, A. niger; 14 days.

Figure 2 — Another series of microbiological evaluations, ANSI test, 6/74.



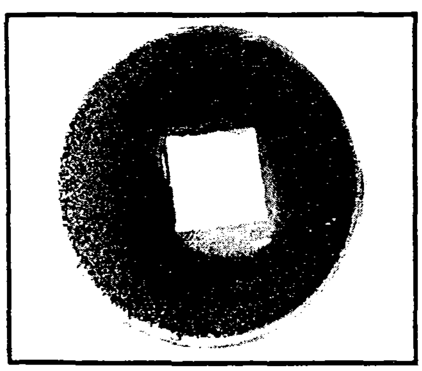


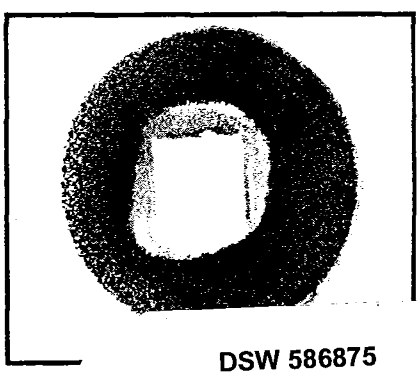
unprotected sample — substantial overgrowth

0.05% A-48 dispersion — clear zone of inhibition

0.10% A-48 dispersion — clear zone of inhibition

0.15% A-48 dispersion — clear zone of inhibition.





times show through wallcoverings (especially nonporous types like vinyls, which cause the paste to remain moist for extended periods, thus promoting mold growth).

- Black mold or red slime (another mold) are sometimes problems in ready-mixed gypsum wallboard joint compounds. Here, because the "glue line" is pretty thick, drying can be slow. Spores of these vigorous molds will grow rapidly into unsightly colonies which can show through a coat of paint.
- Corrugated boxboard has been known to show mold growth in humid, tropical climates; this results from mold feeding on the corrugating adhesive, or possibly on the board itself.

The Market for Biocides

There are no published statistics on the use of biocides in adhesives and sealants. Based on field interviews with technical and purchasing managers at numerous large, medium, and small adhesives and sealants companies, we estimated the 1972 biocide consumption at $1.4 million, broken down as follows:

End use	$ Millions
Construction, including joint compound	$0.6
Packaging	0.3
Sealants	0.2
All other	0.3
Total	$1.4

Source: Abbott Laboratories field market analysis

At the time the analysis was done (late 1972), the leading type of biocide was the mercurial. Other types range from inexpensive chemicals like formaldehyde and phenol, to the parabens and chlorinated phenols, to the higher priced nonmercurial specialty biocides.

Mercurials may no longer be the leading type of biocide, since we know of several companies which have since replaced mercurials with nonmercurials, including Abbott's Amical 48 and Amical 48 Dispersion.

Biocide Cost/Use Economics

Accustomed to using biocides which range in price from $0.10 to $2.50 per pound, both technical and purchasing people in the adhesives and sealants industry tend to react negatively to pecialty biocides which may cost $6 o $17 per pound or more.

The real key to biocide economics is cost per unit protection — not cost per pound of biocide. We refer to this concept as "cost/use economics." The same concept has elsewhere been dubbed "cost/benefit ratio," "efficacy per unit cost" (which is the inverse), and so forth. Here is a simple example of the application of the cost/use factor:

A starch packaging adhesive is well protected by a \$0.50/lb biocide, used at the 0.3 percent weight level. The cost/use factor in this case is 0.5 x 0.3 = 0.15. Suppose that a \$6.00/lb biocide will provide equivalent protection when used at the 0.01 percent level. In this case, the cost/use factor would be only 6 x 0.01 = 0.06. The adhesive maker would actually save 60 percent by using the apparently more "expensive" biocide.

To keep the concept simple, we assign no units to the cost/use factor. As long as two biocides are compared in identical units — dollars/batch, cents/can, etc. — it makes no difference what units are used.

The Environmental Issue: MIC vs. LD_{50}

Early industrial biocides were heavy metal compounds which were well-known poisons. We can point to the mercurials, arsenicals, and lead compounds as examples. The objective was to apply them in such a way that man suffered the least and the pests suffered the most.

As the chemical, pharmaceutical, medical, and environmental communities became more knowledgeable and more concerned, there evolved biocides which were selectively more poisonous to microbes while being less poisonous to mammals, birds, and fish. Classical examples were phenol and its derivatives in the industrial field and quinine and its derivatives in the human and animal health field. Notice now the trend away from compounds based on heavy-metal elements.

Indeed, the commercial antibiotic today (penicillin, tetracycline, erythromycin, streptomycin, etc.) is a biocide with a specifically high toxicity to disease-causing microbes and a low toxicity to the host organism (the patient). In other words, they are biocides with a low MIC value and a high LD_{50} value. The terms MIC and LD_{50} are worth discussing.

MIC stands for minimum inhibitory concentration, and it refers to the concentration of biocide (usually expressed as parts per million) in a controlled medium (such as nutrient agar) which will inhibit growth of a specific microbe. The lower the MIC, the better the biocide. For example, a compound showing an MIC of 1 ppm against *Aspergillus niger* is likely to be a better bathtub-caulk biocide than a compound showing an MIC of 20 ppm against that same organism. The word "likely" is emphasized because the MIC values of the two compounds were determined in a controlled medium *in the laboratory*. In an actual caulk formulation, their effective usage levels may or may not be in a ratio of 1 to 20.

LD_{50} stands for lethal dosage, and it refers to the quantity of a biocide which a group of mammals can withstand (through skin absorption or, more commonly, when administered orally) and statistically have a 50-50 chance of surviving. This test, also carried out in the laboratory, is administered to a variety of test animals, particularly to rats (in which LD_{50} values correlate closely with human LD_{50} values). LD_{50} is usually expressed in milligrams of compound per kilogram of body weight. The higher the LD_{50}, the safer the biocide. Thus, a biocide with an LD_{50} of 10,000 mg/kg will be substantially safer to workers in the plant than a biocide with an LD_{50} of 200 mg/kg.

Finally, TL_{50} data are now required by the Environmental Protection Agency for biocides used in a number of industries where the plant effluent may be deleterious to fish life. TL_{50} stands for median toxic limit, and it refers to the biocide concentration, in parts per million in water, at which a certain species of fish (usually fresh-water fish) will statistically stand a 50-50 chance of surviving. The higher the TL_{50}, the safer the biocide.

Working With Your Biocide Supplier

In our experience, most adhesives and sealants firms do not have microbiologists on their technical staffs. This is understandable, because microbial spoilage problems are 1) minor in relation to the problems of adhesion or sealing, and 2) generally more effectively solved by companies with microbiological facilities and personnel.

Microbiological testing can be costly, and it is not usually precise to the "nth" degree. You may derive some benefit from asking one or two competitive biocide suppliers to evaluate the efficacy of biocides in your formulations. Doing this excessively, however, can only lead to unnecessary overhead expenses for the biocide suppliers, resulting inevitably in higher prices for the biocides.

You and your supplier will get the maximum mutual benefit if you will first discuss your microbiological problem with a representative of your biocide supplier. He may want to communicate with his home office before he commits them to perform tests. Assuming mutual prior agreement, you *should then submit a reasonable* number of samples always including both a blank control (containing no biocide) and a standard production control. Whenever possible, stick with standard ASC, ASTM, MIL tests, etc. If not, arrive at a mutual understanding of the test parameters before tests are initiated. Code the samples, and request a written and pictorial report of the results. After the tests are complete and you have reviewed the report, discuss the results openly and frankly with the biocide supplier's sales or technical representative.

Summary

Biocides are chemicals or systems of chemicals which either kill or inhibit microorganisms. These microbes, if not inhibited, frequently damage the esthetic or engineering properties of adhesives and sealants. An adhesive or sealant manufacturer having microbial problems should pinpoint whether they are "in-can" problems, "post-application" problems — or both.

In 1972, the adhesive and sealant industry consumed approximately \$1.4 million of biocides, mainly in construction and packaging adhesives and in sealants. Biocide economics should be based not on the price of the biocide alone, but on its cost/use factor. Sometimes a high priced biocide will prove less expensive to use.

Environmental issues are becoming important in the choice of biocides for adhesives and sealants. The ideal biocide has 1) a numerically *low MIC* value against your problem organism, 2) a high oral LD_{50} value in mammals, and 3) a high TL_{50} value in fresh-water fish.

When you ask your biocide supplier to help you evaluate the efficacy of a biocide, you will get the best results if you are 1) specific in stating the problem and possible test methods, 2) reasonable in your expectations, and 3) candid in discussing the test results with the biocide supplier who did the evaluation

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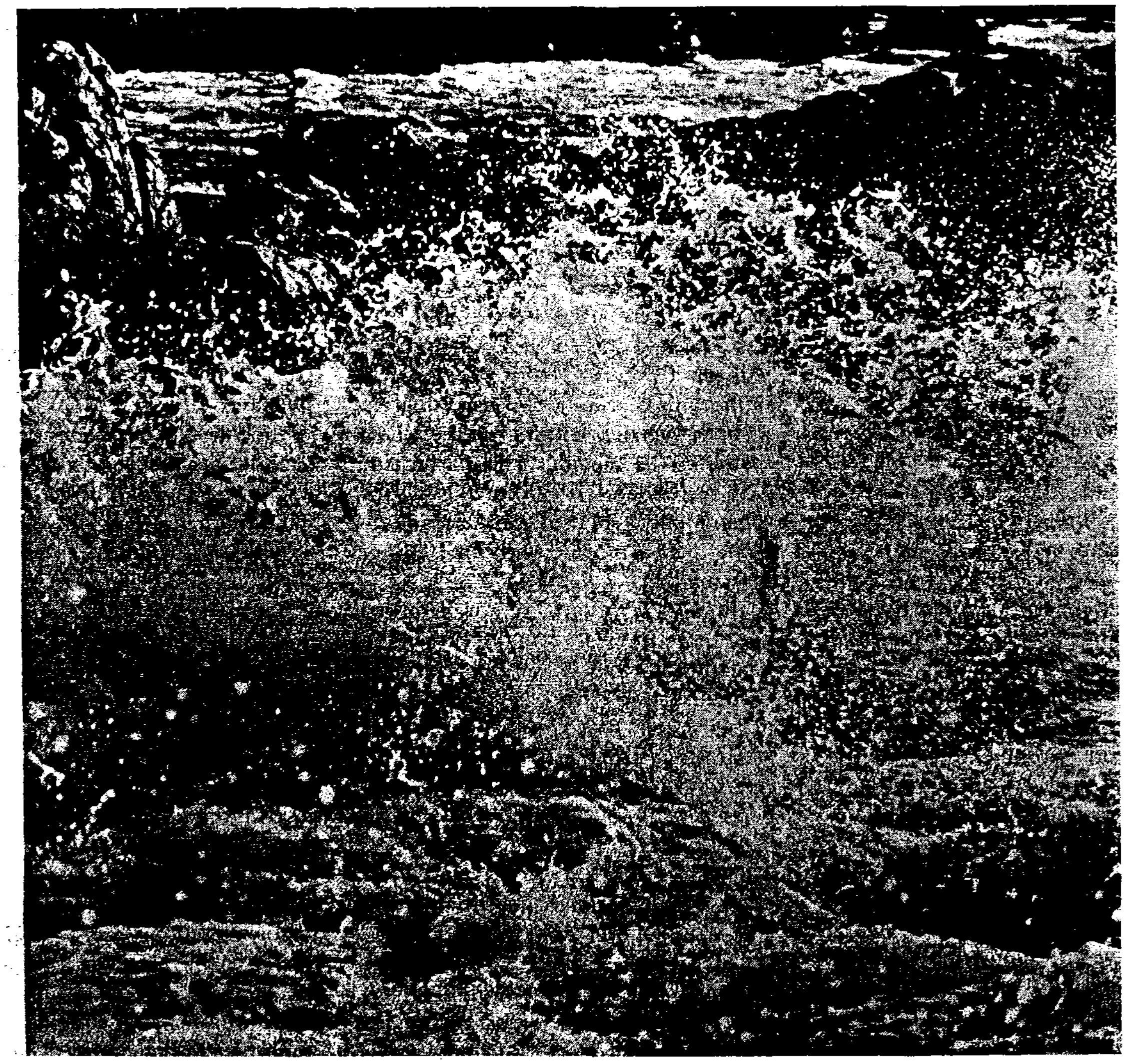

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