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Advances in Quaternary Ammonium Biocides

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ABSTRACT

Several generations of structurally variable quaternary ammonium biocides were developed from approximately 1935 until the present. Demand for products with improved microbiological performance guided each successive step of development. Commercial availability of dialkyl dimethyl ammonium chlorides in 1965 set the stage for significant advances in quaternary biocide practices in the USA and Europe. This trend is continuing today with development of new, fourth-generation quaternary biocides. Regulatory requirements by the US Environmental Protection Agency (organic soil tolerance) and specific consumer/marketing demands (hard water tolerance) provided a renewed challenge for quaternaries meeting those requirements. Development and properties of new, fourth-generation quaternary biocides meeting those challenges are discussed. Some of the functional advantages of quaternaries are outlined. Development of the fourth-generation quaternary biocides has led to products demonstrating significantly superior broad spectrum biocidal activity, specifically designed to meet the new challenges of organic soil and hard water contamination. Strong market gains, made by quaternary biocides over the recent past, have been primarily as a result of the type of work described herein, but some of the gains in quaternary usage can be ascribed to concern over adverse toxicological and environmental impact of other traditional biocides such as phenolics and aldehydes. The outlook for a continued increase in the use of modern-day quaternary biocides is encouraging.

INTRODUCTION

Commercial importance of cationic surface-active agents first became relevant with the discovery of their significant biocidal properties in 1935 (1). Today's cationic surface-active agents, with improved antimicrobial properties, continue to play an increasingly important role as broad spectrum biocides in many and varied applications. These cationic biocides are now commonly referred to as quaternaries or, in short, quats.

Fatty alcohols and/or fatty acids derived from both natural and synthetic processes provide the basic feedstock for today's production of a variety of commercially available quats. The process for conversion of the basic oleochemicals to fatty amines followed by quaternization is well established.

Quaternaries of the type discussed here generally are readily water-soluble and thus lend themselves to easy preparation of simple aqueous solutions or more complex formulated multicomponent systems marketed for a variety of applications.

These modern-day quats exhibit many functional advantages, such as:

—broad spectrum microbiological activity, including bactericidal, fungicidal and virucidal activity,
—microbiological activity over the entire pH range,
—low toxicity at use concentrations,
—high vapor pressure for absence of volatile biocide,
—high aqueous solubility,
—highly surface-active,
—excellent detergency,
—colorless and odorless.

Some of the major applications for biocidal quaternary ammonium compounds are as:

—household, institutional/industrial and hospital disinfectants/sanitizers/cleaners, fungicides, virucides,
—swimming pool algaecides,
—water treatment microbiocides,
—fabric mildew preventatives,
—laundry bacteriostat/sanitizers,
—oil field biocides,
—topical antiseptics,
—preservatives, industrial/cosmetics/pharmaceuticals.

GENERAL BACKGROUND

Over the years, the search for biocides with improved microbiological and functional performance characteristics has led to the development of several generations of quats which may be broadly segmented. Quaternaries of the initial discovery were alkyl dimethyl benzyl ammonium halogens of mixed alkyl chain distributions. Work by Cutler (2) describes the performance characteristics of a homologous series of odd- and even-chain alkyl dimethyl benzyl ammonium chlorides. It was found that, generally, biocidal activity for this structural type of quaternary was centered at an alkyl chain range from 12 to 16 carbons. The product of greatest commercial significance today is alkyl benzyl dimethyl ammonium chloride with an alkyl chain distribution of C_{14} = 15%, C_{12} = 40%, C_{16} = 10%.

Second-generation quats are primarily modifications of the first-generation by substitution within the benzene ring or at the quaternary nitrogen, as shown in Figure 1.

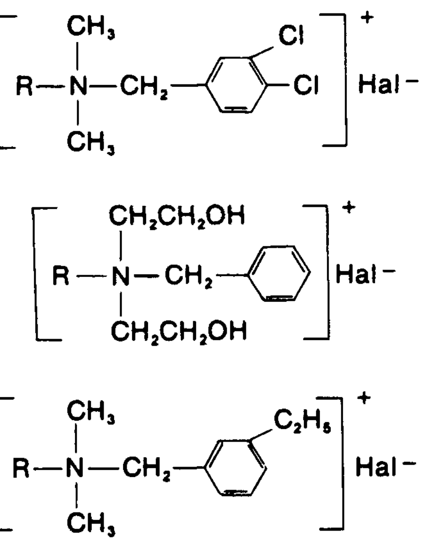


FIG. 1. Second-generation quaternaries (1955): substituted alkyl dimethyl benzyl ammonium halogens.

Also, at this stage, combinations of first- and second-generation quats, which improved microbiological performance, became commercially significant.

The product of primary commercial significance presently is a mixture of equal proportions of alkyl dimethyl benzyl ammonium chlorides and alkyl dimethyl ethyl benzyl ammonium chlorides of a specific alkyl chain distribution, as shown in Figure 2.

The advent of patented dialkyl amine technology (3) made possible the economical production of dialkyl dimethyl ammonium chlorides. These new structures provided significant advances in quaternaries with microbiological performance characteristics (4-6).

In contrast to first- and second-generation products, the primary biocidal activity of the dialkyl quaternaries is found in the C_8-C_{10} alkyl chain range. The products of current commercial significance are (a) dioctyl dimethyl ammonium chloride; (b) octyl decyl dimethyl ammonium chloride (50%), dioctyl dimethyl ammonium chloride (25%), didecyl dimethyl ammonium chloride (25%); and (c) didecyl dimethyl ammonium chloride.

DEVELOPMENT OF THE FOURTH GENERATION

Discussion

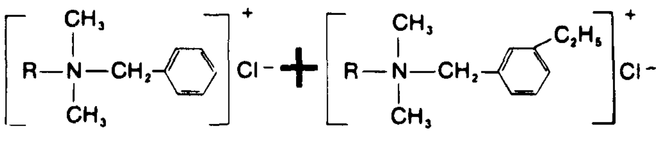
Distribution of biocides, their microbiological performance characteristics and the resultant claims for control of microorganisms are controlled in many parts of the world by a host of laws and regulations. Efficacy requirements vary from country to country and for each specific use.

Our findings, presented hereafter, on the development of new quaternary biocides of the fourth generation are confined to US requirements and regulations under the Federal Insecticide Fungicide Rodenticide Act (FIFRA) of the Environmental Protection Agency (EPA), which regulates such products in the USA.

Over the recent past, two new challenges emerged for surface disinfectant products based on quaternaries: (a) improved organic soil tolerance mandated by EPA regulations for the inclusion of 5% organic soil during the required efficacy testing by the AOAC Use-Dilution Test; and (b) increased hard water tolerance for surface disinfectants by challenge of the disinfectant use solution with hard water contaminants during efficacy testing. Although the level of hard water contamination may vary, a level of 400 ppm calculated as $CaCO_3$ appears to have become the industry norm.

Although first-, second- and third-generation quats provide some of the answers to these challenges, it became clear that further improvement would be a benefit.

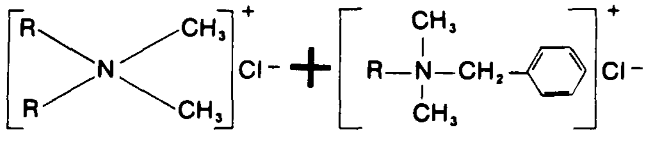
Continued research in our laboratories investigating structural aspects of biocidal quaternaries and their relationship to each other has led to significant further advancement in biocidal quaternary technology. Many experimental products were evaluated exhibiting varying degrees of promise in the improvement of overall biocidal activity and, more specifically, the improvement of disinfectant activity in the presence of both organic soil and hard water contamination. Guidance was drawn from the performance characteristics of first-, second- and third-generation quaternaries. Also, these products provided the baseline on which to improve. Our work culminated in the commercialization of a fourth generation of quaternary biocides consisting of synergistic combinations of dialkyl dimethyl ammonium chlorides and alkyl dimethyl benzyl ammonium chlorides, such as shown in Figure 3.



Alkyl (C_{14}, 60%; C_{16}, 30%; C_{12}, 5%; C_{18}, 5%) Dimethyl Benzyl Ammonium Chlorides

Alkyl (C_{12}, 68%; C_{14}, 32%) Dimethyl Ethylbenzyl Ammonium Chlorides

FIG. 2. Product of greatest commercial significance today.



Octyl Decyl Dimethyl Ammonium Chloride 50%
Dioctyl Dimethyl Ammonium Chloride 25%
Didecyl Dimethyl Ammonium Chloride 25%

Alkyl (C_{14}, 50%; C_{12}, 40%; C_{16}, 10%) Dimethyl Benzyl Ammonium Chlorides

FIG. 3. Dialkyl dimethyl ammonium chlorides and alkyl dimethyl benzyl ammonium chlorides.

The new fourth-generation quat and commercial alkyl dimethyl benzyl ammonium chlorides and dialkyl dimethyl ammonium chlorides were compared for disinfectant, sanitizing and fungicidal performance under organic soil and hard water contamination conditions. For purposes of identification, the following product codes apply: quat A = alkyl (C_{14} = 50%; C_{12} = 40%, C_{16} = 10%) dimethylbenzyl ammonium chloride; quat B = dialkyl (C_8-C_{10}) dimethyl ammonium chlorides; and quat C = synergistic combination A and B at a 40:60 ratio.

Data presented in Figure 4 show the minimum concentration of quat, in ppm, required to demonstrate disinfectant activity via the AOAC Use-Dilution Test in the presence

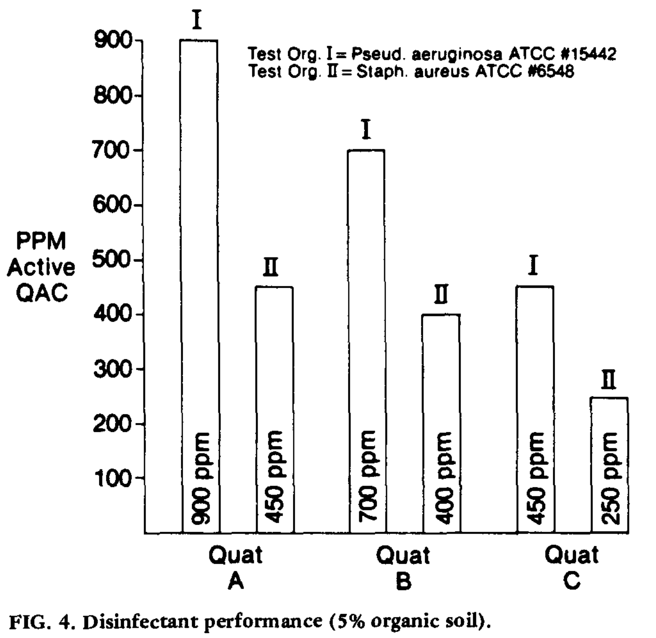


FIG. 4. Disinfectant performance (5% organic soil).

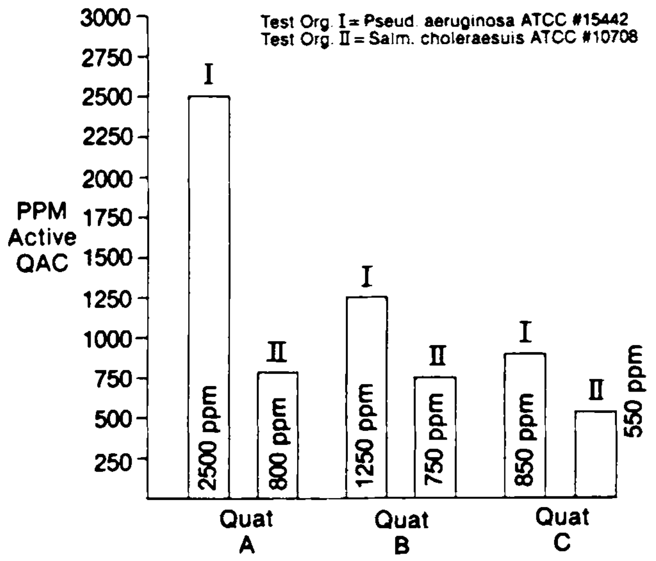


FIG. 5. Disinfectant performance (400 ppm water hardness, 5% organic soil).

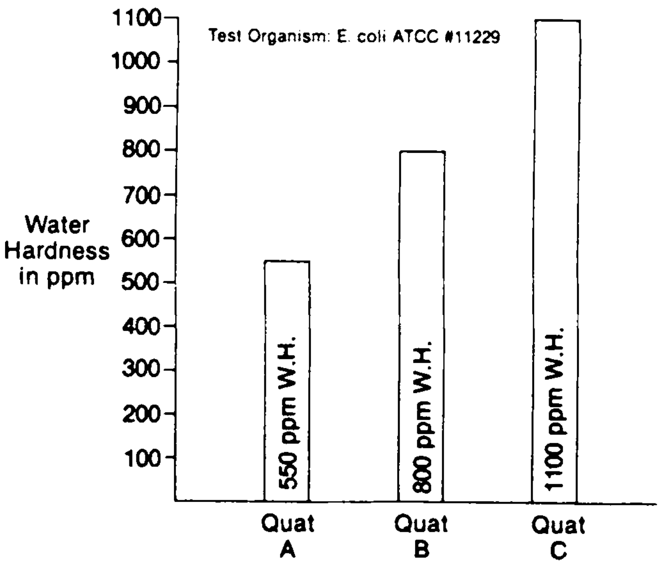


FIG. 6. Sanitizing performance (quaternary concentration, 200 ppm).

of 5% organic soil.

These data demonstrate clearly the superior performance of quat C when tested by the AOAC Use-Dilution procedure against *Pseudomonas aeruginosa* and *Staphylococcus aureus* in the presence of 5% organic soil.

Data in Figure 5 show the minimum concentration of

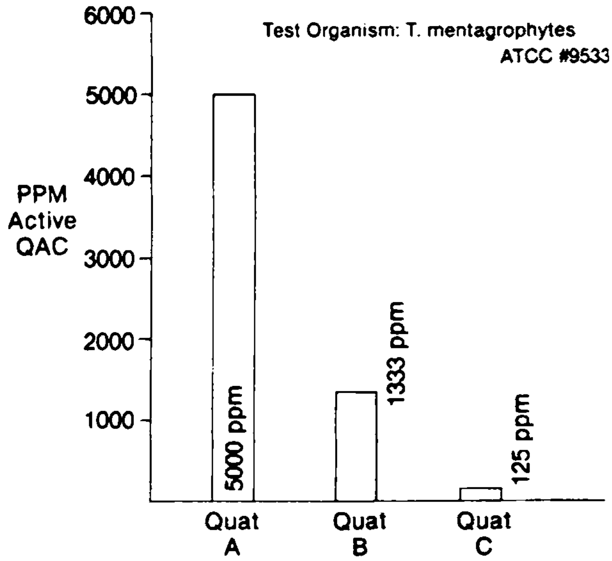


FIG. 7. Fungicidal performance (5% organic soil).

quaternary, in ppm, required to demonstrate disinfectant activity via the AOAC Use-Dilution Test in the presence of 400 ppm water hardness and 5% organic soil. The superior disinfectant performance of quat C, this time, in the presence of both 400 ppm hard water contamination and 5% organic soil, is shown.

An important function of a quaternary biocide is its ability to sanitize under varying hard water conditions. Figure 6 shows the hard water tolerance by the AOAC Detergent Sanitizer Test, in the presence of 5% organic soil, at a standard quaternary concentration of 200 ppm.

Quat C, at up to 1100 ppm water hardness, shows excellent sanitizing capacity in comparison to quats A and B.

Figure 7 shows the minimum concentration of quaternary, in ppm, required for fungicidal activity, in the presence of 5% organic soil, by the AOAC Fungicidal procedure. Outstanding fungicidal activity of quat C, with 10-40 times the concentration of quats B or A required to obtain similar performance, is shown.

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