THE CHEMISTRY AND FUNCTIONAL CHARACTERISTICS OF BIOCIDAL QUATERNARIES, AAC's

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Introduction

The commercial importance of cationic surface active agents first became relevant with the discovery of their significant biocidal properties by Domagk[1] in 1935. 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. Among the more recent applications is wood preservation.

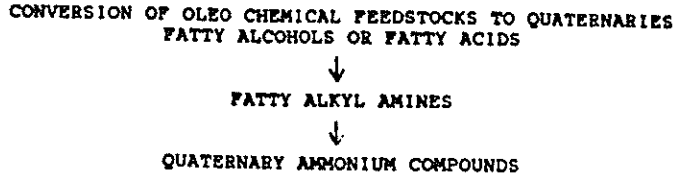
These cationic biocides are now commonly referred to as Quaternaries or Quats.

During their evaluation as new wood preservatives and now in specific commercial wood preservation applications, these compounds have collectively become known as Alkyl Ammonium Compounds or short AAC's.

The term "cationic surfactant" generally refers to compounds containing at least one hydrophobic long alkyl chain group and a positively charged nitrogen.

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 quaternaries. The processes for conversion of the basic oleo chemicals to fatty amines followed by quaternization are well established. Typically, conversion of the basic raw materials proceeds as outlined in Figure 1.

FIGURE 1



The resultant quaternary products find a wide range of uses, with only a specific segment of the quat products, exhibiting biocidal properties. Hence, application for wood preservation and other biocidal uses is limited to those compounds exhibiting microbiological activity.

Since World War II, many new uses for quaternaries have been developed. Among the most prominent areas of utility other than biocidal uses are fabric and textile softening, lubrication and static control, along with hair conditioning and static control in personal care products.

Other areas of utility include corrosion inhibition, and foam depression, ore flotation, asphalt and petroleum additives, textile dying, emulsification-demulsification. The biocidal quaternaries of the type discussed hereafter generally are readily water soluble and thus lend themselves for easy preparation of simple aqueous solutions or more complex formulated multicomponent systems marketed for a variety of applications including of late various facets of wood preservation. These modern day quaternaries exhibit many functional advantage such as:

Figure 2

FIGURE 2

----BROAD SPECTRUM MICROBIOLOGICAL ACTIVITY, INCLUDING FUNGICIDAL BACTERIACIDAL AND VIRUCIDAL ACTIVITY

----MICROBIOLOGICAL ACTIVITY OVER THE ENTIRE PH RANGE

----STRONG ELECTROSTATIC BONDING CHARACTERISTICS

----LOW VAPOR PRESSURE FOR ABSENCE OF VOLATILE BOICIDE

----HIGH AQUEOUS SOLUBILITY

----HIGHLY SURFACE ACTIVE - IMPROVED PENETRATION

----COLORLESS AND ODORLESS

----LOW TOXICITY AT USE-CONCENTRATIONS

Aside from wood preservation, some of the more important areas of utility for biocidal quaternaries are outlined in Figure 3.

Figure 3

MAJOR AREAS OF APPLICATIONS FOR
BIOCIDAL QUATERNARY AMMONIUM COMPOUNDS

Preservatives, Including Wood,
Industrial/Cosmetics/Pharmaceuticals

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

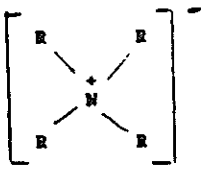
General Discussion

The most significant functional feature of a cationic, setting it apart from other types of ionically charged or non-ionic compounds, is the positively (+) charged cation, usually a quaternized nitrogen; e.g.,

Figure 4

FIGURE 4

GENERAL STRUCTURE OF CATIONICS



This property causes strong electrostatic attraction toward negatively (-) charged substrates of all types. Thus one can speak of cationic surfactants as being "preferentially" absorbed or adsorbed onto wood, fibers, hair, skin, floors & walls, fungi, bacteria. This phenomenon is often referred to in practical terms as substantivity, deposition or exhaustion, depending on practical application.

By means of synthesis variation, primarily that of the hydrophobic alkyl chains and the hydrophillic anions such as halides, sulfates, and others, basic performance properties, such as solubility, foaming, substantivity, biocidal activity, softening, conditioning, lubrication, charge dissipation (static control) can be controlled.

Quaternaries are derived directly from the reaction of a primary, secondary, or tertiary amine and a quaternizing agent, such a methyl chloride, benzyl chloride, dimethyl sulfate, diethyl sulfate and others.

The resultant quaternaries may be present as mono, di, or trialkyl derivatives. They may be of straight chain alkyl, cyclic or imidazoline structure. Additional variations can include ethoxylation, propoxylation and polymerization.

The designations biocidal, fungicidal, germicidal, antibacterial quaternaries describe a functionally most important feature of such products. That is, their ability to eliminate or prevent undesirable microbial and fungal growth or contamination at low concentrations

These biocidal quaternaries are effective against both gram (+) and gram (-) microorganisms as well as fungi and viruses.

Some investigators have described the mechanism of action of a biocidal quaternary as follows:

The quaternary interferes with the respiration and glycolysis (an aerobic breakdown of foodstuff) of the microorganism with particular effect in inhibiting the oxidation of certain carbohydrates.

This means that the quaternary essentially tampers with the cell metabolism, thereby bringing the cellular activity to a halt, with the ultimate result of killing the cell.

A number of additional modes of action have been postulated, but it appears safe to say that two of the most important features of the quaternaries ability to destroy or control microbial growth are surface activity and substantivity.

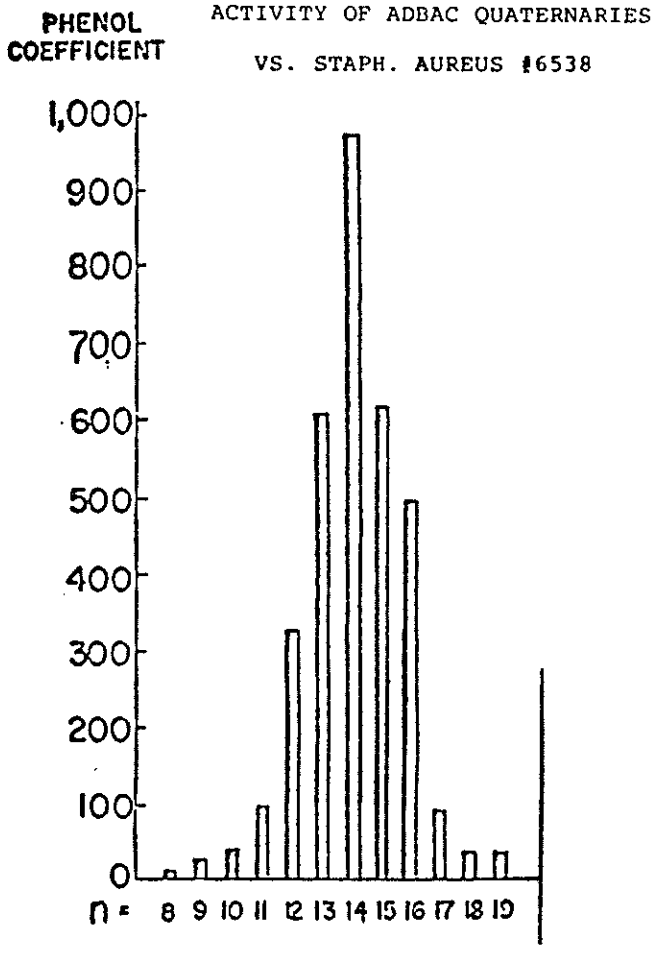
Over the years the search for quaternary biocides with improved mocribiological and functional performance characteristics has led to the development of several generations of quats which can be broadly segmented. Aside from the desire to maximize biocidal performance the availability of suitable raw materials was and is a determining factor in the production and further development of these products.

Let us briefly review the most important development stages of these quaternary biocides.

The First Generation - 1935-Present

Quaternaries of the initial discovery were Alkyl Dimethyl Benzyl Ammonium halogens of mixed alkyl chain distributions. Work by R. A. 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.

FIGURE 5

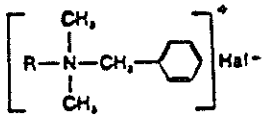


Data developed by R. A. Cutler[2] et al utilizing the phenol coefficient procedure provides an example of the microbiological activity exhibited by Alkyl Dimethyl Benzyl Ammonium Chlorides of varying alkyl chain length, Figure 5.

FIGURE 6

FIRST GENERATION QUATERNARIES - 1935

Alkyl Dimethyl Benzyl Ammonium Halogen



PRODUCT OF GREATEST COMMERCIAN SIGNIFICANCE TODAY

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

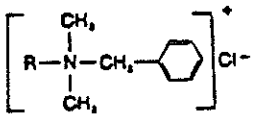


Figure 6 shows the structure of a typical alkyl benzyl dimethyl ammonium halide, along with the product of greatest commercial significance today, an alkyl benzyl dimethyl ammonium chloride with an alkyl chain distribution of C_{14}-50%, C_{12}-40%, C_{16}-10%.

From approximately 1950 the development of second generation quats led to the synthesis and evaluation of more complex and varied molecules.

Figure 7

FIGURE 7

SECOND GENERATION QUATERNARIES - 1955

Substituted Alkyl Dimethyl Benzyl Ammonium Halogens

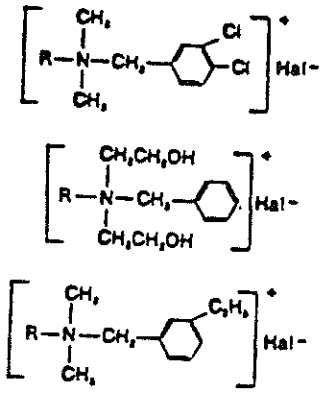


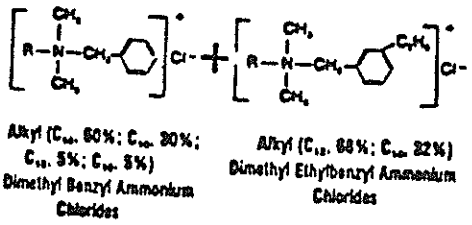
Figure 7 shows that second generation Quats are primarily modifications of first generation Quats by substitution within the benzene ring or at the Quaternary nitrogen.

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

Figure 8

FIGURE 8

PRODUCT OF GREATEST COMMERCIAL SIGNIFICANCE TODAY



Alkyl (C_{14}, 50%; C_{16}, 30%; C_{12}, 5%; C_{18}, 5%) Dimethyl Benzyl Ammonium Chlorides

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

Figure 8 shows that 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

The Third Generation - 1965-Present

The advent of patented dialkyl amine technology by Dadekian, (Lonza Inc., US) made possible the economical production of dialkyl dimethyl ammonium chlorides. These new structures provided significant advances in biocidal quaternaries. The microbiological performance characteristics of these dialkyl quaternaries have been aptly discussed by Dadekian[3] Ditoro[4] and Angele[5][6].

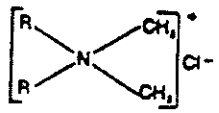
In contrast to first and second generation products, the primary biocidal activity of the dialkyl quaternaries is found in the C_8 - C_{10} alkyl chain range. The products of current commercial significance are shown in Figure 9.

Figure 9

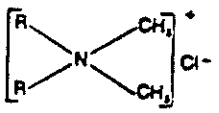
FIGURE 9

THIRD GENERATION QUATERNARIES - 1965

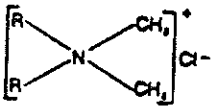
Dialkyl Dimethyl Ammonium Chlorides



Dioctyl Dimethyl Ammonium Chloride



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



Didecyl Dimethyl Ammonium Chloride

Quaternaries of the dialkyl type, particularly didecyl dimethyl ammonium chloride and octyl decyl dimethyl ammonium chloride, were found to significantly improve on the overall microbiological performance of first and second generation quats. That is to say, these new compounds can be employed at lower use concentrations for the intended tasks of controlling microbial contamination.

Of particular interest to wood preservation is the fact that these dialkyl quaternaries are highly fungicidal. Reductions of 10-50 fold in the concentration required to eliminate fungi, used in screening tests, were demonstrated over quats of the first and second generation. This performance advantage has been investigated and reported by a number of researchers interested in the development of new wood preservatives. A. F. Preston and Darrel D. Nicholas[7], A. F. Preston[8], A. F. Preston and J. N. R. Ruddick[9].

Summary

Biocidal quaternaries (AAC's) have undergone several milestones of development leading to ever improved microbiological performance for this class of cationic biocides.

Of these developments the dialkyl dimethyl ammonium chloride quats and most specifically didecyl dimethyl ammonium chloride show the greatest degree of promise and utility for various facets of wood preservation.

Along with the advantages discussed earlier, these compounds are ideally suited for these applications. Some commercial use of system incorporating quaternaries have commenced in above ground applications with additional research in progress.

Work on the development of suitable in-ground contact treatment systems with AAC's is ongoing.

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