DSDMAC in Germany, and assuming that there is complete adsorption at the crude effluent sludge, DSDMAC in sludge should be ca. 1.6% (related to dry weight). It appears from all examinations made so far on the behavior of cationic surfactants and their electrically neutral salts under anaerobic conditions such as e.g., sludge digestion, that, contrary to the relatively easy aerobic decomposition, they appear to be persistent here and do not degrade. At the same time, the question is thus raised with regard to their toxicity towards microorganisms that normally dominate the biochemical processes in sludge digestion or other anaerobic effluent processes. Further studies (22) on anaerobic sludge digestion, when having DSDMAC contents of digested sludge up to 2.5%, is not inhibited. According to Janicke et al. (20), electrically neutral salts of DSDMAC and LAS do not affect the anaerobic sludge treatment either, when they appear at concentrations up to 67 mg/L TS and at digestion times of 70-80 days. In general, one may assume that the cationic surfactants used in fabric softeners, including their neutral salts, are not biodegradable under anaerobic conditions and that, at the same time, when occuring at concentrations that are possible in practice, they do not inhibit the anaerobic wastewater or sludge treatment processes.

The present knowledge about environmental properties of cationic surfactants used in fabric softeners has not given the EEC or West Germany cause to draw up legal specifications on their minimum degradability, as is the case for anionic and nonionic surfactants. However, new shorter-chain cationics that are used as specialty chemicals in some new heavy-duty powders have different properties and might require a different environmental analysis. Their solubilities and the fact that they do not complex with LAS raises some questions about their toxicity. Their fate, however, is governed by a very high and rapid biodegradability.

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Organoclay Rheological Additives: Past, Present and Future

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ABSTRACT

Rheological or flow properties have important implications in many and diverse applications. Often, an additive is used to impart the desired flow behavior. Among these, organoclay products, formed by the reaction of organic cations with smectite clays, are the most widely used additives for solvent-based coatings. The cation – usually a quaternary ammonium salt – used will influence the performance of the resultant organoclay. Criteria to consider in the choice of a cation are molecular size, compatibility with the fluid in which the organoclay is to be used, stability and reactivity. To form a stable organoclay product, the organic cation must contain at least one long-chain alkyl group. Othr groups attached to the cation may be divided into two categories: "filler" groups serve to complete the tetrahedron around the nitrogen, whereas "active" groups contribute beneficially to the performance of the organoclay. Our study of the structure/property relationships has led to the development of new additives described here. These are superior, particularly in terms of use, while providing the same excellent rheological control offered by earlier additives.

INTRODUCTION

The control of rheology, or flow behavior, has application in products ranging from foods to lubricants to paints and other coatings. Often, seemingly contradictory flow behaviors are desired under different conditions. At times, low viscosity at low shear and high viscosity at high shear is desired. Examples of such behavior may be found in the automatic transmission of your car; under low shear conditions, this transmission fluid has very low viscosity, but under the high shear conditions that the fluid experiences while driving, the fluid behaves more like a solid . Water, also, under high shear conditions will assume the properties of a solid, which is partially responsible for the action of boat propellers.

More often, the opposite type of flow behavior is desired; i.e., high viscosity under low shear conditions, and low viscosity under high shear conditions. Lubricating greases, for example, must be sufficiently fluid to maintain coverage of the moving and contacting parts, but thick enough to remain in the bearing. Paints exhibiting this type of flow behavior apply easily, while being more resistant to pigment settling and allowing application of a thick film without sagging.

The rheologist has described several basic types of flow behavior (1), the most important of which are:

- Newtonian flow, in which the viscosity of the fluid is independent of the applied shear (Fig. 1a);
- pseudoplasticity, in which the viscosity of the fluid is a function of the applied shear. The viscosity of a pseudoplastic fluid decreases reversibly as the shear increases (Fig. 1b);
- dilatancy, which is basically the opposite of pseudo-

plasticity. Dilatant fluids increase in viscosity with increasing shear (Fig. 1c); and,

- thixotropy (Fig. 1d). Thixotropic fluids decrease in viscosity with shear and/or time under a given shear condition. The process is reversible, and may occur so rapidly as to be considered instantaneous, in which case thixotropy approximates pseudoplastic flow, or recovery may require minutes, hours, days, or even months to occur.

Note that these are idealized flow behaviors. Real fluids typically exhibit different types of flow depending on the shear range.

The desired rheological behavior may be an inherent property of the product being developed, but more often an additive is used to impart the desired flow properties. Coatings formulators, for instance, have a number of such additives at their disposal to control application properties. Perhaps the most basic of these is the solvent, which, through evaporation, can be used to increase the viscosity of the applied film. This, together with mechanisms such as rapid crosslinking and coalescence of emulsified or dispersed particles are irreversible methods for controlling the application properties of the coating.

Other additives, however, operate in a reversible manner, and provide greater ease in application. Most function by hydrogen bonding and/or polymer chain entanglement, developing a loose three-dimensional structure throughout the fluid. These include:

- thixotropic polymers, such as thixotropic alkyds which are film forming polymers which, as the name implies, impart thixotropy to the coating;
- various waxes and gums such as castor wax and its derivatives;
- inorganic materials, such as finely divided (fumed) silicas. In use, the fumed silicas form long chains of particles interconnected by hydrogen bonds. Thixotropy is provided both by entanglement of these chains and hydrogen bonding between the chains; and
- organoclays, which are the most widely used of the flow modifiers in solvent-based paints, and are the subject of this discussion.

Organoclays are, as the name implies, organometallic compositions formed by the reaction of organic compounds with clay. The clays of interest for the preparation of rheological additives belong to a class known as smectites, and are characterized by a three layer, platey structure. The two most important species are bentonite, an aluminosilicate, and hectorite, a magnesiosilicate (Fig. 2). In nature, these clays exist as stacks of platelets, much as pages in a book.

Bentonite and hectorite are further characterized by a negatively charged layer lattice structure, which arises from the replacement of some of the normal lattice atoms with other, lower valency atoms of similar size (i.e., isomorphic substitution); e.g., magnesium replaces some of the aluminum atoms in bentonite, and lithium some magnesium atoms in hectorite. The negative charges thus developed are reflected to both faces of the clay platelet where they are counterbalanced, in nature, by inorganic cations such as sodium, magnesium and calcium. These cations are not part of the lattice structure itself, and are exchangeable.

The edges of the clay platelet have been less well defined, but are responsible for the rheological activity of these clays and their derivatives. They are presumed to be electrically neutral (although some evidence for the existence of anion exchange sites has been presented [2]), and are composed of inorganic hydroxyl moieties (e.g., Al-OH, Mg-OH and Si-OH). Once dispersed in a fluid, the clay platelets will form a three-dimensional network through interplate hydrogen bonding via these hydroxyl moieties. These hydrogen bonds are similar to their organic counterparts in that they have low bond energies, and are easily disrupted by shear. Thus, during application, which is inherently a high shear process, the three-dimensional network breaks down such that the viscosity of the coating is similar to that of the coating without any rheological additive. Under rest conditions, however, the hydrogen bond reforms rapidly, again providing a three-dimensional network throughout the system, and thereby increasing the viscosity of the applied coating. Note that this process is completely reversible, allowing "working" of the coating during, e.g., brush application (Fig. 3).

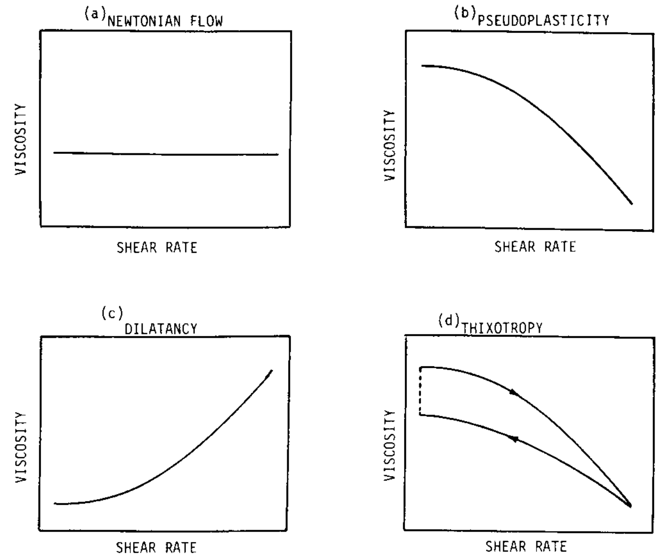

FIG. 1. Typical liquid flow behavior.

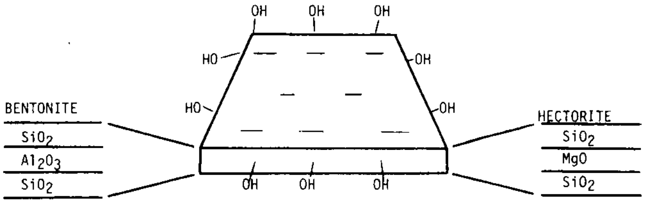

FIG. 2. Schematic diagram of a smectite clay platelet.

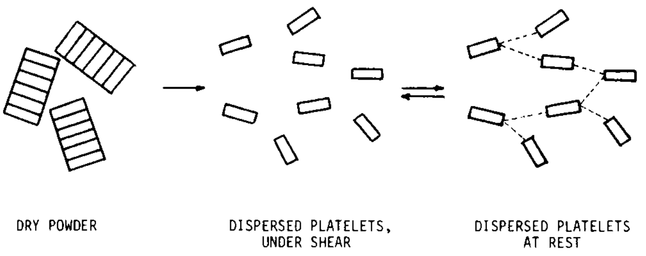

FIG. 3. Dispersion process for smectite clays and organoclays.

Two sequential reactions may occur during the formation of an organoclay (3, 4). First, the clay undergoes an ion-exchange reaction with the aforementioned exchangeable inorganic cations according to the following equation:

$$nR_4N^+X^- + M_n^+clay^{n-} \rightleftharpoons [(R_4N^+)_nclay^{n-}] + nM^+ + nX^-$$

If the organic cation is present in an amount greater than the cation exchange capacity of the clay, the excess will be physiochemically adsorbed onto the faces of the clay. During this latter mechanism, amine salts are neutralized so the actual adsorbed species is an amine (4):

$$mR_aN^+H_{4-a}X^- + [(R_4N^+)_n clay^{n-}] \leftrightharpoons [(R_4N^+)_n$$

$$(R_aNH_{3-a})_m clay^{n-}] + mH^+ + mX^-$$

Quaternary salts are more stable, and are adsorbed onto the clay as the salt:

$$mR_4N^+X^- + [(R_4N^+)_n clay^{n-}] \leftrightharpoons [R_4N^+)_n(R_4N^+X^-)_m clay^{n-}]$$

As a result of these reactions, the clay platelet faces become oleophilic in character. The edges of the clay platelet, however, which are responsible for the rheological activity, remain essentially unaltered except at very high loadings of excess organic cation, and, as with the starting clay, are responsible for the rheological activity of organoclays.

Note that all the above reactions are written as equilibrium processes. These reactions have been studied by several workers, who have independently determined that the equilibrium concentrations are dependent on the number of carbon atoms in the alkyl groups attached to the nitrogen (4, 5). The reaction proceeds essentially to completion only when at least one alkyl group is C_{10} or longer, a fact which has been explained by van der Waals' forces. Surprisingly, the presence of several shorter chains is not as influential on the equilibrium, even though the total number of carbon atoms may be greater than for a single long-chain cation. This, then, is the first requirement for organic cations for use in the commercial preparation of organoclay rheological additives, that it contain at least one long-chain radical. Fortunately, these long chains are readily and economically available from various plant and animal sources (e.g., coconut oil, beef tallow and fish oils).

The performance of the organoclay will depend largely on the spacing between adjacent clay platelets in the dry state, and the compatibility of the organic portion with the fluid media in which the organoclay is to be dispersed. The spacing, in turn, is dependent on the molecular size of the cation and the molar ratio of that cation to the clay (6, 7). Large spacings are generally preferred because of the beneficial contribution to the ease of dispersion of the organoclay. This effect, however, will be largely negated if compatibility with the fluid media is not maintained.

One factor influencing this compatibility is the long-chain alkyl group or groups of the cation. In general, the polarity of the solvent with which a particular organoclay composition will be most compatible is inversely related to the number and length of the alkyl groups attached to the cation.

The long-chain groups will, however, account for only part of the organic cation. We have divided the other moieties that are attached to the cation center into two basic classes – "filler" and "active" groups. Filler groups perform the function of completing the tetrahedron around the nitrogen, but do not appear to offer any other beneficial effects in terms of organoclay performance. They form the base line. Typical examples of filler groups are hydrogen and short-chain alkyl groups such as methyl, ethyl and butyl.

Active groups on the other hand, even though perhaps a small part of the total cation, have a beneficial contribution to the organoclay performance. This may be manifested in a number of ways, including increasing the solvent polarity range over which the organoclay is usable, improving the ease with which the organoclay can be dispersed, or imparting some other unique property, such as improving the usefulness of the organoclay in a particular application. Typical examples of active groups are benzyl and 2-hydroxyethyl. Cations containing these groups will not significantly increase the spacing between the clay platelets versus their filler group analogs, but provide both greater solvent polarity range and improved ease of dispersion to the organoclay.

The desirable characteristics of the organic cation may then be summarized as follows:

- Nitrogen derivatives are preferred due to their ready availability and low cost relative to other cation sources.
- Because of their stability in both the preparation and end uses of organoclay rheological additives, quaternary ammonium salts are preferred versus amine salts.
- The organic cation must contain at least one long chain in order for the reaction with the clay to proceed essentially to completion.
- The organic cation should be compatible with the fluid in which the organoclay is to be used. The compatibility can be derived both by the number and type of long-chain alkyl groups of the cation and the other organic radicals attached to the cation.
- The presence of polar active groups on the cation is usually desirable to improve the ease of dispersing the organoclay.

The study and utilization of the structure/property relationships of organoclays have led to new developments to meet the needs of coatings manufacturers. Organoclay rheological additives provide excellent control of the flow properties of coatings. Their utility has been limited to those applications which could accommodate the high shear conditions necessary to disperse the additive fully since full rheological properties can only be obtained with complete dispersion. Although most paint manufacturers are accustomed to such shear requirements from their pigment dispersing experience, problems have been encountered in varnish manufacture. Adjustment of the viscosity of the finished paint, when the viscosity of the paint is much lower than at earlier stages of the process and only low shear equipment is normally available, has been a difficult and tedious procedure. Also, these high shear requirements have limited throughput and increased energy costs.

Two years ago, we introduced BENTONE 500 rheological additive to the ink industry. (BENTONE is a registered trademark of NL Industries.) Previous organoclay gellants required the preparation of a pregel, or compound, in a portion of the ink solvent, and high shear to achieve full dispersion and development of the rheological properties. Such conditions are not compatible with modern ink manufacturing practice, which utilizes high speed and moderate shear equipment to increase throughput. In such instances, fumed silica was often the rheological additive of choice. BENTONE 500 additive will disperse easily and completely under these lower shear conditions and, in many cases, provides better dispersion than fumed silica (Fig. 4). Also, it does not require the use of either compound or high shear devices to achieve full dispersion, and therefore can be used at any point during the manufacture of the ink.

In terms of rheology, BENTONE 500 additive is somewhat more efficient than fumed silica (Fig. 5), and provides much better viscosity stability on aging (Fig. 6). It gives the ink a short, buttery consistency, which is currently preferred, and reduces misting of the ink on high speed presses. These properties are obtained without any significant effect on print quality and appearance, and often with a reducion in cost.

Last year, we introduced BENTONE SD-1 R/A, the first of a new generation of superdispersible organoclay rheological additives designed principally for the paint

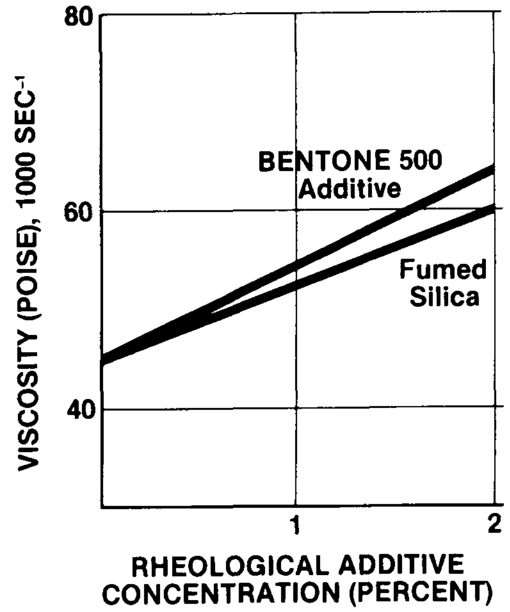

FIG. 4. Comparison of the dispersion properties of BENTONE additives in a web offset heatset ink under high speed dispersion conditions (2% rheological additive).

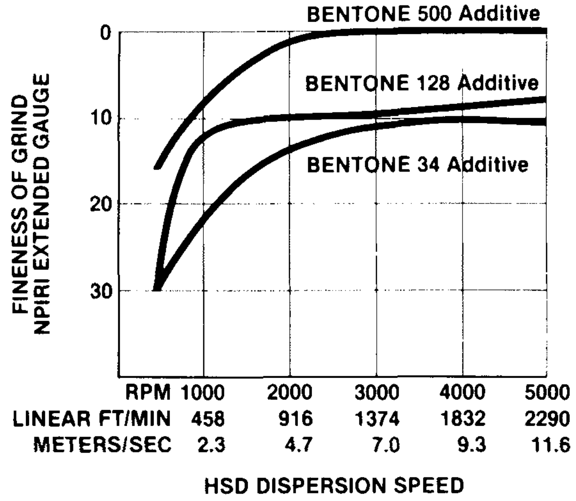

FIG. 5. Comparison of the efficiency of BENTONE 500 rheological additive with fumed silica.

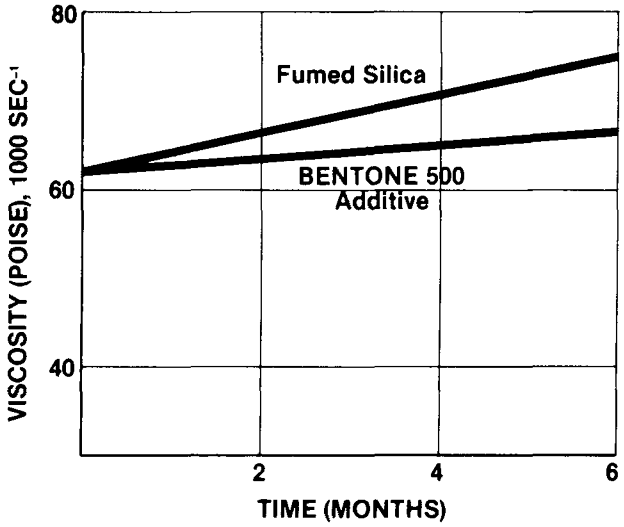

FIG. 6. Viscosity stability of inks with BENTONE 500 rheological additive and fumed silica.

industry. Superdispersibility means that, unlike previous additives, the rheological additive may be incorporated at any point during the paint making process, with full development of the rheological properties. Only minimal shear is necessary to develop the dispersion. The need for chemical activators to achieve dispersion of the additive – a problem area for use of standard organoclay products – and specific point of addition of the rheological additive has been eliminated. The coatings manufacturer, therefore, has at his disposal a versatile rheological additive which will improve his throughput, batch-to-batch uniformity, ease of manufacture and ease of correction, while at the same time, due to the ease of dispersion of the superdispersible additives, reducing his need for post correction and, in many cases, reducing his production costs.

This new rheological additive is designed particularly for use in low polarity solvent-based coatings, such as decorative paints, using aliphatic hydrocarbon solvents. It may also be used in higher polarity systems, such as aromatic solvent-based systems, if more normal organoclay shear levels are employed for incorporation. It is so easy to disperse that full development of the dispersion and rheological properties can be expected even when incorporating the additive during the lowest viscosity stage of the paint manufacturing operation (Table I).

As shown in Table II the rheological efficiency of BENTONE SD-1 additive, when incorporated under very low shear conditions, is fully equivalent to that of BENTONE 34 additive, the conventional product for such applications, when incorporated under optimal, high shear conditions. BENTONE SD-1 additive thus provides the paint chemist with a degree of formulating latitude and the paint production supervisor with ease of manufacture heretofore unachievable.

Shortly, we will introduce BENTONE SD-2 rheological additive, which is designed for use in moderate to highly polar systems using ketone, ester and alcohol solvents. This includes a wide spectrum of coatings such as automotive topcoats and primers, appliance enamels, epoxy and vinyl marine finishes, zinc rich primers and fingernail polish. This new rheological additive offers significant ease of dispersion and efficiency advantages over the conventional BENTONE 27 additive, which requires high shear dispersion of a preformed pregel to achieve optimum performance, and, in many cases, can replace fumed silica on a pound-for-pound basis while providing the additional benefits of easier handling, better viscosity stability on aging, and reduced rheological additive costs (Table III). This additive will provide the same degree of formulating latitude and ease of use to these coatings that BENTONE SD-1 additive does for decorative coatings.

The performance advantages of BENTONE 500, BENTONE SD-1 and BENTONE SD-2 rheological additives were achieved totally through the organic portion of the organoclay; no change to the basic clay lattice structure is involved. It is our goal to continue to develop new products to meet the needs for various industries for new rheological additives. To do so, we intend to continue our study of all facets of organoclay technology, including the basic structure/property relationships. We are therefore interested in any and all new developments in organic cation, particularly amine and quaternary ammonium, chemistry. Of special interest is the continued study of the effects of various "active" groups on the performance parameters of the organoclay.

TABLE I

Incorporate BENTONE SD-1 Additive at Any Point

BENTONE SD-1 point of rheological additive addition	Resin solvent BENTONE SD-1 pigment ↓ Grind ↓ Letdown	Resin solvent pigment ↓ Grind BENTONE SD-1 ↓ Letdown	Millbase ↓ Grind ↓ Resin solvent additives BENTONE SD-1
Fineness of grind	6.5	6.5	6.5
Viscosity, initial			
Stormer (KU)	74	73	75
Brookfield, 100 rpm (cP)	650	650	680
Viscosity, 1 month			
Stormer (KU)	76	76	78
Brookfield 100 rpm (cP)	790	740	790
Sag, Leneta (mils)	4	4	4

TABLE II

Comparison of BENTONE SD-1 and BENTONE 34 Additives

	High gloss enamel	
Thickener	BENTONE SD-1 additive	BENTONE 34 additive
Incorporation method	Dry to letdown	Pregel to grind
Use level by weight (%)	0.2	
lb/100 US gal	1.9	
Fineness of grind	7.0	7.0
Stormer viscosity (KU)	70	69
Brookfield viscosity, 100 rpm (cP)	1180	1100
#4 Ford/DIN Cup (sec)	210	200
Sag, Leneta (mils)	5.5	5.5
Gloss, 20°	97	96

TABLE III

Comparison of BENTONE SD-2 and BENTONE 27 Additives with Fumed Silica in a High Build Vinyl Topcoat

Thickener	BENTONE SD-2 Additive	BENTONE 27 Additive	Fumed silica
Incorporation method	Dry to letdown	Pregel to grind	Dry to letdown
Use level by weight (%)	0.72	0.72	0.72
Fineness of grind (sc)	6.0	6.5	5.5
Stormer viscosity (KU)	99	96	103
Brookfield viscosity, 100 rpm (cP)	1760	1470	1900
Sag, Leneta (mils)	12	10'	12
Gloss, 60°	32	29	32

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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.

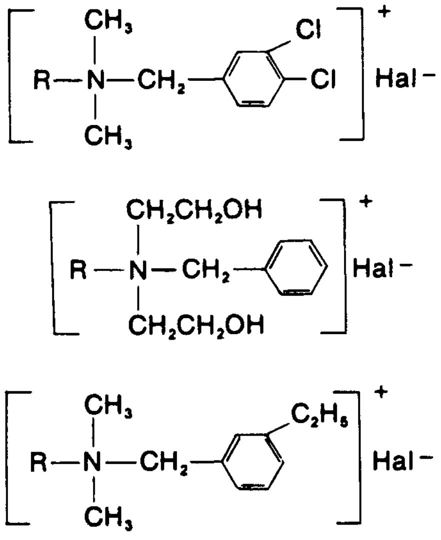

FIG. 1. Second-generation quaternaries (1955): substituted alkyl dimethyl benzyl ammonium halogens.