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**Quaternary and**  
**Cleaner-Sanitizers**  
*in the Dairy Industry*

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# Quaternary and Cleaner-Sanitizers

## *in the Dairy Industry*

By

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The quaternary ammonium compounds are a new type of germicide now being recommended for many of the sanitizing operations for which chlorine compounds (sodium and calcium hypochlorite) have been used. The quaternaries, as they are termed, represent an entirely different type of compound than the hypochlorites from the chemical standpoint. They have certain properties that tend to be more favorable than hypochlorites for some dairy sanitizing operations, and for other specific applications they may be less effective than hypochlorites. The quaternaries also can be incorporated with some cleaning ingredients to make a combined cleaner and germicide known as a detergent-sanitizer or cleaner-sanitizer.

In view of the marked difference in properties between the quaternary ammonium compounds and the more conventional hypochlorite sanitizers, and because of the rather extensive promotion these compounds have been given for application in the dairy industry, it is essential that the dairy plant operator, dairy farmer, and those involved in establishing and administering standards for dairy sanitation procedures be thoroughly familiar with all of the advantages and disadvantages of this new type of sanitizing agent.

## General Properties of Quaternary Compounds

### Stability

The quaternary ammonium compounds, as a group, represent a highly stable form of chemical germicide. In the absence of organic matter or other noncompatible agents, their activity may remain intact over periods of many months. This is a valuable property from the standpoint of transportation, merchandising, and farm and plant sanitation.

### Odor

The better quaternaries now on the market are relatively odorless. That means that equipment sanitized with them should not impart an odor or flavor to the food product handled in it. In the past some of the poorer quaternary products prepared from insufficiently refined constituents have imparted undesirable odors and flavors to foods from sanitized equipment and utensils.

## Flavor

Quaternary solutions have a bitter, puckery flavor. This does not carry over into dairy products from equipment or utensils sanitized with such solutions. If milk is adulterated by addition of quaternary compound, however, the bitter flavor may be apparent with concentrations as low as 10 ppm of quaternary in milk. At concentrations of 25 ppm of quaternary the bitter flavor may be quite pronounced.

## Corrosiveness

Quaternaries are relatively noncorrosive against metals. This is a valuable property for it enables maintaining a residual film on equipment and utensil surfaces for long periods without danger of corrosion.

## Toxicity

The question of possible toxicity of quaternary ammonium compounds for human beings needs considerable clarification at the present time. Most of the studies reported to date indicate that the traces of quaternary that might be transferred into milk or milk products from sanitized utensils or equipment should not prove toxic to human beings. Research studies under way at the present time should provide the necessary information on this problem. Various workers have shown that quaternary solutions in use-dilution do not cause the skin irritation or chapping of hands of workers or teats of cows that sometimes accompanies use of hypochlorites. Concentrated solutions of quaternaries, however, may be irritating and should be handled with care.

## Bacteriostatic action

Quaternaries inhibit growth of some bacteria without necessarily destroying them. This bacteriostatic action is particularly evident against thermophilic micrococci and sporeformers on dairy equipment and accounts for the effectiveness of detergent-sanitizers against thermophilic bacteria on utensils.

The bacteriostatic action of quaternaries has been demonstrated in other instances. Studies have shown that presence of as little as 10 ppm of quaternary added to milk may seriously retard growth of lactic-acid starter bacteria, both in the mother culture and in the cheese vat. Cultures thus inhibited included Streptococcus lactis, Streptococcus cremoris, Streptococcus thermophilus, and Lactobacillus lactis. The quantity of quaternary ammonium compound entering milk through normal sanitation procedures should not be great enough to inhibit organisms such as the lactic-acid bacteria. Intentional adulteration of milk on the farm, however, may result in significant inhibition of acid production in starter or cheese milk. A method has recently been developed in the Experiment Station laboratories that will detect presence of less than 5 ppm of quaternary added to milk. This method, which is relatively simple in procedure, may be applied in any suspected cases of quaternary adulteration (see section on Determination of Quaternary Concentration in Sanitizing Solutions and Milk).

## Precipitate formation

Some difficulty has been encountered in the past in certain sanitizing operations due to the development or accumulation of a brown precipitate where some quaternaries have been used on equipment or in sanitizing tanks. In studies on detergent-sanitizers, such a precipitate has been largely avoided by rinsing as much of the milk solids as possible from the surface before application of the quaternary compound.

## Chemical structure

Various quaternary ammonium compounds, some differing greatly in chemical constitution, have been studied and employed for dairy sanitation procedures. Examples of some widely used quaternary ammonium compounds are alkyl dimethyl benzyl ammonium chloride and diisobutyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride.

An examination of the quaternary compounds reveals a common similarity in the presence of a pentavalent nitrogen. From this is derived the term quaternary ammonium. The anion in the compounds mentioned above is chlorine. The remainder of the molecule constitutes the cation. Since the cation of the molecule contributes the property of a wetting agent and is also the active part of the molecule from the germicidal standpoint, this group of quaternary ammonium compounds often is referred to by the term cationic surface active agents.

## Cost

Quaternary compounds usually cost more on a use or parts per million basis than hypochlorites. The complexity of the quaternary molecules shown above provides the explanation. A sodium hypochlorite ( $\text{NaClO}$ ) or calcium hypochlorite ( $\text{CaCl}_2\text{O}$ ) is much simpler in chemical constitution and therefore somewhat less costly to manufacture.

# Factors Affecting Germicidal Activity of Quaternary Compounds

## Type of compound

There are some significant variations among commercial quaternary compounds on the market with respect to their germicidal activity. Any compounds of questionable germicidal properties should be tested by some reliable procedure to assure use of a highly germicidal preparation. It has been found that the Weber and Black method and a similar method developed in the Experiment Station laboratories are very useful for this purpose. Another excellent method for this purpose is the Johns slide technique. Phenol coefficients are not in every instance a reliable measure of the sanitizing value of a germicide.

## Variation in resistance of different forms of bacteria

There is considerable variation in resistance of different species of non-sporeforming bacteria to quaternary compounds. Gram-positive organisms such as Micrococcus pyogenes aureus appear to be quite susceptible. The thermophilic micrococci appear to be inhibited (bacteriostatic effect) by low concentrations, but bacterial spores are usually far more difficult to destroy with quaternaries than with hypochlorites. The gram-negative coliform species are definitely more resistant to quaternaries than to hypochlorites. Pseudomonas fluorescens, another gram-negative type, also is exceptionally resistant to quaternary action but is destroyed rather easily by hypochlorites. Certain of the Pseudomonas species are psychrophilic types; they may enter milk and milk products from water supplies and frequently are responsible for bacterial growth in pasteurized refrigerated milk, cream, and butter. These facts should be borne in mind when planning the sanitizing operation, especially where the above species are a problem.

## Temperature of sanitizing solution

The germicidal activity of quaternary solutions is increased with an increase in temperature. This effect of temperature on quaternary action is less pronounced than is true with hypochlorites. However, it also represents a significant factor to be considered in preparing the sanitizing solution. A sanitizing solution prepared with tempered water at 90° to 100° F. should provide greater destruction of bacteria on equipment, than a solution prepared with cold well water at 50° to 60° F. Where coliform bacteria present a problem in sanitizing-plant equipment, quaternaries may be more effective if the sanitizing solution is prepared with hot water.

## pH of sanitizing solution

In general, quaternaries exert less buffering effect on the pH of the sanitizing solution than do hypochlorites. Thus a quaternary sanitizing solution tends to approach the pH of the water used to prepare it. The quaternaries most commonly used for dairy sanitizing operations usually exhibit greater germicidal activity in alkaline solutions. With such compounds a solution at pH 9 to 10 may be definitely more germicidal than one at pH 7.

## Presence of organic matter

Quaternaries are more stable in the presence of organic matter than are hypochlorites. Nevertheless, the germicidal activity of quaternaries is seriously impaired in the presence of organic matter as, for example, milk solids. In our studies, we have found that low concentrations of quaternaries are almost completely inhibited in germicidal activity in the presence of milk.

## Water employed for preparing sanitizing solution

Certain ions in water may markedly inhibit germicidal activity of quaternary compounds. It has been shown that calcium, magnesium, and especially iron exert a definite inhibiting effect on quaternary action. The effect may be so pronounced

in some hard waters that four times as much quaternary may be required as would be needed in normal or distilled water. It has been reported that as little as 10 ppm of ferric ionized iron may inactivate 200 ppm of quaternary.

Apparently anions such as chlorides, nitrates, carbonates, and sulfates exert no inactivating effect on quaternaries. A considerable portion of the inactivating effect of some hard waters on quaternaries can be removed by addition of alkaline water-softening compounds. The pH of the solution appears to play a significant role in this regard since merely raising the pH of the germicidal solution prepared in hard water may offset the inactivating effect of some hard water salts.

Some studies indicate that not all hard waters respond equally in this manner to addition of softening or sequestering agents. Further study is needed to provide information on the best means of fortifying quaternary preparations to cope with hard waters. Available evidence emphasizes more and more the need either for a fortified quaternary preparation capable of fast germicidal action in various types of water or a chemical and bacteriological analysis of plant and farm waters to determine their suitability for quaternary sanitizing solutions.

### Effect of certain cleaners and cleaner-ingredients

Soaps and anionic wetting agents inactivate quaternaries. Since anionic wetting agents are a common ingredient in many dairy cleaners, care must be observed to remove all traces of cleaners containing such compounds before applying a sanitizing solution to equipment or utensil surfaces. Some polyphosphates also inactivate quaternaries. Others such as tetra sodium pyrophosphate are compatible with them and may be incorporated with quaternaries to prepare cleaner-sanitizers. Nonionic wetting agents do not inactivate them and may be incorporated with quaternaries without interfering with their germicidal action.

## Specific Applications in Dairy Sanitation

### Farm sanitation operations

Quaternaries have proved themselves satisfactory for a number of farm sanitation operations. They may be employed in the warm water used to wash udders prior to milking. While they effect no appreciable reduction in bacterial count of milk in this operation, they have an advantage over hypochlorites from the standpoint of chapping and irritation. It has been observed that quaternaries show less chapping and irritation of udders and teats than do hypochlorites.

Studies have indicated quaternaries to approximate hypochlorites in destruction of mastitis streptococci on teat cups. They, therefore, can be used in mastitis sanitation procedures for treating teat cups. Removal and destruction of the test organism, Streptococcus agalactiae, on teat cups by dipping in 250 ppm quaternary solution frequently exceeded 99 per cent in Experiment Station

studies. The usual recommendation is to first rinse teat cups in a pailful of lukewarm water to remove excess milk solids and then dip in a bucket of sanitizing solution of at least 200 ppm strength. Use of an extra teat-cup assembly for each milker unit has been recommended to enable soaking one set in germicide while the other set is on the cows.

Quaternary solutions can also be employed in the form of a sanitizing rinse on milking machines and utensils just before use. A concentration of 200 ppm usually is recommended for this purpose. Two important reservations should govern the application of quaternaries for such farm sanitizing steps. First, their use for this purpose must be approved by the regulatory officials responsible for any given area. Second, there should be some assurance that the quaternary provides effective germicidal action in the water being used for the sanitizing solution.

### Plant sanitizing

The same fundamental factors apply to both plant and farm application of quaternaries for sanitizing operations. Quaternaries can be employed for milk-plant sanitizing in the same manner as are hypochlorites. A concentration of 200 ppm usually is recommended for this purpose with an exposure period of at least three minutes to the germicidal solution proper. For either the farm or plant sanitizing operation before use of utensils or equipment, the quaternary provides no advantage over an active hypochlorite solution of equivalent strength. Where gram-negative coliform or Pseudomonas species are a problem, the hypochlorite may have an advantage in germicidal activity.

The tendency of quaternaries to form a bacteriostatic film on utensils or equipment enables their application to equipment after washing. The bacteriostatic film prevents growth of bacteria on the equipment while it is idle. This is especially helpful for surfaces that are difficult to dry. Tanks and tank trucks have been sanitized in this manner after cleaning by spraying the surfaces with quaternary.

Milk cans may be treated with quaternary solution by injection at the steam position. The bacteriostatic film left in the can tends to greatly reduce growth in the can before it is again used. Following are examples of the effect of this application: Average count per can immediately after leaving washer, 29,800; after 24 hours' storage, 42,490; cans from same washer after 24 hours' storage in moist state, 33,690,000; and cans treated with 200 ppm quaternary following washing, 4,690.

## Cleaner-Sanitizers

Quaternary ammonium compounds can be incorporated into so-called detergent-sanitizers or cleaner-sanitizers which include in addition to the quaternary a nonionic wetting agent and compatible polyphosphates and other alkaline cleaner ingredients. This development has radically altered farm sanitation methods in some parts of the country. The introduction of cleaner-sanitizers has met with

mixed success in different parts of the country. This is due in part to the great variation in composition and effectiveness of cleaner-sanitizer preparations now on the market and also to noncompatible constituents in many water supplies. Various methods of application of the compounds also have been recommended with consequent variable results.

This new and somewhat revolutionary farm-sanitation method is based primarily on the bacteriostatic properties of the quaternary film formed on equipment and also on the compatibility between quaternaries and nonionic wetting agents and certain other cleaner ingredients. By combining cleaner and germicide, the essential sanitation steps include a rinse with water immediately after use of equipment, followed by a washing with cleaner-sanitizer. The equipment then is merely racked up to drain without removing the washing compound. The bacteriostatic quaternary film left on equipment should prevent growth of bacteria while equipment is idle. Just before use, the equipment may be rinsed with water or with a sanitizing solution such as quaternary or cleaner-sanitizer or hypochlorite solution.

In an extensive farm trial employing a standard procedure and various cleaner-sanitizer procedures, we have made a number of observations regarding application of these compounds. In many cases where cleaner-sanitizers were used, the numbers of thermophilic bacteria decreased even when other types, chiefly gram-negative, increased. It was found that a flush-wash procedure alone was not sufficient. A thorough rinse with cool or lukewarm water immediately after use and thorough brushing with a warm cleaner-sanitizer washing solution were essential under average conditions. The study emphasized further that thorough cleaning may be more important than rapid germicidal action in the end results attained with cleaner-sanitizers. There is growing evidence that some cleaner-sanitizers on the market have failed simply because they have not supplied the required cleaning ingredients.

Even though the study was conducted in an area where farm water hardness was low to moderate, there was an accumulation of a practically invisible deposit on rubber parts of some milking machines. This is of particular significance because of the high content of sequestering agent in the cleaners used. It was found that this deposit could be removed by a periodic acid treatment. In almost every instance, when the acid cleaning was carried out, the raw bacterial count of the farm milk was immediately reduced. The results emphasized that some form of periodic acid cleaning was desirable in the cleaner-sanitizer procedure. This might be of still greater significance if the farm water supplies carried a high content of hard water salts. The essential steps appeared to include: (1) A thorough rinse with water immediately after use, (2) Brushing with warm cleaner-sanitizer solution, (3) Racking or hanging up to dry with no further treatment, (4) Rinsing with water or germicide just before use, (5) Periodic (preferably weekly) thorough clean up of milking machine with an acid detergent.

# Determination of Quaternary Concentration in Solutions

Various methods of determining quaternary concentration have been examined in our studies. As a result of this investigation, a method was developed which has served during the past four years, both as a sensitive laboratory procedure and a simple, accurate field test. The essential steps include mixing 1 ml. of quaternary solution and 1 ml. of eosin indicator with a small quantity of buffer solution. Presence of quaternary results in formation of a red precipitate. Subsequent titration to a colorless compound with standardized anionic surface active agent may be employed to determine the exact quantity of quaternary present.

Modifications of this method will determine concentrations of less than 5 ppm of quaternary compound in water solutions and in milk. A modification of the method also can be employed for determining concentration of quaternary in alkaline cleaner-sanitizer solutions. Further information on this method is available in Oregon Agricultural Experiment Station Circular of Information 472.