For many years chlorine has been the principal chemical germicide used in the dairy industry. Among its advantages may be included its rapid action, low cost and wide effectiveness against most kinds of microorganisms. Unfortunately, chlorine is irritating to the skin, corrosive to many metals, relatively unstable on standing, and its activity is effectively reduced in the presence of organic matter.

A few years ago there came into prominence a relatively new group of chemicals, the quaternary ammonium compounds, which exhibited germicidal action. Because of this and certain other properties of these compounds, it was felt by some individuals that they might replace chlorine as the general dairy disinfectant.

Quaternary ammonium compounds are a rather heterogeneous group of chemicals classified among the cationic surface active agents, which means that they carry a positive charge when in solution. All of these compounds possess the ability to some degree of lowering surface tension and increasing the wetting power of a solution. As a group the quaternaries are practically odorless and tasteless in the dilutions used. They are noncorrosive and nonirritating. They are very stable and apparently have low toxicity for animals. In fact, young rats fed a diet containing three per cent of a common quaternary ammonium compound (alkyldimethylbenzyl ammonium chloride) showed no ill effects. Other laboratory animals have been supplied with a 0.1 per cent solution of this compound as their sole source of fluid for months without harm. Whether a nontoxic character can be ascribed to all quaternaries is yet to be determined.

Obviously it would be desirable to have a material with the above characteristics for use as a general purpose germicide.

### Germicidal Properties of Quaternaries

The standard Food and Drug Administration method for testing chemical disinfectants and antiseptics was used in early trials with quaternary ammonium compounds. In running this test the ability of the chemical to kill a test organism is compared with that of phenol under rigidly standardized conditions. It is not the purpose of this paper to enumerate the shortcomings of the test, but suffice it to say that most of the investigators who worked with the quaternaries were not satisfied with the results. True, excellent phenol coefficients were reported for the quaternaries, but the results were highly erratic and in many cases were not reproducible.

As a result of the difficulties found in testing quaternaries, modifications of the Food and Drug Administration test have been made. Also, entirely new techniques have been developed by which the quaternaries are tested under conditions more nearly approximating their actual use. The general result is proof that the quaternary ammonium compounds as a group exert considerable germicidal activity. However, individual quaternaries show widely different killing powers. Also, they differ in their effectiveness against different organisms.
In comparing the germicidal action of quaternaries with that of chlorine compounds, investigators have reported that the former are more effective against Gram positive than against Gram negative bacteria, whereas chlorine is more effective against Gram negative forms. One exception to this generalization is the ordinary Gram positive cheese starter bacteria, which are more resistant to quaternaries than to chlorine. In trials against spores certain investigators have found little or no killing effect of quaternaries even in concentrations far above those normally used. Another investigator has reported quaternaries to be much more effective than chlorine against certain spores. It might be well to point out that seldom do the researchers use the same quaternaries under the same conditions and they often use different spore forming organisms for testing. Therefore, it is hazardous to draw a conclusion from the few available reports of trials. Probably it is safe to say that the use of quaternaries for sanitizing milk plant equipment cannot be expected to solve all problems arising from thermoduric bacteria in the milk.

One other property of the quaternaries that deserves particular mention is their bacteriostatic action; that is, their ability to prevent the growth of bacteria in concentrations too low to kill. Whereas chlorine readily evaporates from the rinsed surface of a piece of equipment, the quaternaries tend to remain in the film of moisture on the surface. Thus, these compounds can continue to inhibit bacterial growth during the time equipment is not in use.

**Effect of Various Factors on the Germicidal Activity of Quaternaries and Chlorine**

**Temperature**

Chemical reactions in general increase in rate as the temperature is increased. It is well known that chlorine is a much more effective germicide in hot water than in cold water. Comparisons of the effect of temperature on the action of chlorine and the quaternaries have shown that the quaternaries show nothing like the decided stimulation of activity due to increased temperature that is shown by chlorine. Use of quaternaries in hot water speeds up their action to some extent, but nothing like as much as is true with chlorine.

Conversely, chlorine activity is slowed down in cold water to a much lesser extent than is that of the quaternaries. For example, in one experiment in which the effect of temperature was studied, the concentration of chlorine necessary to kill a test organism in a unit time was the same at 68°, 50°, and 40° F. However, with six different quaternaries tested at the same time, the amount required to kill the test organism was increased from 5 to 400 times as the temperature was reduced from 68° to 40° F.

Thus, it seems apparent that the quaternaries do not show the marked stimulation of activity with increases of temperature that are shown with chlorine, and they may be inhibited even more than chlorine at lower ranges of temperature.

**Hydrogen ion concentration**

Chlorine is most effective in acid solution, and rapidly loses its effectiveness in the presence of alkali. This is one reason why care must be taken to remove all traces of alkaline washing powders from dairy equipment before using chlorine as a germicide.

As a general rule the quaternaries are most effective in alkaline solutions although the degree of alkalinity compatible with optimum activity seems to vary with different quaternaries. With many of the quaternaries a precipitate is formed in the presence of considerable alkali and the germicidal efficiency is lost. For this reason the user must take care in using quaternaries with
alkaline washing powders. This point will be considered further below.

In general, the stimulation in activity resulting from adjustment to optimum pH is not as great with quaternaries as with chlorine. 

Water hardness

Chlorine is not greatly affected by the hardness of water used to make the solution except insofar as the hardness may increase the pH of the water. Tests with chlorine have shown the same germicidal activity in distilled water as in water with 400 ppm hardness. However, studies have shown the quaternaries to be less effective in hard water than in soft water. This has been explained in one instance on the basis of combination of magnesium and calcium ions with the quaternary ammonium compounds, thus reducing their effectiveness.

Organic matter

One of the major limitations of chlorine is its inability to act effectively in the presence of considerable organic matter. Apparently chlorine combines with the organic matter and is thus removed from availability to act on bacteria. However, tests by Johns, indicate that the amount of milk necessary to inactivate or markedly reduce the action of chlorine is considerably greater than was formerly believed.

Trials with the quaternaries indicate that these compounds also are interfered with by organic matter, but not to such an extent as is chlorine. In general it may be said that organic matter interferes with the action of both chlorine and the quaternaries, but to a lesser extent with the latter compounds.

Comparison of Quaternaries and Chlorine for Various Applications

Udder rinse before milking

One of the important uses of chlorine in the dairy is for the washing of teats and udders before milking. Unfortunately this chemical is irritating to the skin of the udder and the hands of the milker. Also, as it is used organic matter is added to the solution and its effectiveness is lost rapidly. It has been estimated that under ordinary conditions, no more than ten cows' udders should be washed with the same pail of chlorine solution. This may necessitate rather frequent changes of the rinsing solution.

Quaternaries have been found satisfactory for the purpose of washing udders and teats before milking. Most persons who have reported on this use claim a reduction in the incidence of chapping and irritation of the skin as compared with chlorine. This would suggest that the quaternaries might be more effective in preventing the initiation of infections. Also, one group of investigators found that from 30 to 40 udders could be washed with a single solution before there was a significant decrease in the germicidal effectiveness of the washing solution due to the accumulation of organic matter.

As to the effect of quaternaries and chlorine rinses on the bacteria count of the milk, little difference has been reported. Kesler and others at Ohio State University compared the bacteria counts in milk from cows whose udders had been rinsed before milking with a quaternary, with chlorine, and with plain water. The chemicals were used in concentrations of 200 and 400 parts per million. These investigators could detect no significant differences in the bacterial content of the milk regardless of the rinsing solution used.

Milking machine sanitizing

Comparisons of quaternaries and chlorine solutions for sanitizing milking machine parts, including teat cups, show little differences in effectiveness. Both reduced contamination considerably, but neither was markedly better than the other. Under practical con-
ditions of exposure neither quaternaries \(^\text{12, 15}\) nor chlorine \(^\text{15}\) completely sterilized milking machine teat cups upon treatment between cows, where the exposure time was only for a few seconds. However, both types of chemicals showed better results when the chemical rinse was preceded by a water rinse to remove much of the milk.\(^\text{15}\)

Quaternaries have been tried as replacement for the lye soak solution used for milking machine rubber parts between uses. As a growth preventive 200 ppm of a quaternary was as effective as 0.5 percent lye, but the quaternary left an undesirable deposit on the rubber in some cases. The quaternary tried appeared to be superior to lye at reducing milk contamination with thermoduric bacteria originating from the milking machine.\(^\text{6}\)

**Dairy equipment sanitizing**

Various quaternaries have been compared with chlorine as sanitizing agents for vats and other large equipment.\(^\text{15}\) Under the conditions of the test the quaternaries were no better than chlorine against a variety of organisms. In fact, they required a longer time to act or higher concentrations than did chlorine to effect the same result. As might be expected, the amount of milk residue left in the equipment affected the results. When considerable milk was present the quaternaries showed to better advantage than did chlorine at equivalent concentration.

**Milk can sanitizing**

Quaternaries have been used to excellent advantage in sanitizing milk shipping cans. They may be applied as an atomized spray into the cans after washing and steaming. The main advantage of the quaternaries in this application over chlorine is that the effect of the former persists for a considerable while after the treatment. Mueller and others \(^\text{12}\) have shown that milk cans treated with a quaternary rinse after cleaning had much lower counts after 24 hours standing than did similar cans that were not so rinsed. In another study Davis \(^\text{2}\) tried solutions of four quaternary compounds as can rinses. He observed a 52 percent reduction in bacteria counts in cans taken immediately from the can washer as compared with untreated cans. After 24 hours the treated cans showed 96 percent reduction, thus illustrating the marked bacteriostatic action of these compounds.

**Mastitis control**

Efforts have been made toward helping control mastitis by washing the teats and milking machine teat cups with chlorine and with quaternaries.\(^\text{4, 15}\) Results of these studies indicate that the quaternaries tried were little if any more effective at destroying the mastitis streptococci on the teats or teat cups than was chlorine. It should be borne in mind, however, that quaternaries are less irritating to the skin of the teats and of the workers' hands than is chlorine.

**USE OF QUATERNARIES IN DETERGENT MIXTURES**

It has been suggested that it would be highly desirable to the dairy industry to have available a mixture of a germicidal quaternary with a suitable detergent for use in cleaning and sanitizing dairy equipment. However, care must be exercised in choosing the components of such a mixture. For example, soaps and other anionic wetting agents are incompatible with the quaternaries, react with them, and dissipate their germicidal effectiveness. Although as a general rule the quaternaries act best in alkaline solution, care must be taken in choosing the alkaline cleaning agent for use with or before the quaternary. For example, certain manufacturers caution against the use of sodium metasilicate, sodium tetraphosphate, and sodium hexametaphosphate with their quaternary ammonium.
compounds. Unless used to considerable excess, trisodium phosphate is compatible with most quaternaries and can be used in conjunction with it. Here again the question of residual organic matter enters the picture, and for this reason it is usually recommended that the quaternaries not be used except on equipment that is already physically clean. Therefore, it might be most desirable to use a compatible cleaning compound such as trisodium phosphate first, followed by a germicidal rinse with a quaternary compound.

**Comparison of Costs**

The quaternary ammonium compounds now on the market are more expensive per unit quantity than are chlorine compounds. For purposes of comparison I have chosen a representative of each as purchased for use in the university. Admittedly these materials were purchased in fairly small quantity, thus adding to the cost, but their general relationship should be about the same regardless of the quantity purchased. The chlorine compound was a common dairy sanitizer consisting chiefly of calcium hypochlorite. When made up to a concentration of 200 ppm available chlorine, as recommended, the material costs 0.2 cent per gallon. The quaternary ammonium compound used for comparison was a 10 percent solution of mixed alkyl dimethyl benzyl ammonium chlorides. When made up to a concentration of 200 ppm this material costs 0.8 cent per gallon. Thus, in this comparison, the quaternary is about four times as expensive as the chlorine compound.

Proponents of the quaternaries point out that these materials are much more desirable than chlorine for many purposes because of their bland, odorless, nontoxic and practically tasteless character. Perhaps in many instances in the food industry these desirable characteristics are sufficient to overweigh their greater cost.

**Advantages of the Quaternaries Over Chlorine**

From the above statements it is apparent that neither chlorine nor quaternary ammonium compounds can be expected to do a good sanitizing job unless the surfaces on which they are to act are already clean. Organic matter reacts with each chemical and dissipates its germicidal strength. Therefore, according to present information there are few places in the dairy where the quaternaries can be expected to do a more effective sterilizing job than chlorine. There seems to be little doubt that for sanitizing clean equipment chlorine acts more quickly and is even slightly more effective than quaternaries at equivalent concentration. However, the residual action of chlorine is slight, and in instances where the equipment is to be left idle for several hours the quaternaries may find a real application. Such an instance is milk shipping cans, where the residual bacteriostatic action of quaternaries offers promise in reducing the bacteria count of milk.

Another possible advantage of the quaternaries is in washing udders before milking. For this purpose the quaternary solutions are less irritating than is chlorine of equivalent strength, and they maintain their effective strength longer because of a lesser susceptibility to the presence of organic matter.

**Summary**

Because of their nonirritating quality, prolonged bacteriostatic action and relatively lesser susceptibility to organic matter, the quaternary ammonium compounds may be preferable to chlorine as a rinse solution for udders before milking and as a rinse for certain articles of dairy equipment. However, these compounds are more expensive than chlorine; they act more slowly, and, in the absence of organic matter, are less effective germicides. Also the quaternaries are more likely to be inhibited by unfavorable...
water hardness, pH, temperature, and incompatible detergents used for cleaning.

REFERENCES


Regular Corps Appointments for Sanitarian Officers (Milk and Food) in the United States Public Health Service

Competitive examinations for appointments in the Regular Corps of the U. S. Public Health Service in the grades of Assistant Sanitarian (1st Lieutenant) and Senior Assistant Sanitarian (Captain) will be held in the near future. This announcement is to acquaint milk and food specialists with opportunities in the Public Health Service.

Regular Corps appointments are permanent in nature and provide opportunities to qualified sanitarians for a life career in public health. Assignments to duty are made with consideration of the officer's preferences, abilities, and experience. There is ample opportunity for professional growth and development.

For officers with dependents, entrance pay (without benefits) is $3811 a year in the Assistant grade and $4489 in the Senior Assistant grade. Promotions are at regular intervals up to and including the full grade of Sanitarian, which corresponds to the rank of Major, at $5822 to $7981 a year. Promotion to the Senior grade (Lieutenant Colonel) and to the Director grade (Colonel) is by selection. Retirement

(Continued on page 51)