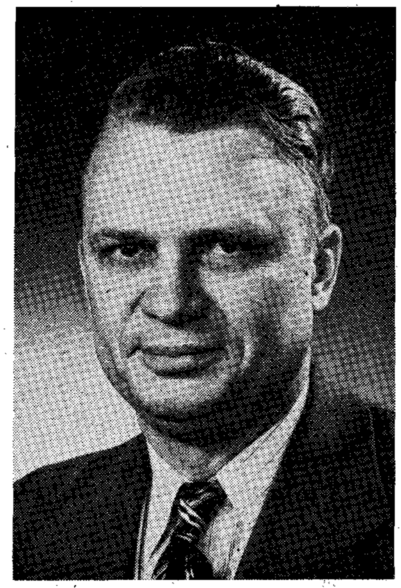
CAUSES AND CONTROL OF CORROSION OF STAINLESS STEEL, ESPECIALLY IN CONJUNCTION WITH MILK AND OTHER FOOD EQUIPMENT[1]

G. M. Riegel

Metallurgical Department, Republic Steel Corporation, Massillon, Ohio

This paper presents background information regarding classified types of corrosion of stainless steels and methods of preventing corrosion. Detergent cleaning is discussed with reference to a general chart. A few examples of dairy equipment corrosion are shown and analyzed.

In-place cleaning has proven to have some very definite advantages for both farm and city dairies. It is thought that sanitizers have been responsible for most of the pitting on stainless dairy equipment.



Garland M. Riegel received the M.S. degree in Chemical Engineering from the University of Illinois in 1935. He began work for Republic Steel Corporation in a general metallurgical laboratory at Canton, Ohio, in September, 1935. He has remained with Republic until the present time. Since 1940 he has been in charge of a laboratory group engaged in development and research work on stainless steels and corrosion.

To understand fully the causes of corrosion of stainless steel and to know how to combat these causes, it is necessary to become familiar with some of the ways by which stainless steels may be affected from corrosive standpoints. For convenience in discussing conditions leading to corrosion, metallurgists and corrosion engineers use a number of terms to classify the types of varieties of corrosion. The forms of stainless steel corrosion may be classified under about ten headings:

1. *General* or etching attack—such as may be caused by an inorganic (mineral) acid used in a cleaning process. Stainless steels are not particularly resistant to corrosion by hydrochloric and sulfuric acids. Therefore, these acids (even though inhibited) are not recommended as satisfactory to use in the cleaning of stainless dairy equipment. However, stainless steels are quite resistant to nitric acid of various concentrations and at various temperatures; but this acid attacks many other materials quite readily and is dangerous to use for several reasons.

   Consequently, less harmful organic acids, such as lactic, citric, acetic, tartaric, gluconic or butyric may be employed for dissolving off mineral (lime-type) deposits on dairy equipment when necessary.
2. *Galvanic* corrosion—which may be produced by contact of dissimilar metals in a solution or electrolyte. Even low ionized or weak solutions may cause attack with flow of current but the strongly ionized electrolytes increase the corrosion.
3. *Electrolytic* imposed or stray current attack—such as stray electric currents producing undesirable pitting attack on installations where electrical equipment is being employed.
4. *Intergranular* corrosion—where a particular set of conditions causes a preferential attack at metallic grain boundaries.
5. *Contact* or crevice corrosion—as may be produced as a result of clinging organic and mineral deposits or overlapping metal conditions plus corrosive sludges.
6. *Stress* corrosion and corrosion fatigue—such as caused by a variety of metallic strain conditions accompanied by pitting and cracking due to some kind of corrosive environment.
7. Regular *chemical pitting*—usually produced by members of the halogen family of elements (fluorine, chlorine, bromine and iodine) and their compounds. Among the compounds capable of causing pits are certain of the fluorides, chlorides, bromides, iodides, sulfides, sulfites, sulfates,

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thiocyanates, and chlorites (or hypochlorites). Of these, the most frequently encountered are the chlorides and acid conditions will usually accelerate the attack.

In connection with dairy equipment, we are occasionally concerned with such chemical pitting. This may result from various sources, as from lactic acid and salt derived from milk and milk products including butter, cheese and ice cream; by cleaning and sterilizing solutions; or it may be produced by some coolants used in heat exchangers which may be utilizing calcium chloride or sodium chloride in the cooling water.

The lactic acid content of milk products is not a factor in corrosion of Type 302 stainless steel when considered alone. However, in conjunction with other factors (e.g., salt) it may aid in corrosion by acting as an acid electrolyte. For this reason it is important that the formation of concentration or galvanic cells be prevented or avoided. This can be accomplished by adequate and frequent cleaning.

Brine refrigerants contain chlorides and, to avoid pit corrosion by these solutions, they should be kept on the alkaline side, about pH 8 to 10. Otherwise, and in addition, an inhibiting agent probably should be used. As a precaution against corrosion, brine tanks should be frequently brushed or wiped clean of deposits around the solution level to prevent concentration cell pitting.

If chlorine solutions are used for sanitizing, they should never be allowed to stand for more than a few hours or, preferably, not longer than one hour in contact with stainless steel at any one time period. Usually chlorine sanitizing can be done in a few minutes or not longer than ten minutes before the equipment is put into service.

8. *Bacteriological* product pitting—has developed in some cases such as where sulfur compounds have been released and have produced corrosion of metals.
9. *Erosion* corrosion—sometimes occurs due to swift movement of materials causing an active condition at sharp bends and at restricted zones as in nozzles.
10. *Fretting* corrosion—caused by rubbing, pressure and resulting strain in metal parts along with an attack by a corrosive environment which causes small pieces of metal to become dislodged, resulting in a roughened surface.

Frequently, there is an overlapping of these forms of corrosion so that two or more are involved at the same time. However, general classifications are convenient for explanation of the processes of attack and methods of preventing or controlling corrosion. In the processing of milk products, several of the conditions ideal for pit corrosion are apt to be present.

Milk and milk products have a tendency to form a tightly adherent substance called "milkstone" which in the presence of slight acidity and/or somewhat salty condition may cause corrosion, especially if the milkstone is allowed to remain for long periods. Thorough and regular removal of the milkstone coat will prevent premature failures.

The removal of milkstone from stainless equipment may be effected by various solvents and detergents, including some organic acids and such alkaline chemicals as caustic soda, sodium metasilicate, soda ash, trisodium phosphate, sodium tetraphosphate, sodium tripolyphosphate, sodium hexametaphosphate and tetrasodium pyrophosphate. Addition of wetting agents usually makes these chemicals more effective in cleaning.

If the milkstone is very tenacious or difficult to remove from the equipment, high grade bristle brushes or nylon brushes, possibly in conjunction with a fine grade of pumice or whiting, may be used. Sometimes stainless steel wool or sponges are employed to remove very tenacious coatings; also, fibrous pads and cellulose or plastic sponges are used. Care should be exercised to prevent undue scratching of the metal surfaces. Likewise contamination should be avoided, as may be caused by employing ordinary steel wool or bronze and brass sponges.

Figure 1 lists the most common detergent ingredients. These may be grouped into three classes for consideration and discussion:

COMMON DETERGENT INGREDIENTS

KEY TO CHART
A.......HIGH VALUE
B.......MEDIUM VALUE
C.......LOW VALUE
D.......NEGATIVE VALUE
★....VIA PRECIPITATION
•....VIA SEQUESTRATION
⊛....ALSO STABLE TO HEAT

INGREDIENTS		Emulsification	Saponification	Wetting	Dispersion	Suspension	Peptizing	Water Softening	Mineral Deposit Control	Rinsability	Suds Formation	Non-Corrosive	Non-Irritating
BASIC ALKALIS	CAUSTIC SODA	C	A	C	C	C	C	C	D	D	C	D	D
	SODIUM METASILICATE	B	B	C	B	C	C	C	C	B	C	B	D
	SODA ASH	C	B	C	C	C	C	C	D	C	C	C	D
	TRI-SODIUM PHOSPHATE	B	B	C	B	B	B	A★	D	B	C	C+	C-
COMPLEX PHOSPHATES	SODIUM TETRA-PHOSPHATE	A	C	C	A	A	A	B•	B	A	C	AA	A
	SODIUM TRI-POLYPHOSPHATE	A	C	C	A	A	A	A•	B	A	C	AA	B
	SODIUM HEXAMETAPHOSPHATE	A	C	C	A	A	A	B•	B	A	C	AA	A
	TETRASODIUM PYROPHOSPHATE	B	B	C	B	B	B	A•	B	A	C	AA	B
ORGANIC COMPOUNDS	CHELATING AGENTS	C	C	C	C	C	A	AA⊛•	A	A	C	AA	A
	WETTING AGENTS	AA	C	AA	A	B	B	C	C	AA	AAA	A	A
	ORGANIC ACIDS	C	C	C	C	C	B	A⊛	AA	B	C	A	A
	MINERAL ACIDS	C	C	C	C	C	C	A⊛	AA	C	C	D	D

Figure 1. The common ingredients variously used in commercially available detergents are listed in this chart. The ratings under the "non-corrosive" column apply to metals in general and not to stainless steel alone.

1. *Basic Alkalis*—Note that caustic soda, or sodium hydroxide, is the most efficient of the chemicals listed on the chart for cleaning butter fat from dairy equipment because of its excellent saponifying characteristic.

The corrosive effects of caustic soda are rated "D", or bad, in this general chart which does not hold for stainless steels. However, dilute and very dilute solutions of caustic soda, especially when hot, are quite corrosive toward tin plate, galvanized coatings, aluminum, brass and bronze. In the concentration and temperatures used in the dairy industry, caustic soda will not harm stainless steels.

Also, it may be observed that although sodium metasilicate rates good in this group, it is surpassed in general by superior properties of trisodium phosphate.

2. *Complex Phosphates*—Generally speaking, the complex phosphates are more valuable cleaning agents than the basic alkalis. Note particularly the excellent and almost equivalent characteristics of the first three listed, namely, the tetraphosphate, tripolyphosphate and hexametaphosphate.
3. *Organic Compounds* — The organic chelating agents are excellent sequestering materials on account of their ability to hold normal hard water deposits, including iron hydroxide, in solution by chemical combination.

The addition of wetting agents is important in order to lower surface tension and allow complete, instead of partial cleaning of surfaces whether irregular or not.

Organic acids, such as lactic, acetic, tartaric, citric and gluconic are excellent for dissolving off mineral deposits or hard water scale because they do not have the corrosivity toward metals which is usually characteristic of the mineral acids. However, dilute solutions of phosphoric acid may be used effectively with stainless steels providing the contact duration is of normal cleaning periods and complete flushing and neutralizing is accomplished after cleaning.

Recently an investigation was completed in regard to a corroded ice cream scraper blade made of Type 410 stainless steel. Its badly pitted condition indicated that it had been in contact with corroding solutions, such as those containing chlorine and/or chlorides for periods of too long duration without rinsing or removing the harmful solutions. (See figure 2.)

Apparently, such scraper blades should be properly cleaned and sanitized by using a detergent and about 200 ppm. of a quaternary ammonium compound solution. A quaternary solution should be employed for such sanitizing to minimize opportunity for corrosion of such stainless steels of lower chromium content and of lower corrosion-resistance. Pumps and various valves should be scrubbed and sanitized in a similar manner to do an effective economical job.

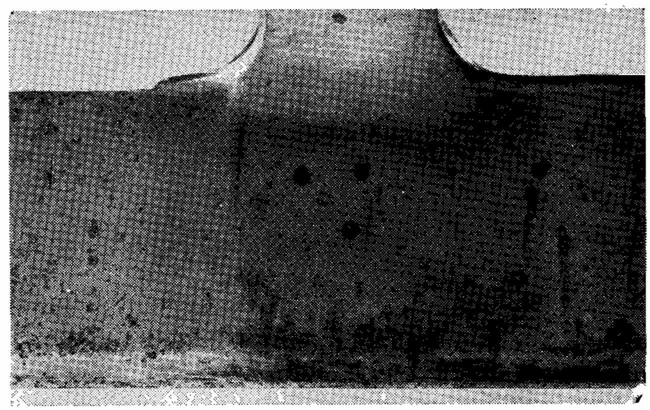

Figure 2. Corrosion or pitted condition on an ice cream scraper blade indicating an apparent lack of proper cleaning and rinsing.

Investigations of localized corrosion on pump shafts have sometimes revealed that milk and milk products (e. g., ice cream mixes) have seeped into packing glands around the shafts; also cleaning and sanitizing solutions have done likewise. Consequently, pitting developed due to long time contact with corrosive solutions plus crevice conditions and possibly electrolytic or galvanic action between dissimilar material, e.g., bronze bushings or graphitized packing and the stainless steel. The smaller shaft shown in photograph was made of Type 416 stainless and the other of Type 303, both showing competitive analyses of free machining quality. (See figure 3.)

Apparently, better designed pump and mixing shafts or methods of sealing off the bearings have greatly reduced failures of this kind in recent years. Also, improved cleaning methods are being employed and more care is being exercised to supply stainless in its best corrosion-resistant condition for the particular applications.

The importance of surface finish and care should not be underestimated nor neglected and may be summarized as follows:

1. For proper sanitation and ease of cleaning, it is first necessary to start with food handling equipment which has smooth, clean surfaces.
2. Next it is very important to keep them that way with the right kind of cleaning methods.
3. Polished finishes have ordinarily proven to be less susceptible to pitting corrosion than rough, coarse ground and as-pickled surfaces.
4. Bright cold rolled or polished surfaces are easier to maintain in the proper sanitary manner.

Many farm and city dairies are now employing, where possible, cleaned-in-place (C.I.P.) methods instead of completely disassembling the milk handling

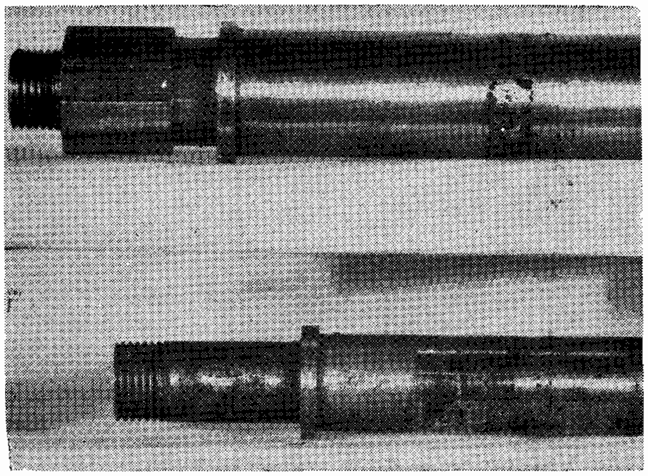

Figure 3. Better design of packing glands and stuffing boxes, as well as pump and shaft arrangements on mixing apparatus, have reduced the frequency of corrosion problems such as those shown here on shafts from earlier machines. Periodical check and replacement of packing materials is advised.

equipment for each cleanup. Various public health departments and their dairy inspectors in more recent years realize that, when done properly, just as good or better cleaning can be accomplished by the C.I.P. process as by the more laborious and time-consuming method of taking apart the equipment and cleaning the various pieces separately. Some health departments are now recommending the C.I.P. methods.

A number of universities through their departments of agriculture, animal experiment stations and dairy science departments are proving that C.I.P. methods can be very effective, speedy or more efficient and economical. It is also being demonstrated that, when balanced detergents are employed properly, there is little or no need for a sanitizer as the equipment is made really clean and practically free of microorganisms. Hot water and hot chemical detergent solutions are still found to be effective germicidal agents.

There are several types of chemical sanitizers available but hypechlorites and quaternary ammonium compounds are most widely used. Chloramines, other organic chlorine compounds and iodophors are some of the other sanitizers on the market. Also receiving some attention an sanitizers are isothiourea alkyl ether derivatives and commercial grade antibiotics. Usually we can expect more corrosion trouble from the halogen sanitizers (which ordinarily liberate free chlorine, bromine or iodine) than from any other chemicals sold by reputable suppliers of cleaning compounds. Such halogen liberating compounds (e.g., sodium hypochlorite and calcium hypochlorite) should be employed at low temperatures such as 60°F. and under, as well as for short time periods (10 minutes, maximum) just before utilizing the equipment in order to be of service at the most effective time and in order to greatly reduce the chances of pitting attack on the metallic surfaces. It has been proven that chlorine has about the same germicidal efficiency in cold water as in hot water and there is lower loss of gaseous chlorine in the cooler solutions.

If other means of sanitizing can be found to be sufficiently effective, halogen sterilizing should be eliminated. Considerably more experimental work needs to be done along this line.

Quoting from a report issued by the Department of Dairy Science at the University of Illinois, ". . . . the quality of milk handled through a stainless steel pipeline cleaned in position did not differ significantly from the quality of milk handled through the same system when the pipeline was disassembled for cleaning after each milking.

"Improperly cleaned and sanitized pipelines may constitute an important source of general and thermoduric contamination of raw milk. Milk pipelines were santized effectively by the use of procedures which included either chlorination or hot water (185°F.) as the germicidal agent.

"A milk pipeline which was allowed to become excessively contaminated through the use of inadequate sanitation procedures was readily restored to a satisfactory bacteriological condition by a resumption of correct rinsing, washing and sanitizing operations. It was not necessary to disassemble the pipeline in order to achieve this result."

Then, quoting from "Detergents in the Dairy Industry" by Charles Schwartz of the Hall Laboratories, Inc., Pittsburgh:

"Surveying our experience broadly, we might say that the best detergent available to the dairy industry today is one in which there is contained an efficient calcium-sequestering material for the control or prevention of alkaline-earth-metal precipitates, an alkali sufficient in amount to do a good cleaning job and a type least harmful to operator and equipment. It might be added, though, that in addition to a good detergent, there is required a reasonably well worked out cleaning procedure, equipment of the proper type and in good condition, and, last but not least, a fair proportion of an ingredient which we have not been able to mix into detergents—common sense."