A STUDY OF SOME PHYSICAL AND CHEMICAL PROPERTIES OF SEVERAL COMMERCIAL DAIRY CLEANERS

THESIS FOR THE DEGREE OF M. S.
MICHIGAN STATE UNIVERSITY

HAROLD J. BARNUM
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Thesis

Submitted to the Faculty of the Michigan State College in partial fulfillment of the requirements for the degree of Master of Science.

by

Harold J. Barnum

1929

THESIS

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INTRODUCTION

Soap has been used since ancient times. The prophets, Jeremiah and Malachi (1) refer to its use during Biblical times. The potash obtained from the burning of several plants growing in salt marshes was mixed with oil to form soap. Pliny (2), the Roman historian, gives an early account of it as having been first made by the Gauls from a combination of goat's suet and the ashes of the beech tree.

Chevreul, a French chemist, early in the nineteenth century, raised soap making from empiricism to a scientific basis. France for many years was the great soap market of the world, but during recent years the manufacture of soap has spread to many countries. Through research and invention, a soap or cleaner for practically every type of cleaning has been developed.

The cleaning process is not thoroughly understood. The foremost investigators have advanced several theories as to how and why soap cleans. Recent investigations show that not one, but several factors play a definite role in the cleaning process. As a result of his experiments, Hillyer (3) in 1903 was the first to advance a partial explanation of the detergent or cleaning power of soap. His theory is accepted today. He made use of the phenomena of interfacial tension between two liquids to explain his theory. According to this theory the interfacial tension will be great between the two liquids when each liquid has strong internal attractive forces, or strong cohesion; and

it will be small when they have slight attraction for one another, or slight adhesion. Small interfacial tension will be caused by a weak cohesion of at least one of the liquids and a strong adhesion of the liquids to one another.

Hillyer concluded from his experiments that, "detergent action was largely or entirely to be explained by the power of emulsifying oily substances, or wetting and penetrating into oily textures, and of lubricating texture and impurities so that they may be removed easily". He thought these effects were entirely explained by the low cohesion of the soap solutions, together with their strong adhesion to oily matter which results in low interfacial tension.

Later investigators have found other factors which are closely related to those aiding emulsification, wetting power and lubrication. Fall (2) states that it is necessary to have the soap in solution. It must be in true solution before it can become oriented and absorbed upon the surface of the dirt particle. Numerous experiments with graphite and lampblack have shown that deflocculation or peptization of the dirt particles is necessary. Chapin (4) found that deflocculation occurs when a certain minimum concentration of absorbed oriented molecules of the detergent upon the dirt particle surface has taken place.

Foaming is not necessary in the cleaning operation, but according to Jackson (5) is a useful property. Shorter (5) has pointed out that the pressure on the convex side of a bubble is greater than on the concave side. When the bubble rests on a surface it tends to become a plane and will wet the surface more readily. Suds also seem to lift the dirt out

of the wash liquor, thereby preventing redeposition.

It may then be said that detergent or cleaning action is dependent on the following factors: solution, emulsification, wetting, lubrication, deflocculation, and foaming. In the ordinary cleaning process these factors operating in conjunction with each other, cause the dirt particle to be loosened from the dirt bearing substance, after which it is carried away by floatation.

Phases of Cleaning Peculiar to the Dairy Industry.

In the cleaning of dairy utensils, the process differs from the cleaning of other substances in a few particulars. In general there are two important considerations in the cleaning of dairy utensils: first, cleaning the surfaces from adhering particles of the dairy product; and second, sterilization of the cleaned surface. The cleaning operation is most important, as no amount of sterilization could produce the desired result if the surface were not first cleaned. Some of the washing solutions themselves possess some germicidal effect.

Cleanliness is the most important factor connected with any food supply. Milk is a universal food product. Therefore, in the handling of milk and its products, cleanliness of utensils is a prime requisite. Milk in its natural state possesses great adhesive properties for surfaces with which it comes in contact. Its fat and solid particles make excellent food and provide breeding grounds for micro-organisms. At room or higher temperatures, bacteria multiply very rapidly in dirty

utensils. If the dirt particles are not thoroughly removed and the surface sterilized, these bacteria readily find their way into the milk or milk product.

Milk is a highly satisfactory media for bacterial growth. If the bacteria are injected into the milk from the surface of dirty utensils, reproduction begins immediately which results in lowered quality of product, waste, and serious losses in many cases. The health of the consumer is endangered if there should happen to be disease organisms present.

When milk is altered by some intrinsic agent such as souring or drying, or by some outside agencies, such as heating, the original emulsions and colloids are changed or denatured and the solid and liquid particles which are thrown out, adhere even more tenaciously than the original milk to the surfaces of utensils. The cleaning process then becomes very difficult. Because of the complex nature of dairy products it is highly essential that all dairy utensils should receive a thorough cleaning after each use. On many milk pasteurizers a substance popularly referred to as "milk stone", is found. This contains nearly all of the original constituents of milk in a denatured form. This milk stone is very difficult to remove and the majority of dairy cleaners on the market will not remove it at all.

A factor of considerable importance in the selection and use of cleaning compounds for dairy equipment, is the effect of the cleaner on the metal. Some metals used in dairy equipment corrode, pit, and dissolve quite readily when they come in contact with alkalies or acids.

According to Hunziker (6), "injury to the flavor and keeping quality of the dairy product may be caused by the presence, even in very minute amounts, of the metallic salts themselves which have a metallic, bitter, puckery flavor; or by bacteria-selective influence of certain metallic salts. Furthermore, it was shown that the salts and oxides of certain metals have distinct toxic properties rendering the product unsafe for consumption". Thus it may readily be seen that a cleaner which will dissolve the metal or the metal surface is very objectionable, as some of the metallic salts will find their way into the milk product. A pitted or corroded surface will be left which will more readily facilitate the solution of the metal by the milk. Some of the dissolved (8) metal or pieces of the broken metal will lodge in the pitted or corroded surface in the washing process and will not be entirely removed by rinsing. When the milk comes in contact with the surface of the container the dissolved metal will be taken up by the milk with consequent lowering of quality. The pitted surface affords ideal lodging places for bacteria and dirt. From an economical standpoint, the factory manager is interested in preserving the life of his equipment as long as possible. Cleaners which wear away the surface of the equipment rapidly are not desirable. The use of such cleaners makes it necessary for the owner to repair and replace equipment frequently. This is very expensive.

In the cleaning of dairy equipment, a satisfactory cleaner must be active enough to remove all adhering dirt particles, and must not be detrimental to the equipment or severe on the hands of the user.

Classification of Dairy Cleaners.

Hunziker (7) gives the following classification for washing powders available for cleaning creamery equipment.

1. Soap powders.

Many cleaners on the market contain varying quantities of soap powder. These soap powders are not desirable cleaners for dairy equipment as they leave a film on the cleaned surface which is difficult to rinse off and serves as a good medium for bacterial growth.

2. Neutral or Dairy Sodas.

This group consists of cleaners containing varying mixtures of soda ash and bicarbonate of soda. They usually contain from 45 per cent to 60 per cent of soda ash and from 25 per cent to 35 per cent of baking soda.

3. Soda Ash Cleaners.

These washing powders consist of straight soda ash.

4. Causticized Ash or Special Alkalies.

This type of cleaners are very powerful cleaning agents. They contain from 30 per cent to 50 per cent of caustic soda ($NaOH$), and the remainder soda ash.

5. Trisodium Phosphate.

The basic ingredient of this type of cleaner is tri sodium phosphate. Some of them contain in addition to the tri sodium phosphate, soda ash, sodium bicarbonate, borax, or sodium silicate.

6. Cleaners Containing Disinfectants.

These washing powders contain in addition to the cleaning element some disinfectant such as hypochlorite or chloramine-T.

7. Colloidal.

Recently a new type of cleaner has appeared on the market which is in colloidal form. They contain a colloidal base such as potatoe starch together with soda ash, tri sodium phosphate, or sodium bicarbonate.

8. Detergents or Scouring Powders.

To this class belong a type of cleaners which depend for part of their cleansing effect on scouring by mechanical friction. Volcanic ash or pumice stone make up about 60 per cent to 70 per cent of the cleanser which gives it its abrasive property. The remainder is largely soda ash and sodium bicarbonate with a little soap.

Washing powders sold for dairy use vary widely in their ability to clean satisfactorily and economically. There is need for more information in regard to types of cleaners most desirable for various kinds of cleaning and equipment. It was for the purpose of shedding

more light on the relative merits and faults of the different types of cleaners that this work was undertaken.

REVIEW OF LITERATURE AND DISCUSSION

Phillips, Mack and Frandsen (8) at the Massachusetts Station made a number of practical tests with each of thirty-six different commercial dairy cleaners. The cleaners were classified into four groups on the basis of their chief constituent. The classes were sodium carbonate, tri-sodium phosphate, free caustic, and soap. All tests were made at 0.6 per cent concentration of the washing powder. The washing powers were tested on milk bottles containing a film of dried milk and the water softening powers determined by the amount of cleaning solution necessary to soften standard hard water sufficiently to make permanent bubbles by a soap solution. The emulsifying power was tested by shaking some of the solution with pure butterfat and the free rinsing properties tested on the finger. They summarized their results by placing the classes in the order of their effectiveness as follows; Water Softening Powers: Sodium Carbonate, Phosphate, Soap, Hydroxide. Washing Powers: Sodium Carbonate, Hydroxide, Soap, Phosphate. Emulsifying Powers: Soap, Phosphate, Sodium Carbonate, Hydroxide. Ease of Rinsing: Sodium Carbonate, Phosphate, Soap, Hydroxide. Soap was not recommended for dairy cleaning because of the suds and scum it leaves on the surface of metal, and the expense as compared with other equally as efficient cleaners. They maintain that free alkali is too caustic for hand washing, but can be used advantageously in power machines. They believe that neither sodium carbonate nor tri-sodium phosphate contain

all of the good properties of a cleaner and best results may be secured by a mixture of the two. The following approximate analysis is recommended by these investigators for the ideal washing powder.

Sodium Carbonate (anhydrous)	60%
Tri-Sodium Phosphate ($12H_2O$)	40%
Total Alkali as NaOH	58%

Germicidal Effect of Washing Powders

The alkalinity in commercial washing powders is of two different types. The first is known as total alkalinity and is found by titration with an acid. The second type is the free or effective alkalinity, which the chemist calls the hydroxyl ion concentration. It has been found that in working with various commercial powders the total alkalinity does not correspond to the free alkalinity. Taylor (9) gives the following explanation of the phenomena of the difference between free alkalinity and total alkalinity. "When acids and alkalies are dissolved in water, they ionize or break up to give positively charged H ions and negatively charged OH ions respectively. The intensity of acidity or alkalinity is due to the number of H and OH ions respectively in a given solution. Hydrochloric and sulfuric acids are strong acids, because in solution they give a large number of H ions. Acetic and boric acids are weak acids because they give comparatively few H ions in solution. In a similar manner sodium bicarbonate is a relatively weak alkali because it gives relatively few OH ions in solution. Sodium carbonate, trisodium phosphate and sodium hydroxide, on the other hand, are strong

alkalies because they give a large number of OH ions in solution".

In the cleaning process with alkaline powders, sterilization is accomplished to a certain degree. According to Sherman (10) and Taylor (9) the germicidal action of washing powders is in a large measure due to the true or free alkalinity. Sherman showed that an alkalinity of pH 12 will kill Bacillus typhosus in the cold with five minutes exposure. The same results were obtained with a solution having a pH of 11 at 113° F. He was successful in killing spore forming organisms at low temperatures in very strongly alkaline solutions. Spores which withstood the temperature of boiling water for two hours, were destroyed at 176° F. in washing powder at a pH of 12. Phillips, Mack and Frandsen (8) say that all powders used in their determinations at a strength of 0.6 per cent acted as disinfectants to such a degree as to make the washing solution sterile.

Mudge and Lawler (11) studied the effect of alkali solutions on bacteria found in unwashed milk bottles. They give the following results for the number of bacteria surviving the action of sodium hydroxide solutions of different concentrations for various periods of holding at 120° F. Eight million bacteria were used in each original case.

Concentration of Alkali

Time	0.1%	0.3%	0.5%	0.7%	1.0%
Minutes	PH 12.3	pH 12.9	pH 13.0	pH 13.2	pH 13.4
1	10,000	3,000	200	100	0
2	5,000	1,000	150	50	0
3	2,500	500	100	30	0
4	1,500	150	50	0	0
5	1,000	50	20	0	0

A study of the above table readily reveals that there is a correlation between time of exposure and concentration of alkali. The 1.0 per cent solution was very effective in germicidal action.

At the same time these investigators studied the effect on bacteria in dirty milk bottles of a popular dairy cleaner containing mixtures of sodium hydroxide and sodium carbonate. Stronger concentrations of alkali were used. Four million bacteria were present in each original sample.

Concentration of Alkali

Time	0.5%	0.7%	1.0%	2.0%
Minutes	pH 10.8	pH 11.0	pH 11.2	pH 11.6
1	30,000	20,000	600	200
2	25,000	10,000	400	80
3	15,000	5,000	250	0
4	10,000	3,000	150	0
5	5,000	2,000	50	0

The results of this test indicate that a higher percentage of sodium hydroxide and sodium carbonate was required in the commercial compound than in the straight sodium hydroxide to give the same germicidal efficiency. The authors conclude that the concentration of hydroxyl ions appears to be an important factor in bacterial destruction.

Levine, Peterson and Buchanan (12) made investigations into the germicidal efficiency of sodium hydroxide, and of sodium hydroxide-carbonate mixtures. A popular commercial washing powder containing 2 per cent NaOH and 2.66 per cent Na_2CO_3 by weight was used in comparison. The concentration of the commercial compound and the mixture of NaOH and Na_2CO_3 was equivalent to a normal alkali and gave a pH of 13.18. The straight NaOH had a normality of 0.5 and a pH of 13.20.

A table was published showing the relation of the composition of the alkalies at the same pH to killing times at 50° C.

	Alkalinity by Titration	Concentration		Killing Time
Sample	N.	NaOH %	Na_2CO_3 %	Minutes
NaOH	0.5	2.00	0.00	40.8
NaOH-Na_2CO_3 Mixture	1.0	1.30	3.50	43.7
Commercial Washing Powder	1.0	2.00	2.66	34.0

A study of the table reveals the fact that it required 6.8 minutes more for the straight NaOH solution to kill 99.9 per cent of the bacteria than for the commercial powder at 120°F. At 141°F. the kill-

ing times were 8.5 and 11.75 minutes respectively. The results indicate that the presence of the carbonate in the commercial product served to increase the germicidal effect of the sodium hydroxide present at the same pH. The authors maintain that the disinfecting action of Na_2CO_3 at 120°F. is nil. They believe the presence of the carbonate enhanced the germicidal efficiency of the hydroxide. It would seem as a result of this experiment that neither the total alkalinity nor the H-ion concentration alone is a direct measure of the germicidal powers of these alkalies. These investigators conclude "It is conceivable that the undissociated NaOH rather than the OH ion, penetrates the bacterial cell. In this case the concentration of the undissociated NaOH becomes the determining factor in the germicidal efficiency of the alkalies. The addition of Na_2CO_3 to the hydroxide would result in an increase in the concentration of undissociated NaOH and a corresponding increase in the germicidal action".

This phase of the cleaning operation is of interest to the operator insofar as bottle and can washing is concerned. Most cleaners which are high in alkalinity are severe on the hands as well as detrimental to equipment and cannot be used in other types of work. It is very desirable to sterilize bottles and cans thoroughly. For this purpose a washing powder should be used which will remove dirt quickly, has high disinfecting properties, and will not severely attach glass or metals used in bottle and can construction.

The Effect of Metals on Milk

Recently a few investigators have made extended studies regarding the effect of metals on milk and its products to determine the cause of many "off" flavors and poor keeping qualities. Hunziker (6) states that, "In order for any metal to suffer corrosion, or to affect the dairy product, it must be capable of entering into solution. Solution may be caused by the attack of acids, mineral salts, and other constituents of milk, washing powders, chemical sterilizers, or brine".

Toxicity Hunziker (13) believes that with the scarcity of available data on the subject of toxicity of metals in milk that no standard of toxicity can be established. Numerous examples may be cited, however, that the salts of such metals as chromium, copper, zinc, and tin are highly poisonous. Since these metals are more or less soluble in milk it is quite important that they be not subjected to operations which will cause them to be more readily soluble if they are to be used extensively in the dairy plant. Seligman (14) suggests that the following metals have certain toxic effects on milk. He arranged them in the order of their toxic effect. 1. Chromium, 2. Copper, 3. Zinc, 4. Lead, 5. Tin, 6. Nickel, 7. Aluminum.

Keeping Quality and Flavor Hunziker (15) found that copper lactates impart an intensely metallic taste to milk and milk products even if present in minute quantities. The action of copper was found to be more intense in this respect than that of iron and iron salts. In cases

where poorly tinned equipment is used or the tin has been dissolved or worn off by improper cleaning methods leaving large surfaces of copper exposed, the dairy product is not protected against the detrimental action of the copper. After a series of tests in regard to the effect of the various metals on milk, Hunziker (6) concluded that those metals which showed definite corrosion in milk and acid solutions also had the most damaging effect on the flavor of the milk product. In his work nineteen metals were used. He found that iron, galvanized iron and copper produced a marked metallic flavor in all products and that zinc, tinned iron and nickel silver caused the metallic flavor in the majority of cases. Allegheny metal, tin and heavily tinned copper had no effect on flavor and showed maximum resistance to corrosion and tarnishing. The work of Hunziker has been substantiated by Guthrie and Roadhouse (16) in regard to copper, poorly tinned copper and nickel silver. Seligman (14) agrees with Hunziker as to the effect of copper and zinc on milk products. All three investigators believe that pure nickel is not entirely negative as to its effect on the flavor of milk.

Effect of Milk on Metals Hunziker (6) made an extensive study of the loss in weight and corrosion of metal strips in sweet and sour milks and cream, and in acid solutions. He used aluminum and aluminum alloys, copper and copper alloys, nickel, zinc, iron and galvanized iron, tin and tinned copper, tinned iron, two ordinary chromium steels and one chromium-nickel steel. The corrosive effect on the metal was greater in the acid solutions than in milk products at the same acidity for both. He suggests that acidity is the chief factor in metallic cor-

rosion and that some of the non-acid milk constituents exert a corrosive protective influence. In general the corrosion was more intense in the high-acid than in the low-acid products, and at higher than room temperatures. He found that zinc, iron, aluminum, galvanized and tinned iron lost considerable weight in acid solution and corroded quite severely. In milk and cream, copper, iron, nickel, tin, zinc, galvanized and tinned iron, monel metal, and nickel silver exhibited the greatest loss in weight. Zinc, iron, copper and galvanized iron suffered the most corrosion. Allegheny metal, tin, and heavily tinned copper showed maximum resistance to corrosion and loss of weight in all the tests. Guthrie and Roadhouse (16) carried on a similar experiment with metals immersed in cream. They found that pure nickel lost heavily in weight in raw cream and that monel metal and pure nickel lost considerable weight in pasteurized cream.

Effect of Alkalies on Metals

Very little literature is available on the effect of alkalies on metals for dairy equipment. Phillips, Mack and Frandsen (8) immersed strips of aluminum, copper, nickel, tin and zinc in solutions of washing powders having a strength of 0.6 per cent by weight. They found that cleaners containing hydroxide attacked aluminum, copper, and tin severely. Sodium carbonate cleaners also attacked aluminum, copper, and tin, but less severely. They state that tri-sodium phosphate attacks aluminum and has very little effect on the other metals.

Hunziker, Cordes and Nissen (17), in a recent investigation, studied the effect of washing powder solutions on nineteen different

metals. They used 0.5 per cent solutions of sodium hydroxide, special alkali, modified soda, sodium carbonate, tin cleaner (containing Na_3PO_4 and Na_2CrO_4), tri-sodium phosphate, and a 0.16 per cent solution of tri-sodium phosphate. The corrosion and weight losses totaled greatest in sodium hydroxide and special alkali solutions. The next greatest total losses occurred in the case of 0.5 per cent solutions of tri-sodium phosphate and sodium carbonate in the order named. The action of the modified soda was next in order. The 0.16 per cent solution of tri-sodium phosphate and the 0.5 per cent solution of trisodium phosphate treated with sodium chromate gave the smallest loss in weight.

The aluminum products used in these tests suffered by far the most intense corrosion and loss of weight in all the washing solutions used. The tinned copper and tinned iron products ranked next in loss of weight, although the tinned equipment was much more resistant. Nickel silver tarnished considerably in tri-sodium phosphate and tin cleaner. Copper, iron, galvanized iron, and zinc exhibited more severe corrosion than the tin-plated products. Nickel and monel metal showed only negligible weight losses. The alloys: Allegheny metal, Ascoloy, and Enduro, were most resistant and practically immune to the action of all the alkalies.

The presence of a very small amount of silicate of soda in the sodium carbonate prevented corrosion on the aluminum products. Corrosion in the case of tin-plated copper and tin-plated iron was prevented by adding a small amount of chromate of soda to the tri-sodium phosphate washing solution.

Dr. Prucha (18) of the Illinois Station studied the effect of chlorine sterilizing solutions and washing powders on milk apparatus. His results show that polished Allegheny metal was completely resistant to the various sterilizing solutions, as well as to caustic, trisodium phosphate, and sodium carbonate.

Summary of Review of Literature

Washing powders for dairy use may be divided into groups based upon their composition. A few investigators are of the opinion that a mixture of two or more of these compounds is more desirable than those containing just one compound.

Washing powders contain two kinds of alkalinity, free and combined.

Investigators are not agreed as to the cause of bacterial destruction by alkalies. Some suggest that it is due entirely to the OH ion concentration and others believe it may be due to the OH ion concentration and the undissociated NaOH together.

Metallic salts are without doubt the cause of many off flavors and poor keeping quality in milk and milk products.

The metals used in the handling of milk and milk products differ considerably in their ability to resist solution and corrosion by milk, acids, and alkalies.

The chromium alloys appear to be the most resistant to the action of alkalies.

OBJECT OF THE EXPERIMENT

The primary objects of this experiment were to determine:

1. By chemical analysis the composition of each cleaner studied.
2. The relative solubility of the cleaners in water.
3. The pH and buffer action under dilution.
4. The relative emulsifying powers as measured by the drop number in benzene and butterfat.
5. The relative water softening powers.
6. The effect of cleaner abrasives on metals.
7. The effect of each cleaner solution on metals.

PLAN OF EXPERIMENTAL WORK

Chemical Analyses

Samples of each cleaner were taken at random from barrels and containers as they are sold on the market. The cleaners were analyzed for the following compounds: total alkali as Na_2O, sodium carbonate, sodium bicarbonate, sodium hydroxide, tri-sodium phosphate, sodium hypochlorite, and free alkalinity. All tests were run in duplicate.

Neutral or Modified Sodas

Total Alkali (Na_2O) (19) Four grams of the cleaner was dissolved in 500 c.c. of freshly distilled water. A 25 c.c. aliquot containing .2 gram of cleaner was pipetted off and titrated with .1 NHCl, using

methyl orange as an indicator. The per cent of Na_2O was calculated from the formula:

$$\frac{\text{C.C. .1 N HCl x .31}}{.2}$$

Sodium Bicarbonate ($NaHCO_3$) (19) Eight and four tenths grams of the sample was dissolved in 50 c.c. of distilled water. This was titrated with N NaOH until a drop of the solution added to a drop of freshly prepared silver nitrate indicator on a spot plate gave instantly a dark color. The per cent of $NaHCO_3$ was calculated from the formula:

$$\frac{\text{C.C. N NaOH x 8.4}}{\text{Weight of sample}}$$

Sodium Carbonate (Na_2CO_3) (19) The per cent of Na_2CO_3 was calculated from the formula:

$$(\%Na_2O - (\%NaHCO_3 \times .3690) \times 1.7097)$$

Soda Ash.

Total Alkali Expressed as Sodium Carbonate (19) Five and three tenths grams of the sample were dissolved in 100 c.c. of distilled water. 100 c.c. of N H_2SO_4 were added from a burrette. The solution was boiled for five minutes to expel the CO_2. It was then titrated against .1 N NaOH using four drops of methyl red as indicator. Correction was made for the temperature of the acid. The equivalent of total alkali, expressed as per cent, Na_2CO_3, was calculated from the formula:

$$\frac{\text{C.C. N } H_2SO_4 \text{ (corrected)} - \left(\frac{\text{c.c. .1 N NaOH}}{10}\right) \times 5.3}{\text{Weight of Sample}}$$

Total Alkali Expressed as Na_2O (19) Equivalent of total alkali expressed as $\%Na_2CO_3 \times 0.5849$.

Sodium Bicarbonate ($NaHCo_3$) The same method was used as in neutral sodas.

Sodium Carbonate (Na_2CO_3) (19) The per cent of Na_2CO_3 was calculated from the formula:

Equivalent of total alkali expressed as $\%Na_2CO_3 - (\%NaHCO_3 \times 0.6309)$

Super Alkalies.

Preparation of Sample (19) A sample was prepared for analysis by washing about 40 grams of the cleaner into a 500 c.c. graduated flask with distilled water. The solution was cooled to room temperature, diluted to the 500 c.c. graduation and thoroughly mixed. Aliquot portions of the solution were used for determinations.

Total Alkali (Na_2O) (19) A 25 c.c. aliquot was titrated with NH_2SO_4 using methyl orange as indicator. The per cent of Na_2O was calculated from the formula:

$$\frac{\text{C.C. N } H_2SO_4 \times 62}{\text{Weight of original sample}}$$

Sodium Hydroxide (NaOH) (19) One hundred c.c. of $BaCl_2$ was added to a 25 c.c. aliquot of the prepared solution. This was titrated with NHCl using 6 drops of phenolphthalein as the indicator. The per cent of NaOH was calculated from the formula:

$$\frac{\text{C.C. N HCl} \times 80.02}{\text{Weight of original sample}}$$

Sodium Carbonate (Na_2CO_3) (19) The per cent of Na_2CO_3 was calculated from the formula:

$$(\%Na_2O - \%NaOH \times 0.7748) \times 1.7097.$$

Tri-sodium Phosphate and Colloidal.

Tri-sodium Phosphate (Na_3PO_4) (20) The method followed in the determination of tri-sodium phosphate was the gravimetric method as given in the A. O. A. C. Official Methods of Analysis for P_2O_5. An aliquot of the solution corresponding to .20 gram was neutralized with 10 - 15 grams of ammonium nitrate. 70 c.c. of molybdate solution for every decigram of P_2O_5 present was added to precipitate the phosphoric acid. The mixture was digested for an hour at 65°C, and then filtered and washed with cold water. The precipitate on the filter was dissolved with ammonium hydroxide and hot water. Hydrochloric acid was added to nearly neutralize the solution. While stirring vigorously, 15 c.c. of magnesia mixture for every decigram of P_2O_5 was added drop by drop. After 15 minutes 12 c.c. of concentrated NH_4OH was added. The precipitate was allowed to settle over night. The mixture was then filtered, and washed with dilute NH_4OH until freed from chlorides. The precipitate of magnesium pyro-phosphate was ignited to whiteness, cooled and

and weighed. Calculations were made in terms of P_2O_5, Na_3PO_4, and $Na_3PO_4 .12 H_2O$. The commercial tri-sodium phosphate used in cleaners contains 12 molecules of water of crystallization. As it stands in contact with air some of the water of crystallization is given off. Calculations in terms of Na_3PO_4 12 H2O were invariably high due to this evaporation as the samples aged in their original containers. Because of this unavoidable defect in the analysis, calculations in terms of Na_3PO_4 and P_2O_5 were found to be more accurate and comparable. The following formulae were used in the calculations:

Wt. of $Mg_2P_2O_7$ x 1.4731 equal wt. of Na_3PO_4

$\{$(wt. of Na_3PO_4 ÷ .2) x 100$\}$ equal % Na_3PO_4

Wt. of $Mg_2P_2O_7$ x 3.4146 equal wt. of $Na_3PO_4 .12 H_2O$

$\{$(wt. of Na_3PO_4 ÷ .2) x 100$\}$ equal %$Na_3PO_4 .12 H_2O$

Wt. of $Mg_2P_2O_7$ x .6388 equal wt. of P_2O_5

$\{$(wt. of P_2O_5 ÷ .2) x 100$\}$ equal %P_2O_5

<u>Total Alkali</u> (Na_2O) The same method was used as in neutral sodas.

<u>Sodium Carbonate</u> (Na_2CO_3) Cleaners containing tri-sodium phosphate were analyzed for carbon dioxide, using carbon dioxide apparatus devised by the Michigan Agricultural Experiment Station. .25 gram of the sample was weighed into a small glass container. 1 c.c. of dilute HCl, containing one part HCl, one part water, and 2 drops of amyl alcohol, were placed in a 20 c.c. glass bottle, together with the sample. This container was placed in an upright position. The bottle was connected by a rubber stopper and glass and rubber tubing to a graduated tube holding 50 c.c. of

distilled water. The graduated tube was connected with a constant overflow apparatus. The glass container with the sample was tipped over into the HCl. The number of c.c. of water displaced by the liberated CO_2 was taken as the number of c.c. of CO_2 in the sample. Corrections for temperature and barometer readings were made. The per cent of Na_2CO_3 in the sample was calculated from the CO_2 content by the formula:

$$\frac{2.41 \times \text{grams } CO_2}{.25}$$

Sodium Hypochlorite (NaOCl) (21) The method followed in the determination of NaOCl was that used by Treadwell and Hall for the determination of hypochlorous acid. Five grams of the cleaner was dissolved in 500 c.c. of distilled water. Ten c.c. of 10 per cent KI solution was added to a 25 c.c. aliquot of the cleaner solution. The solution was slightly acidified with HCl. The iodine set free was titrated with .1 N $Na_2S_2O_3$. The per cent of NaOCl in the sample was calculated from the formula:

$$\frac{\text{C.C. } .1 \text{ N } Na_2S_2O_3 \times .003725}{.25} \times 100$$

Free Alkalinity.

A pH determination was made on all cleaners to determine the correlation between the titratable or total alkalinity and the free alkalinity or hydroxyl ion concentration. La Motte indicators and color standards were used for the tests. pH on one per cent solutions was found by weight.

Solubility Tests

Tests were made on each cleaner to determine the relative per cent of total solubility in distilled water at room temperature. 200 c.c. of distilled water was placed in a beaker. An excess of cleaning powder was added to the water and thoroughly stirred. The mixture was allowed to stand undisturbed over night. 25 c.c. of the clear solution was transferred with a pipette to a weighed porcelain evaporating dish. The dish with the solution was weighed and the weight of the solution calculated by difference. The moisture was allowed to evaporate and the residue dried slowly in a vacuum oven to a constant weight. The weight of the dried residue divided by the weight of the solution was the percentage of total solubility at room temperature.

pH and Buffer Action Under Dilution

The pH and relative buffer action of each cleaner under different dilutions with distilled and tap water at room temperature was obtained. The pH, which is the value of the hydroxyl ion concentration, and commonly called the free alkalinity is also a measure of the germicidal effect of the cleaner solution. The tests gave the pH at stronger concentrations than the cleaners are ordinarily used and at different dilutions up to .1 per cent concentration by weight. The ability to resist change in pH upon dilution is what is commonly referred to as

buffer action. Buffered solutions may be diluted with distilled water without affecting the pH value. The stability or change in pH as the dilution progressed was an accurate measure of the buffer action of the cleaner when subjected to dilution. This also gave the effect of hard water on the pH and the buffer action when observations with the same concentration with distilled and tap water were made.

La Motte indicators and standards were used in the tests. Solutions were made with concentrations of one gram of powder made up to 100 c.c. with water, 1 to 200 c.c., 1 to 300 c.c., 1 to 400 c.c., 1 to 500 c.c., 1 to 600 c.c.,1 to 800 c.c., and 1 to 1000 c.c.

The Relative Emulsifying Powers as Measured by the Drop Number in Benzene and Butterfat

Hillyer (3) advanced the theory that two substances having a low interfacial tension toward each other would have high emulsifying powers. A liquid having a low cohesion for itself and strong adhesion for oil or grease, will have a low interfacial tension toward the oil or grease and high emulsifying power. A liquid having great cohesion and low adhesion will have high interfacial tension toward the oil and consequent low emulsifying power. Hillyer (22) devised an apparatus to measure the comparative emulsifying powers of different soap solutions toward typical oils. He compared the number of drops of typical soap solutions issuing from a capillary tube beneath the surface of kerosene with the number of drops formed in the same manner with water. Water forms large drops in

kerosene because of its great cohesion and small adhesion to oil. A soap solution forms small drops because of its low cohesion and its high adhesion to the oil. Soap solutions issuing from the capillary will vary in size of drops. According to the theory, those giving the smallest drops at the same concentration will lower the interfacial tension most, and are the best emulsifiers.

Later investigators have found this method of comparing emulsifying powers to be satisfactory. Baker and Schneidewind (24) made investigations in metal cleansing with alkaline cleaning solutions. They measured the emulsifying power by comparing the size of drops of the aqueous alkaline solutions issuing from a capillary tube beneath the surface of typical mineral oils to the size of drops formed in the same manner by distilled water.

A modification of the two methods mentioned was used in this experiment. An apparatus similar to Hillyer's was constructed. Figure I is a drawing of the apparatus. Pure benzene and pure butterfat respectively, were used in the tests.

In benzene the cleaner solutions were made up to .625 per cent concentration by weight. All determinations were made at room temperatures. With butterfat, it was necessary to reduce the concentration to .02 per cent by weight. At a stronger concentration the strong alkalies ran down in a stream and no drops were formed. The tests with butterfat were carried out at 110° F., the temperature being kept constant in a water bath. The results of both tests were tabulated in number of drops and the comparative size of drops with distilled water.

APPARATUS FOR MEASURING THE EMULSIFYING POWERS OF CLEANER SOLUTIONS

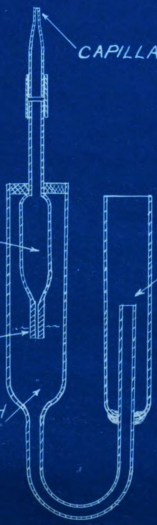

FIG. 1

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The Relative Water Softening Powers

A portion of the cleaner solution in the washing process is used up in softening the water. Softening, or the removal of the calcium and magnesium compounds present in hard water, takes place simultaneously with the cleaning process. The effectiveness of the cleaning operation is dependent upon the thoroughness of the removal of this hardness. If the hardness is not removed, thorough cleaning cannot be accomplished. Some of the alkaline powder is used to precipitate the calcium and magnesium. The remaining powder is used in the cleaning. process. The alkaline powders used in cleaning dairy equipment differ in their ability to soften water. These tests were made for the purpose of measuring the amount of each necessary to soften a given amount of standard hard water. The methods used were those of the American Public Health Association in "Standard Methods of Analysis".

Preparation of Standard Hard Water Solution Eight grams of $CaCl_2$,6 H_2O was made up to four liters with distilled water. This solution was analyzed for CaO by the following method. Five c.c. of reagent HCl was added to 100 c.c. of the solution. Ammonia water was added to make the solution faintly alkaline. 25 c.c. of hot 10 per cent ammonium oxalate was added to the boiling solution. After boiling for twenty minutes the precipitate was allowed to settle, filtered, and washed with warm water and ammonia until freed from chlorides. The precipitate was washed into the original beaker with hot water and hot H_2SO_4 respectively. The solution was titrated at 60°C. with .1N K M NO_4. The number of grams of CaO in the sample was calculated by the formula.

$$C.C.\ .1\ N\ K\ M\ NO_4 \times .0028$$

The number of grams of CaO or parts of hardness per million was calculated by the formula.

Grams CaO in 1 c.c. x 1,000,000.

Preparation of Standard Soap Solution (23) One hundred grams of dry Lux was dissolved in one liter of 80 per cent alcohol. This solution was allowed to stand several days before standardizing. It was then diluted to five liters with 70 per cent alcohol. Ten c.c. of the standard hard water solution together with 90 c.c. of distilled water was titrated with the soap solution. It required 7.1 c.c. of soap solution to produce a permanent foam in the 100 c.c. of hard and distilled water. By titration it required 1.7 c.c. of soap solution to produce a permanent foam with 90 c.c. of distilled water. The number of grams of CaO removed by 1 c.c. of soap solution was calculated by the formula:

$$\frac{\text{Grams CaO in 10 c.c. standard hard water solution}}{5.4}$$

Measuring the Water Softening Powers of Cleaner Solutions (23) All cleaner solutions were made up at the rate of five pounds per 100 gallons of water, or a concentration of .625 per cent by weight. Trials were made in each case to determine the number of c.c. of cleaner solution required for 125 c.c. of standard hard water, so that not more than 12 c.c., nor less than 2 c.c. of soap solution should be used in the final titration, when a 100 c.c. aliquot of the filtrate was used. If more than 12 c.c. of soap solution were used the alcohol contained in it would greatly affect the surface tension and erroneous results would be ob-

[illegible] lowed to stand several days before standardizing. It was [illegible] to five liters with 70 per cent alcohol. Ten c.c. of the [illegible] water solution together with 90 c.c. of distilled water [illegible] with the soap solution. It required 7.1 c.c. of soap so- [illegible] to produce a permanent foam in the 100 c.c. of hard and distilled [illegible] titration it required 1.7 c.c. of soap solution to produce [illegible] foam with 90 c.c. of distilled water. The number of grams [illegible] by 1 c.c. of soap solution was calculated by the formula:

$$\frac{\text{Grams CaO in 10 c.c. standard hard water solution}}{5.4}$$

(23) Testing the Water Softening Powers of Cleaner Solutions

[illegible] solutions were made up at the rate of five pounds per 100 [illegible] water, or a concentration of .625 per cent by weight. Trials [illegible] each case to determine the number of c.c. of cleaner soln- [illegible] for 125 c.c. of standard hard water, so that not more than [illegible] c.c., or less than 2 c.c. of soap solution should be used in the final [illegible] on a 100 c.c. aliquot of the filtrate was used. If more [illegible] c.c. of soap solution were used the alcohol contained in it would [illegible]

tained. In all cases the total was made up to a volume of 175 c.c.

Cleaner solution was added to the hard water solution, thoroughly mixed and allowed to stand over night. It was then filtered and two aliquot portions of 100 c.c. and 50 c.c. respectively were pipetted off and titrated with the soap solution until a permanent lather formed. The number of c.c. of soap solution used, multiplied by the equivalent of CaO removed by one c.c. of soap solution was the number of grams of CaO left in the sample. All tests were made in duplicate.

Since it was impossible to use the same number of c.c. of cleaner and hard water in each case, the only comparable method of expressing the results was in terms of the number of grams of CaO removed per c.c. of cleaner solution, and the number of grams of CaO removed by one gram of the cleaner powder.

The number of grams of CaO removed by one c.c. of the cleaner solution was calculated from the formula:

$$\frac{\text{Total grams CaO present} - \text{total grams CaO left}}{\text{Number c.c. of cleaner in sample}}$$

The number of grams of CaO removed by one gram of cleaner powder was found by dividing .00625 by the number of grams of CaO removed by one c.c. of the cleaner solution.

It was found that the College Creamery tap water contains 240 p.p.m. of hardness in terms of CaO. 100 gallons of tap water contains 94.5 grams of CaO. The number of grams of cleaner powder needed to remove the hardness in 100 gallons of water was calculated by the formula:

94.5

No. of grams CaO removed by 1 gram Cleaner

The amount of cleaner solution, hard water solution, distilled water and soap solution used and number of grams of CaO removed in each case are given in table VI.

The Effect of Abrasives on Metals

A well known brand of detergent was selected for this part of the experiment. The original volcadotte, which is the screened and dried material that makes up a large percentage of the cleanser, was obtained from the company. A portion of this volcadotte was rubber briskly over the surface of the metal for a period of ten minutes to determine whether or not the abrasive scratched the metal. This effect was studied under a ten power binocular microscope. The results were tabulated under the heads of affected or not affected, and the degree of scratching.

The Effect of Each Cleaner on Metals

Metals

The metals, aluminum, pure copper, pure nickel, tinned copper, tinned steel, stainless steel, and Allegheny metal were selected for the test. The metals were cut into strips three inches long and one and seven-eighths inches wide. Each strip was numbered and labeled and a small hole bored in the center of one end. Each strip was cleaned thoroughly with carbon tetra chloride, rinsed with water and wiped dry;

placed in a vacuum oven and dried, cooled, and then carefully weighed to the fourth decimal place. A mark was made with a red pencil at the exact center of each side.

Solutions.

All cleaner solutions were made up at the rate of five pounds of powder per hundred gallons of water, or .625 per cent by weight.

Method of Making the Tests.

A pH of the cleaner solution was made. 210 c.c. of the solution was placed in a 300 c.c. lipless pyrex beaker. One end of a small silk thread was stuck to the side of the beaker with a gummed label. The other end of the thread was run through the hole in the metal. The metal was suspended to the half way mark in the solution by adjusting the loose end on the opposite side of the beaker from the stationary end. After this adjustment was made the thread was securely fastened to the side of the beaker by a gummed label. A glass petri dish was placed over the beaker to exclude dirt and dust and to prevent evaporation. The metal was allowed to remain in the solution undisturbed for a period of two weeks. This was done with the idea of duplicating factory conditions as nearly as possible over a period of years. The results showed only the effect of the cleaner on the metal when left in contact with it without the factors of rubbing or brushing, and exposure to air. Each of the seven metals was subjected to the test with each of the sixteen cleaners.

Observations were made at intervals to note the effect on the metal and change in color of the solution. At the end of the two weeks period

the metals were removed from the solution, washed with distilled water, dried with a cloth, placed in a vacuum oven, dried and cooled, and then carefully reweighed. The loss or gain in weight was calculated from the original weight. The corroding, pitting, and tarnishing effect below the air-liquid line and the corroding and tarnishing effect above the air-liquid line was observed and recorded.

The change in color of the solution was observed and the presence of any precipitate noted. This gave some idea as to the extent of solution of the metal in the alkali. A pH of the final solution was taken to determine if there were any correlation between the loss in weight and change in pH. The stability and the change in pH also gave some idea as to the buffer action of the cleaners when exposed to these metals.

Photographic Work

Actual size photographs of each metal were taken to show the effect of each cleaner on each metal. The pictures were arranged in order on a background and a group picture taken. The photographs are placed in the appendix of this thesis.

RESULTS OF EXPERIMENTAL WORK AND DISCUSSION

Chemical Analyses

Chemical analyses brought out the fact that some of the cleaners studied were of nearly identical composition. The others varied considerably. The analyses made possible a division of the cleaners into five classes according to composition. The types of cleaners included: modified or neutral sodas, soda ash, causticized or special alkalies, tri-sodium phosphate, and colloidal. This division of the cleaners enables the reader to compare the effects of the different cleaners within each class, as well as the effect of the different classes as a whole, with one another. Following is a classification of the cleaners by number.

Neutral Sodas	Soda Ash	Special Alkalies	Tri-Sodium Phosphate	Colloidal
No.	No.	No.	No.	No.
1	5	6	9	16
2		7	10	
3		8	11	
4			12	
			13	
			14	
			15	

The commercial tri-sodium phosphate used in the manufacture of dairy cleaners contains water of crystallization. As the cleaners age in their

original containers some of this water of crystallization is given off. Because of this property, accurate analysis for the form of commercial tri-sodium phosphate (Na_3PO_4 12 H_2O), as ordinarily expressed, could not be determined. The samples were analyzed for phosphorus by precipitating the phosphorus as magnesium pyro-phosphate. It was thought best to express the results in terms of the three compounds, Na_3PO_4 (anhydrous), Na_3PO_4 .12 H_2O, and P_2O_5. The amount of water of crystallization given off affected the accuracy of the results least when expressed in terms of P_2O_5, and most, when expressed in terms of Na_3PO_4 .12 H_2O.

A complete analyses of the cleaners is given in table I. In some cases the figures given do not total 100 per cent. This was due to the small amount of undetermined matter and the moisture content. The moisture content will vary in different brands and types of cleaners. All cleaners when analyzed were in dry powdered form as they are ordinarily obtained in large bulk containers.

An interesting fact brought out by the analyses for total and free alkalinity was the difference in the amount of each found in the different classes. The modified sodas were high in total alkalinity, but low in free alkalinity. The soda ash cleaner gave a similar reaction. The special alkalies were high in both types. The tri-sodium phosphate cleaners as a group were low in total alkalinity and comparatively high in free alkalinity.

Table I. Chemical Analyses.

Number of Cleaner	Free Alkalinity 1% by Weight pH	Total Alkali (Na_2O) Per cent	Sodium Carbonate (Na_2CO_3) Per cent	Sodium Bicarbonate ($NaHCO_3$) Per cent	Sodium Hydroxide ($NaOH$) Per cent	Trisodium Phosphate (Na_3PO_4 Anhydrous) Per cent	Trisodium Phosphate (Na_3PO_4 12 H_2O) Per cent	Phosphorus Penta-oxide (P_2O_5) Per cent	Sodium Hypochlorite ($NaOCl$) Per cent
1	10.0	45.86	61.03	27.55					
2	10.0	45.22	56.90	32.36					
3	10.0	44.85	59.12	27.84					
4	10.0	46.17	58.25	32.76					
5	10.6	57.83	90.98	12.51					
6	12.6	67.03	51.56		47.59				
7	12.6	63.56	49.00		45.05				
8	12.4	66.44	54.30		44.76				
9	11.6	20.15	4.00			40.77	93.75	17.68	
10	11.4	32.37				42.94	99.52	18.62	3.52
11	11.6	37.74	44.24			27.87	65.25	12.09	.
12	11.8	25.42				57.01	131.96	24.72	
13	11.8	27.82	24.39			42.37	97.91	18.38	
14	10.8	26.50	18.34			59.07	136.91	25.62	
15	11.8	22.32	4.66			54.75	126.84	23.73	
16	10.6	42.08	66.40			6.77	15.36	2.87	

1	1.0	40.00	55.00				
2	1.0	50.00	55.00				
3	10.0	50.00	55.00	55.00			
4	10.0	50.00	55.00	55.00			
5	10.0	40.00	55.00	55.00	10.00		
6	10.0	30.00	55.00				
7	10.0	20.00	55.00	55.00			
8	10.0	10.00	55.00	55.00			
9	10.0	0.00	55.00				
10	10.0	0.00					
11	10.0	0.00	0.00				
12	10.0	0.00					
13	10.0	0.00	0.00				
14	10.0						
15	10.0	0.00	0.00				
16	10.0						
17	10.0	0.00	0.00				
18	10.0	0.00	0.00				
19	10.0	0.00	0.00				
20	10.0	0.00	0.00				

Total Solubility

The total solubility of the cleaners studied varied considerably. By the total solubility is meant the percentage by weight of the cleaning powder in a saturated solution. The lowest total solubility at room temperature was 11.12 per cent in the case of number 16. This means that 11.12 pounds of the cleaner will completely dissolve in enough water to make the solution up to 100 pounds. The highest total solubility was 25.82 per cent in the case of the soda ash cleaner. Under ordinary conditions it would not be necessary to make a washing solution stronger than one per cent by weight. All the cleaners were soluble to 10 per cent or more, which insures their going into solution without much difficulty. Those cleaners with high solubility appeared to go into solution more readily than those with lower solubility.

The modified sodas were very nearly identical in their percentage solubility and were next to the soda ash cleaner in total solubility. The special alkalies were third in total solubility. The members of this class varied more in this property than the modified sodas. The tri-sodium phosphate cleaners were more variable in their solubility as a class than the others. This variability ranged from 11.13 per cent with cleaner number 15 to 24.80 per cent in the case of number 11. The colloidal cleaner, number 16, had the lowest percentage of total solubility. The results of the solubility tests are given in table II.

Table II.

Showing Weight of 25 cc. of Saturated Cleaner Solutions; Weight of Dried Powder Contained in 25 cc.; and Total Solubility in Per Cent at Room Temperature.

Cleaner No.	Weight of Solution	Weight of Dried Residue	Total Solubility
	Grams	Grams	Per Cent
1	29.2612	7.1176	24.32
2	28.7528	6.8531	23.83
3	28.7736	6.6352	23.06
4	29.6700	7.2176	24.33
5	30.4961	7.8754	25.82
6	29.9479	5.9232	19.78
7	31.5569	7.0649	22.39
8	29.8707	5.8185	19.48
9	27.3880	4.8764	17.80
10	26.5294	4.4279	16.69
11	29.2322	7.2496	24.80
12	27.2770	4.5205	16.57
13	28.4501	6.5873	23.15
14	28.7074	4.5447	15.83
15	26.5868	2.9597	11.13
16	27.7738	3.0872	11.12

pH and Buffer Action Under Dilution.

The pH value of any solution, as has been explained, is the measure of its H ion or OH ion concentration. In the case of alkaline cleaner solutions this test is a measure of the free alkalinity. This free alkalinity plays a disputed role in the washing process, especially in regard to its germicidal effect. From this standpoint, the constancy or change in pH of the solution from concentrated to very dilute form is a direct criterion of the extent to which it would be advisable to dilute the washing solution without seriously affecting its detergent value. The ability to resist change in pH as the dilution progresses is a measure of the buffer action, or the extent to which the solution is buffered. A solution in which the pH is not changed or but very slightly changed after a series of dilutions is highly buffered. One in which the pH value is lowered considerably upon dilution is not highly buffered. It seems correct to state that all cleaner solutions should be highly buffered.

A marked similarity in the pH and buffer action of cleaners of the same class was noted. The effect of hard or tap water on the pH as compared with distilled water, was a feature brought out by the tests. It was rather interesting to observe the difference in the pH and buffer properties between cleaners of the different classes.

The results of these tests are given in table III. The table is self explanatory. It will be observed that cleaners, numbers 1, 2, 3, and 4 were very similar and constant in their pH and buffer action. In distilled water cleaner number 1 lost .6 pH by increasing the dilution

ten times. This was the largest variation in tap water. Cleaner number 4 exhibited a pH of 9.2 at 1000 dilution which was the lowest.

Number 5, the soda ash cleaner, remained quite stable and constant in all dilutions. Numbers 6, 7, and 8, the special alkalies, contained the greatest amount of free alkalinity of all the samples on test. These three cleaners would no doubt contain the greatest germicidal efficiency. Number 8 had the lowest initial pH. There was little difference between the three when subjected to the other dilutions, or between distilled and tap water.

The tri-sodium phosphate cleaners as a group exhibited a wider variation in buffer action than the other groups. The highest initial pH with distilled water was 11.8 in the case of numbers 12, 13, and 15. The lowest was 10.8 in the case of No. 14. No. 14 also had the lowest pH of 10.2 at the high dilution. With tap water a greater variation occurred. The difference in pH between distilled and tap water up to the 300 dilution was nil in every case except with number 11, in which case the variation was only .2 pH. At higher dilutions the difference became apparent, being as much as 1 pH in some cases at a dilution of 300. The lowest pH reached at 1000 dilution with tap water was 9.0 with cleaners number 12 and 14.

The colloidal cleaner was very stable in buffer action in distilled water. With tap water at high dilutions, the buffer action was not so effective. The results of the tests on this cleaner paralleled those with the soda ash cleaner.

The cleaners may be classified in the order of the amount of free alkalinity as the solutions are ordinarily used, and the relative stability of buffer action under dilution by the following. Those showing least alkalinity and least stability of buffer action are listed last.

	Free Alkalinity	Stability of Buffer Action
Class	Special Alkalies	Modified Soda
Class	Tri-Sodium Phosphate	Soda Ash and Colloidal
Class	Soda Ash and Colloidal	Special Alkalies
Class	Modified Soda	Tri-Sodium Phosphate

Relative Emulsifying Powers as Measured by Drop Number and Size

This phase of the experiment is based upon theoretical phenomena and not on practical tests. Investigators are agreed that the emulsifying power of a cleaning solution is dependent on the lowering of the interfacial tension between the grease or oil and the solution. A measure of this lowering of interfacial tension is a measure of the effectiveness of the dissolved substance or substances used as cleaning agents.

In this work the method used for measuring the relative emulsifying powers of cleaners was the number and size of drops of the same volume of each cleaner solution in benzene or butterfat, compared with the number of drops of distilled water.

Table III.

Showing pH of Cleaner Solutions under Different Dilutions with Distilled and Tap Water.

Dilutions	No. 1 Distilled	No. 1 Tap	No. 2 Distilled	No. 2 Tap	No. 3 Distilled	No. 3 Tap	No. 4 Distilled	No. 4 Tap
1 - 100	10.0	9.8	10.0	10.0	10.0	10.0	10.0	9.6
1 - 200	10.0	9.8	10.0	10.0	10.0	10.0	10.0	9.6
1 - 300	10.0	9.8	10.0	10.0	10.0	10.0	10.0	9.6
1 - 400	10.0	9.6	9.8	9.8	10.0	10.0	10.0	9.6
1 - 500	10.0	9.6	9.8	9.8	9.8	9.8	10.0	9.4
1 - 600	9.8	9.6	9.6	9.6	9.8	9.8	10.0	9.4
1 - 800	9.6	9.4	9.6	9.6	9.8	9.8	9.8	9.4
1 - 1 000	9.4	9.4	9.6	9.6	9.8	9.8	9.8	9.2
	No. 5		No. 6		No. 7		No. 8	
1 - 100	10.6	10.6	12.6	12.6	12.6	12.8	12.4	12.4
1 - 200	10.6	10.4	12.3	12.3	12.3	12.3	12.3	12.3
1 - 300	10.6	10.2	12.1	12.2	12.2	12.2	12.2	12.2
1 - 400	10.6	10.2	12.1	12.1	12.1	12.1	12.1	12.1
1 - 500	10.6	10.2	12.0	12.0	12.0	12.0	12.0	12.0
1 - 600	10.6	10.0	11.8	11.8	11.9	12.0	11.8	11.8
1 - 800	10.4	10.0	11.8	11.7	11.8	11.8	11.8	11.6
1 - 1000	10.0	10.0	11.7	11.4	11.6	11.6	11.7	11.4

Table III. (Continued)

Showing pH of Cleaner Solutions under Different Dilutions with Distilled and Tap Water.

Dilutions	No. 9 Distilled	No. 9 Tap	No. 10 Distilled	No. 10 Tap	No. 11 Distilled	No. 11 Tap	No. 12 Distilled	No. 12 Tap
1 - 100	11.6	11.6	11.6	11.4	11.6	11.4	11.8	11.8
1 - 200	11.6	11.6	11.6	10.8	11.5	11.4	11.8	10.7
1 - 300	11.6	11.6	11.4	10.4	11.4	10.4	11.4	10.6
1 - 400	10.6	10.0	11.4	10.2	11.4	10.4	11.4	10.4
1 - 500	10.6	10.0	10.8	10.0	11.0	10.4	10.8	10.0
1 - 600	10.6	10.0	10.6	10.0	10.8	10.0	10.8	10.0
1 - 800	10.6	10.0	10.6	9.8	10.6	10.0	10.8	9.4
1 - 1000	10.6	10.0	10.6	9.8	10.6	9.8	10.5	9.0
	No. 13		No. 14		No. 15		No. 16	
1 - 100	11.8	11.8	10.8	10.8	11.8	11.8	10.6	10.6
1 - 200	11.6	11.6	10.6	10.6	11.4	11.4	10.6	10.4
1 - 300	11.4	11.2	10.6	10.6	10.8	10.7	10.6	10.2
1 - 400	11.4	10.2	10.6	10.0	10.8	10.6	10.6	10.1
1 - 500	11.4	10.0	10.6	9.6	10.8	10.0	10.6	10.0
1 - 600	11.0	10.0	10.6	9.6	10.8	10.0	10.6	10.0
1 - 800	10.6	10.0	10.6	9.4	10.6	9.8	10.6	10.0
1 - 1000	10.6	10.0	10.2	9.0	10.6	9.6	10.4	9.8

I = 1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
I = 2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
I = 3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
I = 4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
I = 5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
I = 6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
I = 7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
I = 8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

I = 1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
I = 2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
I = 3	0.0	0.0	0.0	8.0	0.0	0.0	0.0	0.0
I = 4	0.0	0.0	0.0	8.0	0.0	0.0	0.0	0.0
I = 5	0.0	0.0	0.0	8.0	0.0	0.0	0.0	0.0
I = 6	0.0	0.0	0.0	8.0	0.0	0.0	0.0	0.0
I = 7	0.0	0.0	8.0	8.0	0.0	0.0	0.0	0.0
I = 8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Many investigators have used benzene as the dropping medium in testing soap solutions. Pure butterfat was used so that conditions might be made as near that found in dairy plants as possible. It was found that there was no correlation between the effect of benzene and of butterfat on the number of the drops. The fat in milk possesses great adhesive properties to metal equipment. Dirt particles also tend to stick to butterfat very readily. Thus it may be seen that the butterfat on the surface of the metal serves as a binder to hold the dirt particle to the metal, as well as being a source of contamination itself. Therefore, it is desirable to employ a cleaner which will emulsify and remove the butterfat readily, which in turn will carry the adhering dirt particles away in the wash water. Since butterfat is the predominating oily substance found on dirty dairy utensils, it would appear that those cleaners having the highest emulsifying powers toward butterfat would be most desirable for use in cleaning dairy equipment. Since benzene is entirely absent from dairy utensils and butterfat is predominant, it appears correct to state that emulsifying tests on butterfat are more reliable than on benzene.

The results of the tests are given in table IV. With benzene the tri-sodium phosphate cleaners as a class had the smallest drops. The special alkalies were next in order, and the modified sodas last. Cleaner number 10 gave the highest emulsifying powers in benzene and cleaners number 3, 4, and 5 were the poorest emulsifiers. With butterfat the special alkalies gave considerably more drops than the others. The soda ash cleaner and the colloidal cleaner were next, in the order named. The mod-

Table IV.

Showing Drop Numbers of Cleaner Solutions and Relative Drop Sizes

As Compared with Drops of Distilled Water.

Number of Cleaner	Benzene 70° F. Concentration of Cleaner Solution .625%		Butterfat 110° F. Concentration of Cleaner Solution .02%	
	Drop Number	Drop Size	Drop Number	Drop Size
1	17.5	.886	17.0	.941
2	17.5	.886	17.2	.932
3	17.0	.912	18.5	.865
4	17.0	.912	17.8	.897
5	17.0	.912	29.0	.552
6	18.0	.861	42.7	.375
7	18.0	.861	42.0	.381
8	18.3	.846	45.0	.355
9	18.8	.823	16.0	1.000
10	19.5	.795	15.8	1.011
11	17.5	.895	17.7	.905
12	18.0	.861	16.2	.989
13	17.5	.886	16.0	1.000
14	19.3	.802	15.8	1.011
15	18.0	.861	17.0	.941
16	19.0	.816	18.5	.865
Distilled Water	15.5	1.000	16.0	1.000

1.000	16.0	1.000	
.868	16.6	.815	
.941	17.0	.185	
1.011	16.8	.905	
1.000	16.0	.886	
.989	15.5	.861	
.908	15.7	.885	
1.011	16.8	.985	

ified sodas as a class were higher in emulsifying power toward butterfat than the tri-sodium phosphate cleaners. Cleaner number 8 was the best emulsifier as measured by this test and cleaner number 10 was poorest.

Chart I is a graphic representation of the relative drop sizes of the different solutions as compared with distilled water in benzene and butterfat.

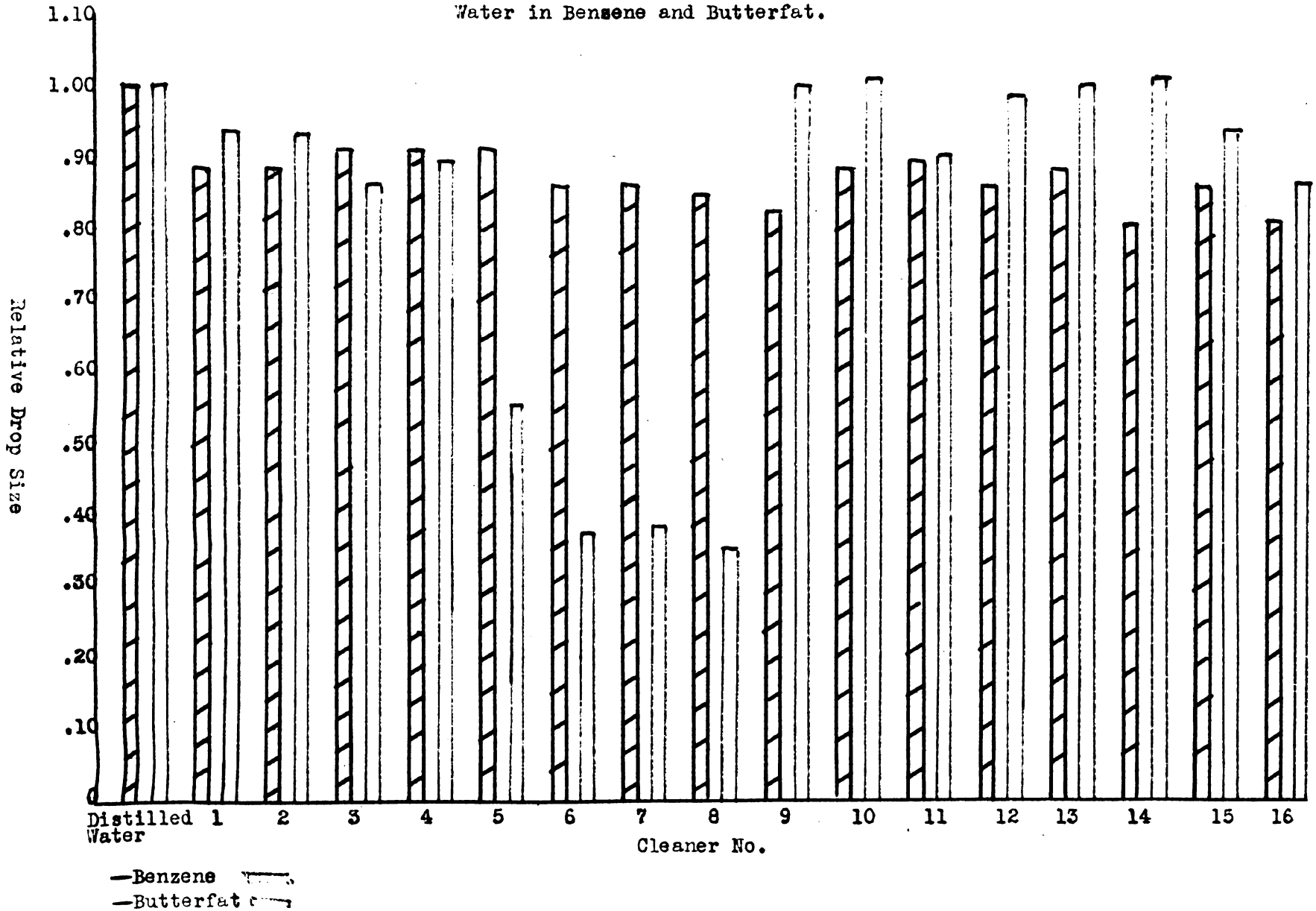
Relative Water Softening Powers

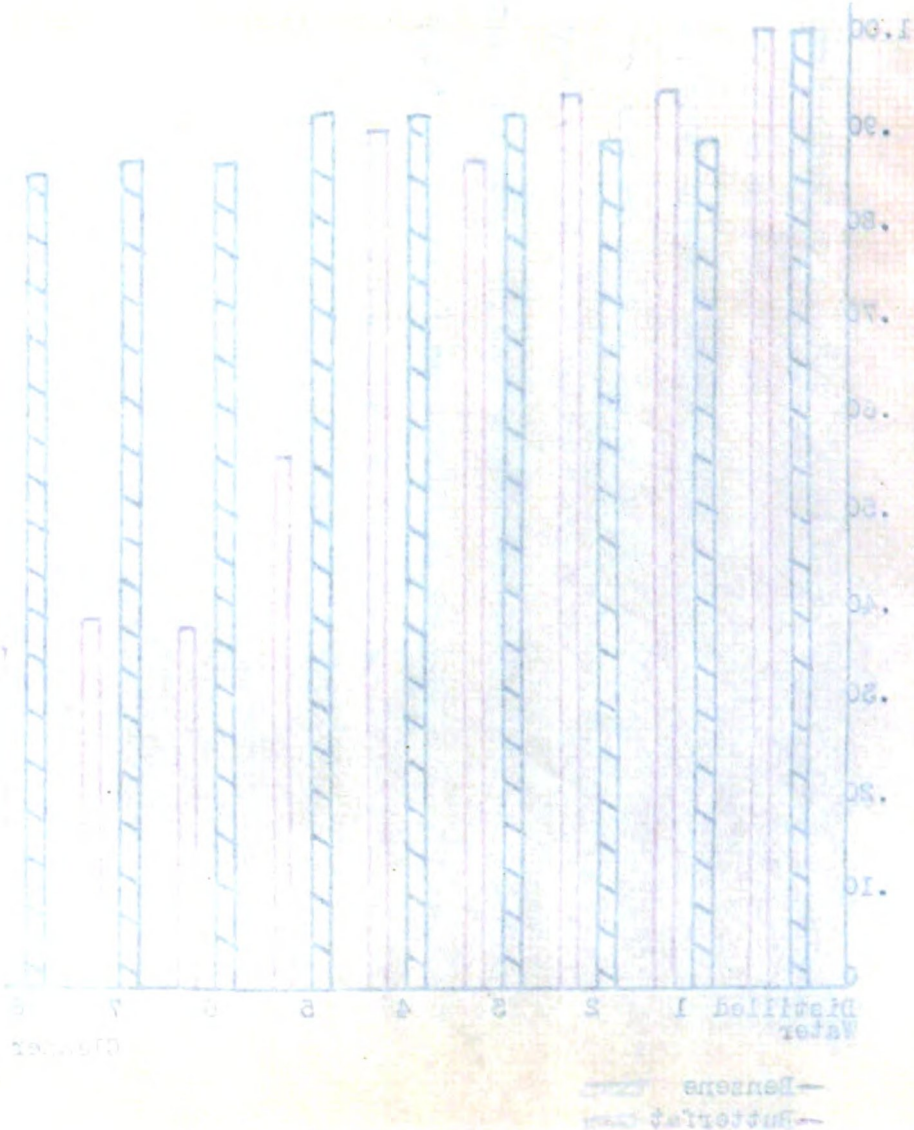
The cleaners under study differed in their ability to remove the soap destroying hardness of water. Table V shows the amount of hard water, distilled water, and cleaner solution used in each case to make up to a volume of 175 c.c.; the amount of CaO present in each case to be removed; the average number of c.c. of soap solution used in each case to produce a permanent foam; and the amount of CaO removed by each cleaner solution.

Table VI shows the amount of CaO removed by one c.c. of each cleaner solution, the amount of CaO removed by one gram of cleaner, and the number of grams and pounds of each cleaner necessary to remove the hardness in 100 gallons of tap water having a hardness of 240 p.p.m.

The soda ash cleaner proved to be the most efficient water softener. The colloidal cleaner, as a class, was next. The modified soda cleaners were quite consistent in their ability to remove hardness and ranked third in this respect, as a class. The members of the special alkali class were

Chart I. Showing Relative Drop Sizes of Cleaner Solutions as Compared with Distilled Water in Benzene and Butterfat.




1.00
.90
.80
.70
.60
.50
.40
.30
.20
.10
0
Relative Mean Size
Distilled Water
1
2
3
4
5
6
7
8
Chamber
Benzene
Butterfly

very uniform in this ability and were almost as efficient as the modified sodas. The tri-sodium phosphate cleaners varied quite markedly from each other in their ability to remove hardness. Number 14 was most efficient of the tri-sodium phosphates and was second among all the cleaners in its water softening ability. Number 10 was least efficient. The tri-sodium phosphate cleaners as a class ranked poorest in removing soap destroying hardness.

Chart II is a graphic representation of the number of pounds of each cleaner necessary to remove the hardness in 100 gallons of tap water.

The Effect of Abrasives on Metals

The abrasive substance or volcadotte does not have the same scratching effect on all metals. Copper, aluminum, tinned copper and tinned steel are very readily scratched with it. With just a few rotations of the material on these metals, scratches could be seen without the aid of the microscope. Nickel was not so readily scratched, but small scratches could be readily detected without magnification. All observations were verified under the microscope. Stainless steel and Allegheny metal were negative to the effect of the abrasive. With continued rubbing and observation under the microscope, no scratching effect whatever could be detected. This led to the belief that these two metals are harder in character than the abrasive substance contained in the volcadotte.

Table V. Showing Preliminary Results of Water Softening Tests.

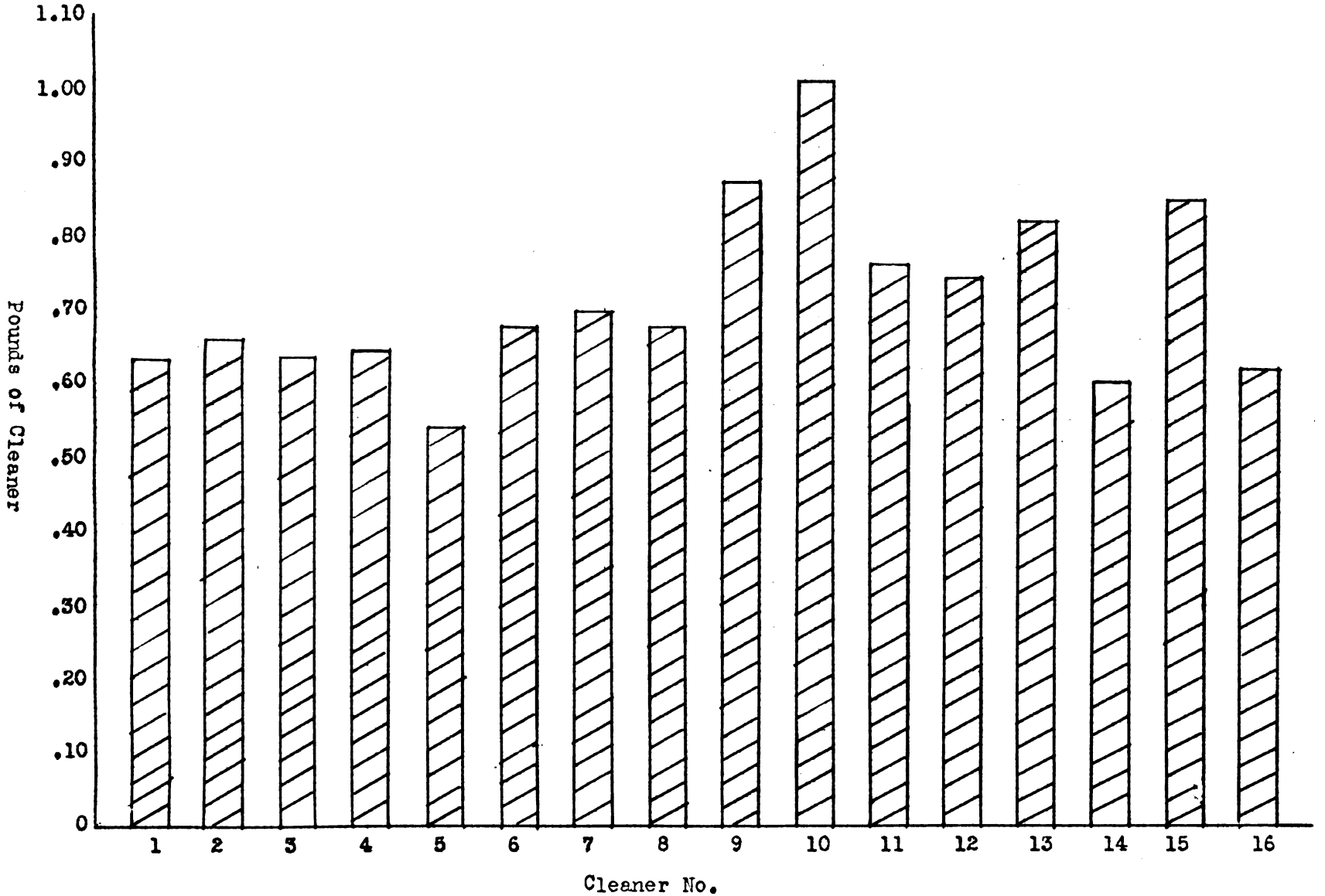
Cleaner No.	C.C.H.W. Used	C.C. Distilled H_2O Used	Total Grs. CaO	C.C. Cleaner Solution Used .625%	Ave. C.C. Soap Solution used in Titration	Ave. Grs. CaO Removed
1	125	15	.09581	35	9.675	.07192
2	125	15	.09581	35	10.800	.06905
3	125	15	.09581	35	9.725	.07175
4	125	15	.09581	35	9.95	.07096
5	125	15	.09581	35	4.625	.08438
6	125	10	.09568	40	7.625	.07683
7	125	10	.09568	40	8.425	.07497
8	125	10	.09568	40	7.425	.07732
9	125		.09541	50	8.375	.07472
10	100	25	.07700	50	6.6	.06013
11	125		.09541	50	3.1	.08775
12	125		.09541	50	4.175	.08552
13	125	10	.09568	40	6.575	.07930
14	125	10	.09568	40	3.75	.08641
15	125		.09541	50	7.55	.07681
16	125	10	.09581	40	4.4	.08473

1	[illegible]	1	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	1	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	1	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]		[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
11	125		.09641	50	3.1	.09775
12	125		.09641	50	4.175	.09852
13	125	10	.09808	40	5.375	.09920
14	125	10	.09808	40	3.75	.09841
15	125		.09641	50	7.55	.09821
16	125	10	.09881	40	4.4	.09975

Table VI. Showing Results of Water Softening Tests.

Number of Cleaner	Grs. CaO removed by 1 c.c. solution	Grs. CaO removed by 1 gr. of cleaner	Grs. Cleaner to remove CaO in 100 gals. tap H_2O	Lbs. Cleaner to remove CaO in 100 gals. tap H_2O	Rank in Water Softening powers
1	.002055	.3287	287.49	.6337	4
2	.001973	.3156	299.42	.6600	7
3	.002050	.3280	288.10	.6350	5
4	.002027	.3243	291.39	.6432	6
5	.002411	.3857	245.00	.5401	1
6	.001921	.3073	307.51	.6780	9
7	.001874	.2998	315.21	.6950	10
8	.001933	.3092	305.62	.6740	8
9	.001494	.2391	395.20	.8712	15
10	.001203	.1924	491.13	1.0827	16
11	.001710	.2737	345.31	.7612	12
12	.001755	.2808	336.53	.7419	11
13	.001587	.2539	372.19	.8205	13
14	.002160	.3456	273.43	.6027	2
15	.001536	.2458	384.45	.8475	14
16	.002118	.3389	278.84	.6147	3

Chart II. Showing Pounds of Cleaner Necessary to Remove Hardness in 100 Gallons of Tap Water.



Cleaner No.
T
S
2
V
P
C
A
B
D
0
.10
.20
.30
.40
.50
.60
.70
.80
.90
1.00
Sounds of Cleaner

Most detergents are made up largely of this abrasive substance. As a result of this investigation it seems proper to state that detergents should not be used in cleaning equipment containing the metals aluminum, copper, tinned copper, tinned steel, or nickel.

Detergents are quite effective in the removal of some types of dirt. In cases where the dirt is baked on to the metal it would be advisable to use a detergent on stainless steel and Allegheny metal since the detergent has no effect on these metals. Manufacturers (21) state that Allegheny metal may be scoured without destroying the surface, and that the more it is polished the more resistant it becomes.

The metals are listed in the following table showing the scratching effect of the abrasive on the metal.

Aluminum	ssss
Copper	ssss
Tinned Copper	sss
Tinned Steel	sss
Nickel	ss
Stainless Steel	N.E.
Allegheny Metal	N.E.

Code: N.E., no effect; s, slightly scratched; ss, moderately scratched; sss, severely scratched; ssss, very severely scratched.

Label	2a
Stainless Steel	N.E.
Aluminium Metal	N.E.

[illegible] ; [illegible] ; severely scratched; case, very severely scratched.
[illegible] ; [illegible] ; no effect; a, slightly scratched; 2a, moderately

Results of the Effect of Cleaner Solutions on Metals.

Discussion of results shown in tables VII, VIII, IX, and X.

In table VII are shown the individual weight losses of all metals arranged according to the number of the washing solution used. Table VII gives the visible corrosion, tarnishing and pitting effect on each metal by each cleaner. Table IX shows the change in pH of each solution when exposed to the different metals for 14 days. Table X shows the change in appearance of the solution after the metals had been partially immersed in the solution for 14 days.

The weight losses were greatest in special alkali solutions. The next greatest losses occurred in tri-sodium phosphate and soda ash cleaner solutions respectively. The colloidal cleaner ranked next, while the modified sodas caused the smallest loss in weight. Of the metals, tinned steel suffered the most severe loss of weight in all solutions except in the case of modified sodas. Aluminum was next in order of weight loss. Tinned copper lost heavily in the special alkalies, and in numbers 9, 14 and 15 of the tri-sodium phosphate cleaners. Copper gained in weight in contact with the soda ash and special alkali cleaners, due to the oxidation which took place. It suffered the greatest loss in weight in the colloidal cleaner and modified sodas respectively. Tri-sodium phosphate caused the least loss of weight on copper. Nickel was comparatively resistant to all the washing solutions, the greatest loss of weight for nickel occurring in cleaners numbers 4, 7, 12, and 15. Stainless steel and Allegheny metal were both very resistant to the attack of each wash-

ing solution used.

The corroding effect was closely correlated with the loss in weight, as may be observed from a study of tables VII and VIII. The special alkalies caused severe corroding on aluminum, tinned steel, and tinned copper, the extent of corrosion being in the order named. The tri-sodium phosphate solutions were next in severity of corroding effect. Tinned steel suffered the most corrosion in contact with tri-sodium phosphate, and aluminum was second. Tinned copper underwent considerable corrosion in contact with the three cleaners numbers 9, 14, and 15. Copper and nickel suffered slight corrosion, and stainless steel and Allegheny metal were entirely resistant to the action of tri-sodium phosphate. The colloidal, and soda ash cleaners and the modified sodas were very similar to each other in their corroding effect. Aluminum suffered most in these cleaners and tinned steel was next. Copper, nickel, and tinned copper corroded slightly in most cases. The three cleaners numbers 1, 3, and 4 did not produce any corrosion on tinned copper. Stainless steel and Allegheny metal were entirely resistant to all three cleaners.

The tarnishing effects both above and below the air-liquid line are recorded in table VIII. The special alkalies produced the most tarnishing effect. Copper suffered both above and below the air-liquid line. Below the line copper turned black, which was due no doubt to oxidation. Tinned steel tarnished considerably at and above the line. Aluminum, copper, and tinned copper showed slight tarnishing by the special alkalies. The metals, nickel, stainless steel, and Allegheny

metal were completely resistant to tarnishing by any of the cleaners. Tri-sodium phosphate solutions caused more tarnishing on tinned steel than the soda ash, modified sodas, or colloidal cleaners. Exclusive of the special alkalies the other cleaners caused about the same effect on aluminum, copper, and tinned copper.

The special alkalies also caused the greatest degree of pitting, Aluminum pitted most severely and tinned copper next. Tinned steel pitted slightly. The modified sodas caused slight pitting on aluminum, and the three tri-sodium phosphate cleaners numbers 9, 14, and 15 pitted tinned copper slightly.

Table IX shows the change in pH of each solution caused by the metals. It may be noted that the tri-sodium phosphate cleaner solutions were lowered most in pH. With one exception there was a lowering of pH in every case. This was greatest in the case of number 9, in which the pH was lowered 2.4, when the cleaner solution stood in contact with tinned steel. The special alkalies were next and the colloidal cleaner third in this respect. The modified soda solutions exhibited the most resistance to the lowering of pH. In the case of copper and tinned copper with modified sodas, a raise in pH was noted. No satisfactory explanation could be found for this except that perhaps the dissolved copper in the sodium carbonate and sodium bi-carbonate solutions acted upon the indicator in such a way as to make the solution appear red. If the pH had lowered, the color of the solution would have been purple.

[illegible] special alkalies were used and the colloidal cleaner [illegible] product. The modified soda solutions exhibited the most [illegible] lowering of pH. In the case of copper and tinned copper [illegible] soda, a raise in pH was noted. No satisfactory explanation [illegible] found for this except that perhaps the dissolved copper [illegible] carbonate and sodium bi-carbonate solutions acted upon [illegible] such a way as to make the solution appear red. If the [illegible] the color of the solution would have been purple.

Table X shows the change in appearance of the cleaner solutions. No change in appearance of any of the solutions after having been in contact with stainless steel and Allegheny metal could be detected. All solutions except number 10 changed in appearance with tinned steel. Aluminum caused the next most visible change. A heavy white precipitate appeared in special alkalies in contact with aluminum. Copper caused a green appearance in the modified sodas, soda ash, and colloidal solutions. Tinned copper caused a light green color to appear in the modified sodas.

A study of the four tables reveals the fact that there is a rather close correlation between loss in weight, corroding, and pitting effect, lowering of pH and change in appearance of the solution during the test. Of the metals tinned steel suffered the most and aluminum was almost as badly affected.

Cleaner number 10, containing tri-sodium phosphate and sodium hypochlorite, caused the least effect of all the cleaners on the metals studied. Cleaner number 7 exhibited the most destructive effect, altho it was closely followed by the other two special alkalies, number 6 and 8.

Photographs of the effect of each solution on each metal are shown in the appendix. Plate I is a group picture of all the metals showing the effect of each cleaner solution. The plates, number II to and including number XIX, are actual size photographs of the metals showing the effect of each cleaner solution on each metal. The immersed end of the metal is the right half, or the end opposite the number and code on the metal.

Table VII.

Showing Loss in Weight of Metal Strips in Cleaner Solutions of .625% Concentration; Partial Immersion for 14 Days at Room Temperature.

Cleaner No.	Aluminum	Copper	Nickel	Tinned Copper	Tinned Steel	Stainless Steel	Allegheny Metal
	mg	mg	mg	mg	mg	mg	mg
1	13.4	2.0	0.4	1.9	4.7	0.1	0.3
2	13.1	3.6	0.6	1.8	2.9	0.3	0.2
3	16.9	2.2	0.4	2.4	4.1	0.1	0.3
4	13.4	3.0	1.3	2.2	2.0	0.1	0.2
5	56.2	4.9*	0.9	1.4	116.1	0.4	0.6
6	216.1	2.2*	0.9	93.4	461.9	0.1	0.5
7	271.0	1.4*	1.2	120.2	445.1	1.4	0.4
8	95.3	3.7*	0.7	73.6	319.8	0.2	0.2
9	69.5	1.0	0.6	78.6	219.3	0.4	0.5
10	63.8	0.6*	0.6	1.0	0.6*	0.5	0.3
11	31.3	0.1	0.1	0.8	210.2	0.1	0.4
12	26.6	0.3	1.6	1.8	121.9	0.4	0.1
13	20.0	0.2	0.6	1.4	122.9	0.2	0.1
14	47.4	2.4	0.7	78.7	199.4	0.1	0.7
15	76.4	1.9	1.0	101.9	315.5	0.1	0.1
16	37.0	3.9	0.5	3.6	0.5	0.5	0.6

* Indicates gain in weight.

1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
2	1.1	[illegible]	1.	[illegible]	[illegible]	[illegible]	[illegible]
3	1.	[illegible]	[illegible]	[illegible]	0.1	[illegible]	[illegible]
4	1.	[illegible]	1.0	[illegible]	[illegible]	[illegible]	[illegible]
5	[illegible]	[illegible]*	[illegible]	1.	11.1	[illegible]	[illegible]
6	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.	[illegible]
7	[illegible]	1.[illegible]*	1.[illegible]	1.[illegible]	[illegible]	1.[illegible]	[illegible]
8	[illegible]	[illegible]*	[illegible]	7.	[illegible]	[illegible]	[illegible]
9	[illegible]	1.[illegible]	[illegible]	7.	[illegible]	[illegible]	[illegible]
10	[illegible]	[illegible]*	[illegible]	1.[illegible]	[illegible]*	[illegible]	[illegible]
11	31.3	0.1	0.1	0.8	210.3	0.1	0.4
12	26.0	0.3	1.6	1.8	121.9	0.4	0.1
13	20.0	0.3	0.6	1.4	122.9	0.3	0.1
14	47.4	2.4	0.7	78.7	199.4	0.1	0.7
15	76.4	1.9	1.0	101.9	318.5	0.1	0.1
16	37.0	3.9	0.8	3.6	0.5	0.8	0.6

* Indicates gain in weight.

Table VIII.

Appearance of Metal Strips after Immersion in 0.625% Cleaner Solutions;

Partial Immersion for 14 Days at Room Temperature.

Cleaner No.	Aluminum	Copper	Nickel	Tinned Copper	Tinned Steel	Stainless Steel	Allegheny Metal
1	t / cccp	N.E. / c	N.E. / c	N.E.	t / cc	N.E.	N.E.
2	t / cccp	t / c	N.E. / c	N.E. / c	t / cc	N.E.	N.E.
3	t / cccp	t / c	N.E. / c	N.E.	t / cc	N.E.	N.E.
4	t / cccpp	N.E. / c	N.E. / c	N.E.	N.E. / c	N.E.	N.E.
5	t / cccpp	t / tttt	N.E. / c	N.E.	tt / ccc	N.E.	N.E.
6	t / ccccppp	t / tttt	N.E. / c	t / cccp	tt / ccccp	N.E.	N.E.
7	t / ccccppp	t / tttt	N.E. / c	t / cccpp	ttt / ccccp	N.E.	N.E.
8	t / ccccppp	N.E. / tttt	N.E. / c	t / cccpp	ttt / ccccp	N. E.	N.E.
9	t / cc	N.E. / c	N.E. / c	t / cccpp	ttt / ccc	N.E.	N.E.
10	t / cc	tt / N.E.	N.E. / c	t / c	tt / c	N.E.	N.E.
11	t / cc	N.E. / c	N.E. / c	N.E.	tt / ccc	N.E.	N.E.
12	t / cc	N.E. / c	N.E. / c	N.E.	tt / cc	N.E.	N.E.
13	t / ccp	t / c	N.E. / c	N.E.	t / ccc	N.E.	N.E.
14	t / cc	N.E. / c	N.E. / c	t / cccp	tt / ccc	N.E.	N.E.
15	t / ccp	N.E. / c	N.E.	t / cccpp	ttt / ccc	N.E.	N.E.
16	t / cccp	N.E. / c	N.E. / c	N.E. / c	N.E. / c	N.E.	N.E.

N. E. No Effect
c slightly corroded; cc corroded; ccc heavily corroded; cccc very heavily corroded.
t slightly tarnished; tt tarnished; ttt heavily tarnished; tttt very heavily tarnished.
p slightly pitted; pp pitted; ppp heavily pitted.

The position of the key letter above or below the dash indicates the condition of the metal above or below the air-liquid line.

13	ccp t	c	c N.E.	N.E. t	ccc tt	N.E.
14	cc t	c N.E.	c	ccc t	ccc ttt	N.E.
15	ccp t	c N.E.	N.E. N.E.	cccp N.E.	ccc N.E.	N.E.
16	cccp	c	c	c	c	N.E.

N. E. No Effect
c slightly corroded; cc corroded; ccc heavily corroded; cccc very heavily corroded.
t slightly tarnished; tt tarnished; ttt heavily tarnished; tttt very heavily tarnished.
p slightly pitted; pp pitted; ppp heavily pitted.

The position of the key letter above or below the dash indicates the condition of the metal above or below the air-liquid line.

Table IX.

Showing Change in pH Produced by Metal Strips Partially Immersed in Cleaner Solutions for 14 Days.

Cleaner No.	Initial pH	Aluminum	Copper	Nickel	Tinned Copper	Tinned Steel	Stainless Steel	Allegheny Metal
1	10.0	-.4	+.5	0	+.5	-.2	0	0
2	10.0	-.4	+.5	0	+.5	-.2	0	0
3	10.0	-.4	+.6	0	+.6	-.2	0	0
4	10.0	-.6	+.5	0	+.5	-.4	0	0
5	10.6	-.6	0	-.5	0	-.6	-.5	-.5
6	12.4	-.5	-.2	-.2	-.6	-1.0	-.2	-.2
7	12.4	-.4	-.2	-.3	-.6	-.8	-.2	-.2
8	12.4	-.5	-.3	-.3	-.6	-1.0	-.2	-.2
9	11.6	-2.2	-1.0	-1.6	-1.8	-2.4	-1.8	-1.6
10	11.4	-1.6	-1.2	-1.6	-1.2	-1.8	-1.8	-1.8
11	11.8	-1.8	-1.3	-1.7	-1.3	-1.8	-1.6	-1.6
12	11.2	-1.8	-.7	-1.2	-.9	-2.0	-1.4	-1.2
13	10.6	-.8	-.0	-.6	-.1	-1.0	-.6	-.6
14	10.8	-1.2	-.3	-.8	-.3	-1.4	-1.0	-.8
15	10.8	-.8	-.4	-1.0	-.8	-1.4	-1.0	-.8
16	10.6	-.8	-.1	-.6	-.1	-.8	-.6	-.6

+ Indicates raise in pH.

- Indicates lowering of pH.

Table X.

Showing Appearance of Cleaner Solutions After 14 Days Contact With Metals.

Cleaner No.	Aluminum	Copper	Nickel	Tinned Copper	Tinned Steel	Stainless Steel	Allegheny Metal
1	--	Green	--	Light Green	Slight White ppt	--	--
2	--	Green	--	Light Green	Very light Green	-	--
3	--	Green	--	Light Green	Slight White ppt	--	--
4	--	Green	--	Light Green	Slight White ppt	--	--
5	--	Light Green	--	--	Greenish Yellow	--	--
6	Heavy White ppt	--	--	--	Slightly Cloudy	--	--
7	Heavy White ppt	--	--	--	Slightly Cloudy	--	--
8	Heavy White ppt.	--	--	--	Slightly Cloudy	--	--
9	Light Blue	--	--	--	Greenish Yellow	--	--
10	--	--	--	--	--	--	--
11	Slightly Cloudy	--	--	--	Light Yellow	--	--
12	--	--	--	--	Light Yellow	--	--
13	--	--	--	--	Light Yellow	--	--
14	--	Very Light Blue	--	Light Blue	Light Yellow	--	--
15	Slightly Cloudy	--	--	--	Yellow	--	--
16	Medium Cloudy	Light Green	Slighly Cloudy	--	Slightly Yellow	--	--

Note: Where no notation is made, no visible change in the color or appearnace of the solution could be detected.

CONCLUSIONS

I. Cleaners may be divided into five classes on the basis of their chemical composition. These classes are, modified sodas, soda ash, special alkalies, tri-sodium phosphate, and colloidal. The cleaners studied in this work were very similar in composition within each class. There was no correlation between the total alkalinity, as measured by titration, and the free alkalinity as measured by pH value.

II. The cleaners were found to vary in total solubility. All cleaners are soluble enough to go into solution readily at the concentration at which they are ordinarily used. There appeared to be a close relation between the rapidity with which the powders went into solution and the total solubility. By classes, the order of solubility was: soda ash most soluble, modified sodas, special alkalies, tri-sodium phosphate, and colloidal least.

III. All the cleaners studied were quite highly buffered. In most cases tap water caused a lower pH than distilled water. The classes may be placed in the order of their free alkalinity as they are used under practical conditions; special alkalies highest, tri-sodium phosphate, soda ash and colloidal, and modified sodas lowest. The stability of buffer action was as follows: modified sodas most stable, soda ash and colloidal, modified sodas, and tri-sodium phosphate least stable.

IV. There was no relationship between the action of the cleaners as emulsifiers in benzene and in butterfat. The results in butterfat are most practical, since butterfat is the oily substance to be removed

from dairy equipment. The special alkalies were found to be the best emulsifiers of butterfat. The soda ash and colloidal cleaners were about the same in this property and the modified sodas were third. The tri-sodium phosphate cleaners were the least efficient as emulsifiers of butterfat. Cleaner number 10 was the poorest emulsifier and cleaner number 8 was the best.

V. Water used for washing in dairies contains varying amounts of hardness. This hardness is due largely to the calcium and magnesium compounds in the water. A portion of the cleaner is used up to remove the calcium and magnesium simultaneously with the cleaning process. The cleaners used were found to vary in the amount of each it took to remove the soap destroying hardness.

By classes, the soda ash cleaner was the most efficient hardness remover. The colloidal cleaner was next and the modified sodas third. The special alkalies ranked fourth in this respect and the tri-sodium phosphate cleaners last. Cleaner number 5 was the best water softener and cleaner number 10 was the poorest.

VI. The cleaning agents commonly called "Detergents" are made up largely of an abrasive substance taken from volcanic ash. It was found that this abrasive substance will scratch the metals, aluminum, and copper very severely; tinned copper and tinned steel severely; and nickel moderately. The abrasive will not scratch stainless steel or Allegheny metal.

phosphate cleaners last. Cleaner number 3 was the best water softener and cleaner number 10 was the poorest.

VI. The cleaning agents commonly called "detergents" are made up largely of an abrasive substance taken from volcanic ash. It was found that this abrasive substance will scratch the metals, aluminum, and copper very severely; tinned copper and tinned steel severely; and nickel moderately. The abrasive will not scratch stainless steel or Alclad metal.

VII. In the tests for effect on metals when partially immersed in the cleaner solutions for 14 days, it was found that the special alkalies caused the greatest loss in weight, the greatest corrosive effect, the most tarnishing and the most pitting. Tri-sodium phosphate solutions caused the next greatest loss in weight and corrosive effect. Soda ash was third in weight loss and corrosion. The colloidal cleaner and the modified sodas exhibited the least destructive effect on the metals.

Tinned steel suffered the greatest loss in weight and the most corrosion. Aluminum was next in this respect and suffered the most pitting. Tinned copper was third and copper fourth. Copper tarnished the most of all the metals. In the special alkalies the exposed surface of copper turned black. Nickel suffered slight loss of weight and corrosion in all solutions. Stainless steel and Allegheny metal were completely resistant to the attack of alkali solutions.

The pH of tri-sodium phosphate solutions was lowered most in contact with metals. The modified sodas exhibited the most resitance to change in pH.

There appeared to be a close correlation between the loss in weight, corrosion, pitting, and change in appearance of the solution.

Cleaner number 10 caused the least destructive effects on the metals studied and cleaner number 7 was most severe on the metals.

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A P P E N D I X

Plate I. Showing the Effect on Metal Strips of Cleaner Solutions after Half Immersion for 14 Days

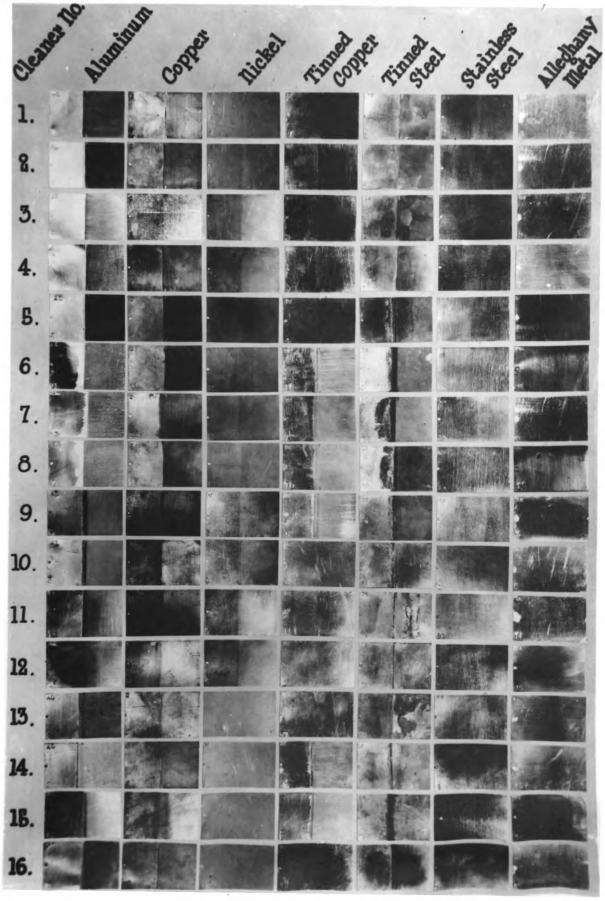

Plate II. Showing the Effect of Modified Soda Cleaner Solutions On Aluminum.

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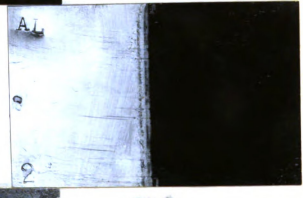

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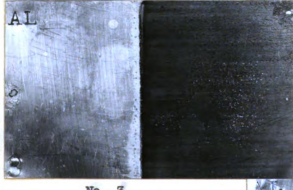

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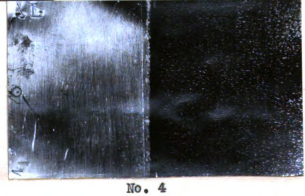

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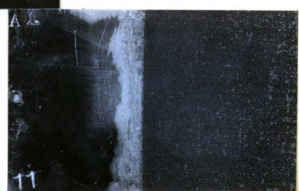
Plate III. Showing the Effect of One Soda Ash Cleaner Solution (No. 5), and Three Special Alkali Cleaner Solutions on Aluminum.

No. 5



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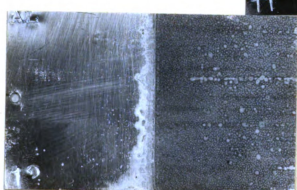

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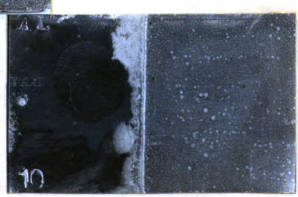

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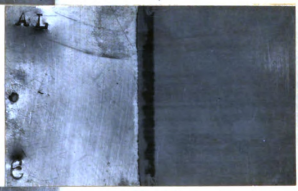
Plate IV. Showing the Effect of Tri-Sodium Phosphate Cleaner Solutions on Aluminum.

No. 9



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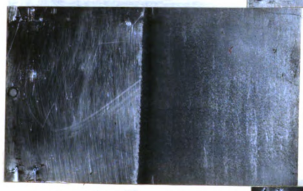

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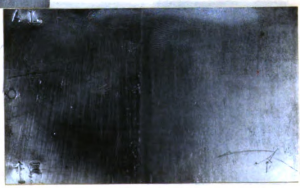

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Plate V. Showing the Effect of Three Tri-Sodium Phosphate Cleaner Solutions, and One Colloidal Cleaner Solution (No. 16) on Aluminum.

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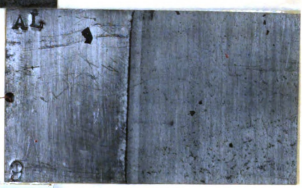

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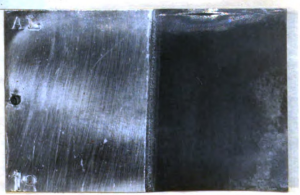

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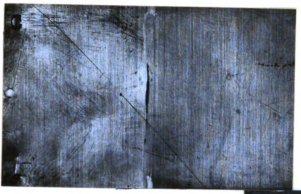
Plate VI. Showing the Effect of Modified Soda Cleaner Solutions on Copper.



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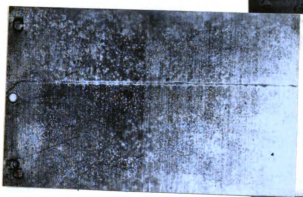

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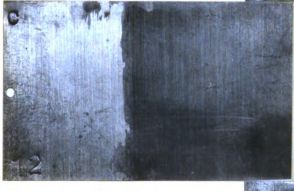
Plate VII. Showing the Effect of One Soda Ash Cleaner Solution (No. 5), and Three Special Alkali Cleaner Solutions on Copper.

No. 5

No. 6



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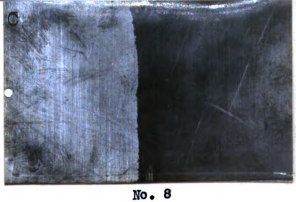

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Plate VIII. Showing the Effect of Tri-Sodium Phosphate Cleaner Solutions on Copper.

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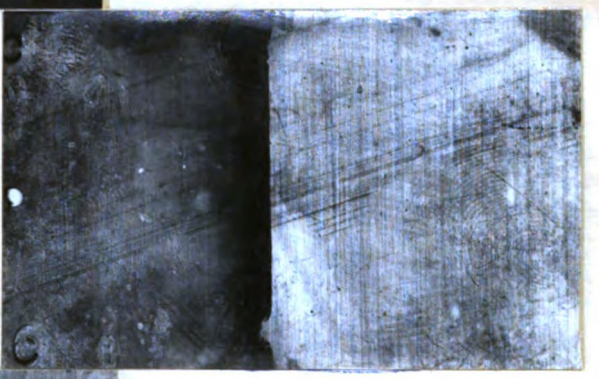

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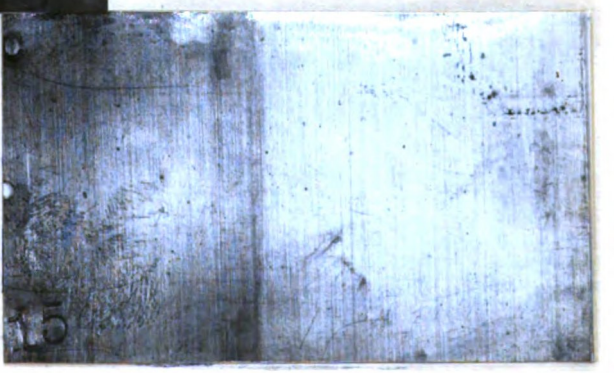

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Plate IX. Showing Effect of Three Tri-Sodium Phosphate Cleaner Solutions, and One Colloidal Cleaner Solution (No. 16) on Copper.

No. 13

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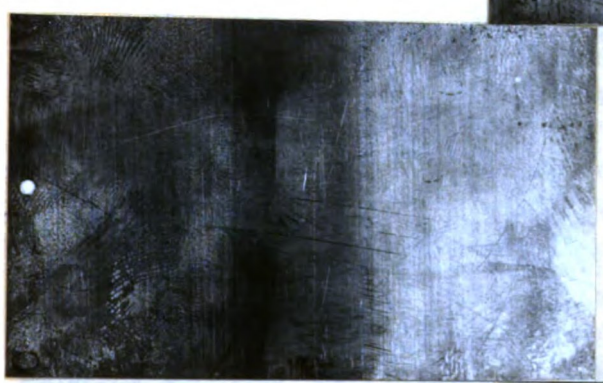

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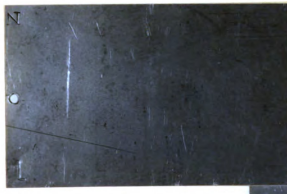
Plate X. Showing the Effect of Modified Soda Cleaner Solutions on Nickel.



No. 1

No. 2

No. 3

No. 4

Plate XI. Showing the Effect of One Soda Ash Cleaner Solution (No. 5), and Three Special Alkali Cleaner Solutions on Nickel.

No. 5

No. 6

No. 7

No. 8

Plate XII. Showing the Effect of Tri-Sodium Phosphate Cleaner Solutions on Nickel.

No. 9

No. 10

No. 11

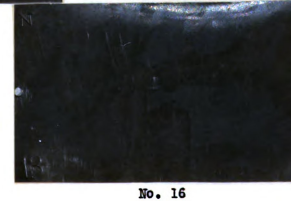
No. 12

Plate XIII. Showing the Effect of Three Tri-Sodium Phosphate Cleaner Solutions, and One Colloidal Cleaner Solution (No. 16) on Nickel.

No. 13

No. 14

No. 15



No. 16

Plate XIV. Showing the Effect of Modified Soda Cleaner Solutions on Tinned Copper.

No. 1

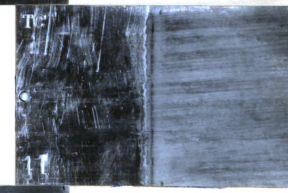
No. 2

No. 3

No. 4

Plate XV. Showing the Effect of One Soda Ash Cleaner Solution, and Three Special Alkali Cleaner Solutions on Tinned Copper.

No. 5



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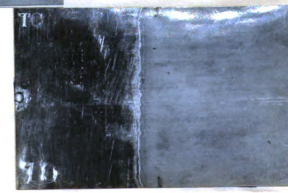

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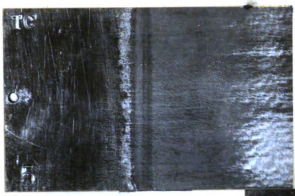
Plate XVI. Showing the Effect of Tri-Sodium Phosphate Cleaner Solutions on Tinned Copper



No. 9

No. 10

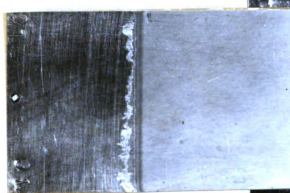
No. 11

No. 12

Plate XVII. Showing the Effect of Three Tri-Sodium Phosphate Cleaner Solutions, and one Colloidal Cleaner Solution (No. 16) on Tinned Copper.

No. 13

No. 14



No. 15

No. 16

Plate XVIII. Showing the Effect of Modified Soda Cleaner Solutions on Tinned Steel

No. 1

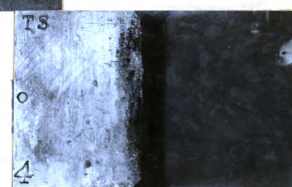
No. 2

No. 3

No. 4

Plate XIX. Showing the Effect of One Soda Ash Cleaner Solution (No. 5), and Three Special Alkali Cleaner Solutions on Tinned Steel.

No. 5



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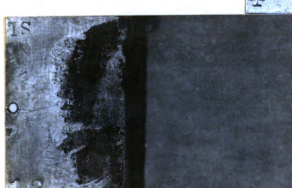

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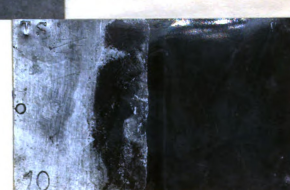
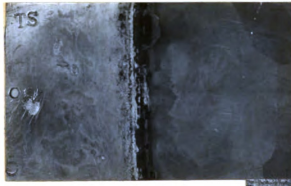


No. 8

Plate XX. Showing the Effect of Tri-Sodium Phosphate Cleaner Solutions on Tinned Steel.



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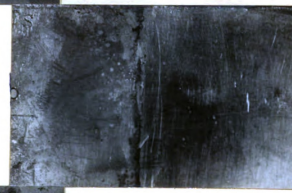

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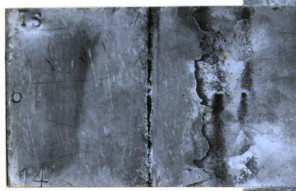

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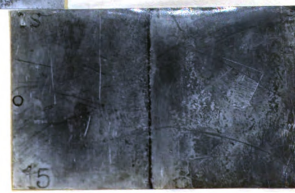
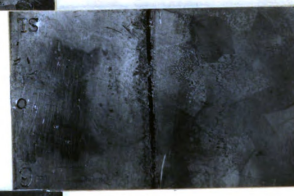


No. 12

Plate XXI. Showing the Effect of Three Tri-Sodium Phosphate Cleaner Solutions and one Colloidal Cleaner Solution (No. 16) on Tinned Steel.

No. 13



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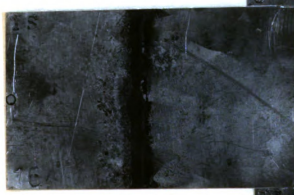


No. 15

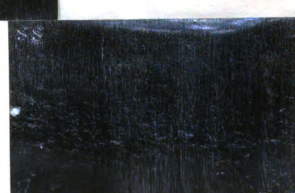
No. 16

Plate XXII. Showing the Effect of Modified Soda Cleaner Solutions on Stainless Steel.

No. 1

No. 2

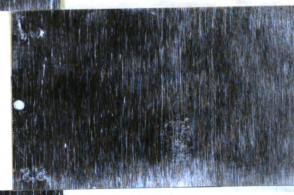
No. 3



No. 4

Plate XXIII. Showing the Effect of One Soda Ash Cleaner Solution (No. 5), and Three Special Alkali Cleaner Solutions on Stainless Steel.

No. 5



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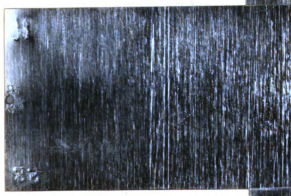


No. 7

No. 8

Plate XXIV. Showing the Effect of Tri-Sodium Phosphate Cleaner Solutions on Stainless Steel.

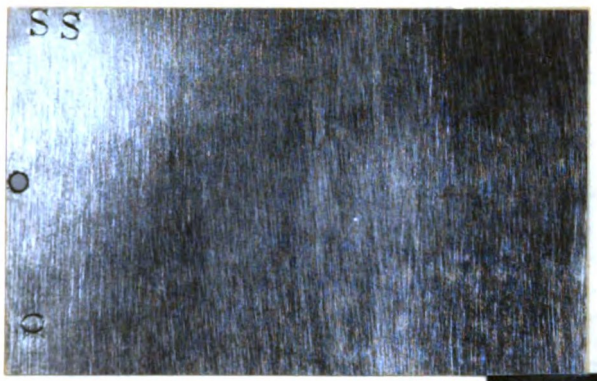
No. 9

No. 10

No. 11

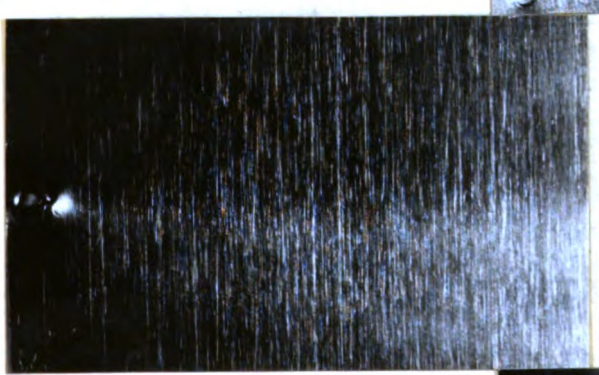
No. 12

Plate XXV. Showing the Effect of Three Tri-Sodium Phosphate Cleaner Solutions and One Colloidal Cleaner Solution (No. 16) on Stainless Steel.



No. 13

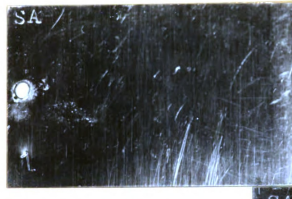
No. 14



No. 15

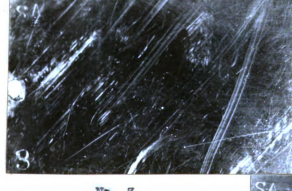
No. 16

Plate XXVI. Showing the Effect of Modified Soda Cleaner Solutions on Allegheny Metal.



No. 1

No. 2



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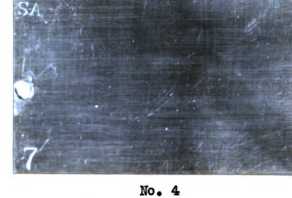
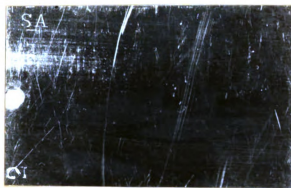


No. 4

Plate XXVII. Showing the Effect of One Soda Ash Cleaner Solution (No. 5), and Three Special Alkali Cleaner Solutions on Allegheny Metal.



No. 5

No. 6

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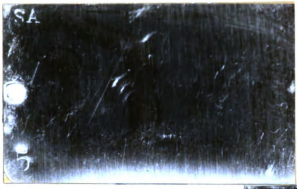
No. 8

Plate XXVIII. Showing the Effect of Tri-Sodium Phosphate Cleaner Solutions on Allegheny Metal.



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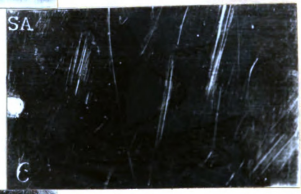

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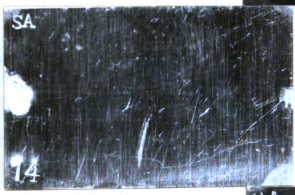

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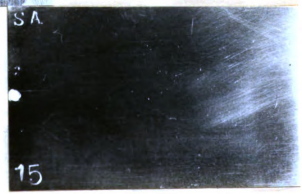


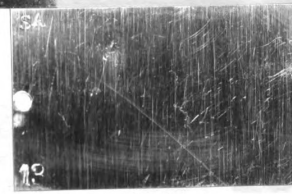
No. 12

Plate XXIX. Showing the Effect of Three Tri-Sodium Phosphate Cleaner Solutions and One Colloidal Cleaner Solution (No. 16) on Allegheny Metal.

No. 13

No. 14

No. 15



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