

the stabilizing effect. Typical compositions would be 35 to 40 per cent soap, 25 to 30 per cent soda ash, 5 to 10 per cent sodium silicate, 25 per cent moisture, and 5 per cent sodium perborate.<sup>90</sup> A soap designed to make cotton flame resistant after washing is made from a paste containing dry powdered soap and a sodium silicate, 180 parts to 24.<sup>91</sup> The liquid portion of the paste is glycerin, 7 parts; potassium carbonate, 8 parts; and sodium tungstate, 4 parts.

Metal polishing compositions often contain soluble silicates.<sup>92</sup> A detergent composition which does not harden and inhibits rusting is suitable for impregnating pads of steel or aluminum wool used for cleansing operations in kitchens. It contains a hydrocarbon sulfonate, a resinate, alkali metasilicate, an amorphous or microcrystalline petroleum wax with a melting point of 77 to 79°C, and water.<sup>93</sup> Various soaps, phosphates, and plasticizers, such as ethylene or diethylene glycol, may be added.

Numerous complex cleansers have been made, the functional relation of the ingredients of which is not comprehended by the present writer.<sup>94</sup> They contain soluble silicates and appear to be based on successful experience of the inventors, but it is to be doubted whether they are the most efficient or economical means of arriving at the particular goals sought.

## Part 2

### Application at Inorganic Surfaces

Differentiation between industrial modification of interfaces at inorganic and organic surfaces is convenient. Inorganic surfaces offer a wide variety of structures and surface reactions which are important in determining treatment. Cleaning nonporous metal, glass, and mineral surfaces is in some cases a problem of deflocculating solid dirt such as abrasion residues and electrolytic oxide smudges held by static charges or weak bonds. More often cleaning depends on preferential wetting to separate a film of soil. Emulsification or saponification of the soil components and deflocculation of the solids permit good rinsing.

The other large fields in which modification of the interface is paramount are dispersion and deflocculation of small particles and the selective separation of such materials, usually minerals. In these fields, cleaning is often of major significance, but in the final steps the surface layers, either adsorbed by chemical action or as fluid, dynamic concentrations of ions near the physical surface, are controlling. Industry long has recognized the

<sup>90</sup> Angus, J. B., *Ind. Chem.*, **15**, 268 (1939).

<sup>91</sup> *Chem. Ind.*, **44**, 293 (1939).

<sup>92</sup> Snell, C. T., *Chem. Ind.*, **66**, 701 (1950).

<sup>93</sup> Goldsmith, H. A., and Humbert, A. L., U. S. Pat. 2,483,135 (1949).

<sup>94</sup> Lara, F., U. S. Pat. 1,335,246 (1920); Milson, J. R., U. S. Pat. 1,430,099 (1922).

advantage of the dual function of silicates in providing controlled alkalinity with colloiddally active anions. With knowledge of these properties, dispersion, flocculation, cleaning, and flotation may be effected in proper sequence.

In the following pages the progression from cleaning of extensive metallic and glass surfaces to the dispersion of finer mineral particles leads to a review of the more complex problems of separating ore constituents.

### METAL CLEANING

Clean metal surfaces are, in an absolute sense, extremely rare, since minute films detectable by electron diffraction or other refined techniques are usually present. From an industrial point of view the proper question is whether the surface is fit for its intended use. Extremely thin, perhaps monomolecular, films of oil can prevent the adherence of electrodeposited metals, although perfect adherence might be obtained in the presence of oxide films of similar dimensions. The test of whether the metal, after the cleaning process, usually followed by a short acid dip and rinse, shows a "water break" is practical because water fails to flow smoothly over a metal surface in the presence of oil or grease. The inorganic oxide films which may be present,<sup>95</sup> though not indicated by the test, are not necessarily detrimental.

The general principles of cleaning metals in aqueous solutions, in which the silicates play a leading role, are closely akin to the problems of detergency in other fields. They differ greatly in particulars, however, because the cleaning step is usually followed by further processing, the nature of which dictates the standards of cleaning performance and the formulations necessary to remove foreign matter and to protect the surfaces of metals which can be injured by contact with strongly alkaline solutions.<sup>96</sup>

A study aimed at giving numerical expression to the cleaning activity of industrial alkalies was made in which steel sheets were coated with various types of oil and placed under controlled conditions in a bath of agitated detergent solutions.<sup>97</sup> The numerical value assigned was the time necessary to clean the metal so that it would not show a water break. The data were found to be reproducible and appear to be a reliable index of cleaning activity. The comparisons in Table 6.3 of the action of solutions of 2 per cent concentration at 95°C are significant.

An ingenious test for comparing metal cleaners uses a spot of burnt transformer oil on a metal strip. The test is not applicable to all such oils. Cleanser solutions to be compared are heated to boiling and the time to cause the disappearance of the spot measured. When sodium metasilicate

<sup>95</sup> Smith, C. W., and Karle, I. I., *Proc. of Am. Electroplaters' Soc.*, **33**, 117 (1946).

<sup>96</sup> Liddiard, P. D., *Chemistry & Industry*, **1948**, 435.

<sup>97</sup> Firgau, W., private communication, Düsseldorf (1933).

is used as the cleaner, boiling starts at the location of the spot and continues there until the spot disappears, after which the formation of steam spreads over the whole specimen. Cosgrove, who developed the test, describes this action as a unique phenomenon which might be called selective cleansing action since, contrary to prior experience, the dirtiest place was cleaned first.<sup>98</sup> The test led to the introduction of sodium metasilicate in the

TABLE 6.3

The time in minutes necessary to clean steel coated with various oils is a useful index of cleaning activity. (Ferguson)

2% Solution of:	Kidney Fat, min.	Machine Oil, min.	Compressor Oil, min.	Rape Oil, min.	Linseed Oil, min.
A. $\text{Na}_2\text{SiO}_3 \cdot 6\text{H}_2\text{O}$	8.2	2.2	15.2	17.7	9.0
B. $\text{Na}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$	9.5	9.6	28.5	26.3	25.0
C. $\text{NaOH}$	120.0	120.0	120.0	18.0	120.0
D. $\text{Na}_2\text{CO}_3$	120.0	91.0	120.0	96.0	120.0
50% A	6.6	3.5	15.0	24.0	42.0
50% B					
70% A	7.8	2.2	12.2	17.0	12.5
30% B					
30% A	14.5	5.5	23.0	24.8	51.0
70% B					
20% A	12.5	32.0	120.0	15.8	35.0
80% C					
20% B	8.0	13.8	120.0	16.0	120.0
80% C					
77% A	4.2	2.0	10.0	14.5	3.2
23% C (Orthosilicate ratio)					
95% A	1.8	8.0	30.0	2.5	4.0
5% Soap (powdered)					
95% A	0.9	0.9	3.1	4.1	1.7
5% Synthetic*					
95% A	0.8	1.0	4.2	3.8	3.7
5% Synthetic†					

\* Sodium salt of the sulfuric acid ester of the alcohols of coconut oil.

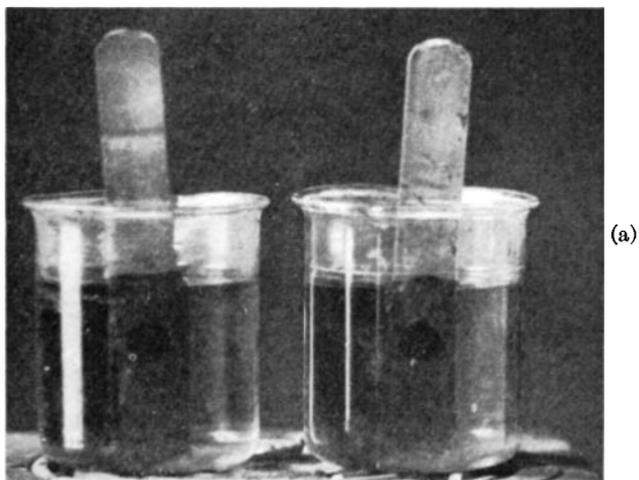
† Mixture of sodium salt of the sulfuric acid ester of lauryl alcohols with tetralin sulfonate.

plant and great simplification of the cleaning steps, all of which, before silicate was used, had been shown to be necessary. An additional use of the test is to determine the remaining useful life of a partly spent cleaning bath (Fig. 6.5).

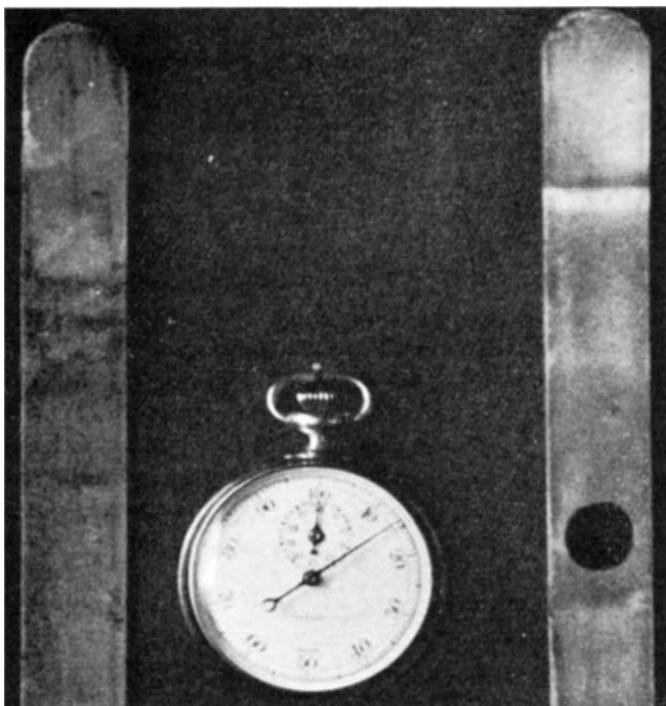
For laboratory studies on the removal of oil from metals by detergent solutions, Morgan made use of the fluorescence of mineral oils in ultra-violet light.<sup>99</sup> Uniformly oiled strips were prepared, subjected to still clean-

<sup>98</sup> Cosgrove, J. M., *Metal Cleaning & Finishing*, **10**, 186 (1938).

<sup>99</sup> Morgan, O. M., *Monthly Rev. Am. Electroplaters' Soc.*, **34**, 430 (1947); Morgan,



(a)



(b)

FIG. 6.5. In a spot test to compare selective cleaning by alkaline solutions, uniform oil spots are deposited on test pieces and the time for removal of the oil is compared. (Cosgrove). (a) Test in process; (b) spot in metasilicate solution disappeared in 15 seconds.

ing solutions of controlled composition for definite times and temperatures, and photographed in ultraviolet light. Very small residues of oil showed white and clean metal, perfectly black. The study was directed to determining the value of alkyl aryl sodium sulfonates with a long alkyl chain, which are compatible with the silicate cleaning solutions. One of these sulfonates was inefficient in combination with sodium hydroxide solutions below 8 per cent of the mixture, but at 3 or 4 per cent of the mixture with  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  and at  $60^\circ\text{C}$  the oil was completely removed in two minutes. While the metasilicate would remove the oil completely at a concentration of 10 per cent, the combination of the organic surface-active compound (5 per cent with 95 per cent metasilicate) enabled an equally satisfactory cleaning job to be done at a concentration of 2 per cent at  $60^\circ\text{C}$  in 10 minutes. Figure 6.6 shows a so-called luminogram representing steel sheets which had been covered with mineral oil and subjected for 5 minutes to still detergent baths. It shows that the sodium metasilicate alone would remove the oil at  $93^\circ\text{C}$ , while a mixture of 95 per cent sodium metasilicate and 5 per cent surface-active agent, at a concentration of 4 per cent, removes all the oil at each temperature tested. A three per cent concentration of the same mixture was effective down to  $60^\circ\text{C}$ , and a 1 per cent solution left visible residues of oil at temperatures below  $93^\circ\text{C}$ . Results at 5 minutes were substantially the same. The cleaning of razor blades was investigated by this method. Two seconds' immersion were sufficient, using 1 per cent of 95 per cent  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  and 5 per cent alkyl aryl sodium sulfonate at  $85^\circ\text{C}$ .<sup>100</sup>

A review of the science and technology of metal cleaning, which compares the technical and economic merits of organic and inorganic cleaners, and includes the consideration of the recovery of oils removed from metal surfaces, is that of Rogner. All the principal processes are discussed, and particular reference is made to the use of alkaline solutions and to the fundamental surface chemistry upon which their usefulness depends.<sup>101</sup> Processes for cleaning metals with alkaline solutions utilize large heated soak tanks, with provision for floating off grease that rises to the surface, and bottom drains to remove solid dirt; electrolytic cleaning tanks so arranged that the work to be cleaned may be made either anode or cathode; and spray washers in which the pieces move continuously through detergent and rinsing sprays and on to a drying section. Various types of con-

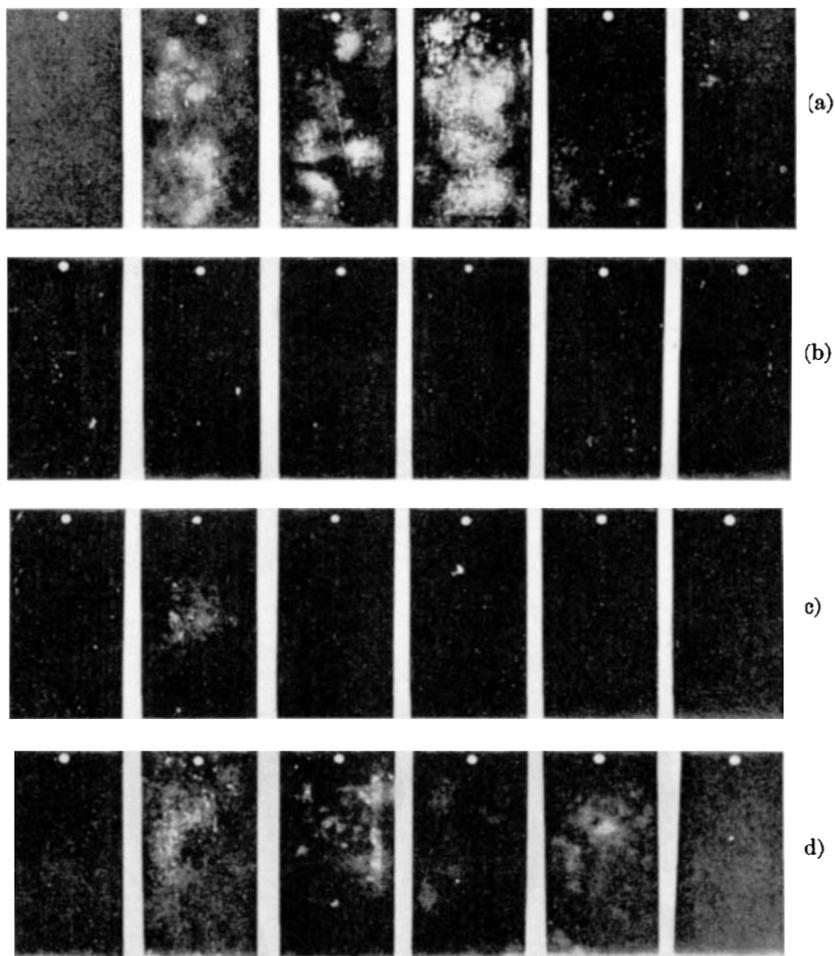
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O. M. and Lankler, J. G., *Ind. Eng. Chem.*, **34**, 1158 (1942), *Ind. Eng. Chem., Anal. Ed.*, **14**, 725 (1942).

<sup>100</sup> Morgan, O. M., Allied Chemical and Dye Corp., National Aniline Division, Report 1942, File No. 9914-8.

<sup>101</sup> Rogner, H., *Korrosion u. Metallschutz*, **17**, (6), 1 (1941); **19** (4), 113, 115 (1943). Bregman, A., *Metal Progress*, **57** (1), 75 (1950); Lesser, M. A., *Soap Sanit. Chem.*, **28**, (4), 50 (1952).

veying equipment, suited to the nature of the work, carry their loads continuously through each of these processes, and drum or other conveyors may be fitted for the cleansing process by the establishment of suitable stations along the route. Specialized cases are the cleaning of continuous



*Courtesy of National Aniline Division  
Allied Chemical & Dye Corporation*

FIG. 6.6. Ultraviolet light shows up faint traces of residual mineral oil on steel test specimens. A 4% solution of a mixture of  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  and synthetic detergent gave efficient cleaning even at  $50^\circ\text{C}$ . (Morgan and Lankler). (a)—100%  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  (4% concn.); (b)—95% A with 5% synthetic detergent (4% concn.); (c)—95% A with 5% synthetic detergent (3% concn.); (d)—95% A with 5% synthetic detergent (1% concn.). From left to right: clean steel;  $49^\circ\text{C}$ ;  $60^\circ\text{C}$ ;  $71^\circ\text{C}$ ;  $82^\circ\text{C}$ ;  $93^\circ\text{C}$ .

strips of metal between the rolling operation and tinning or galvanizing steps, and the establishment of production line techniques, in which processes such as anodizing, phosphate coating, or the electrodeposition of metallic films are linked directly with the cleaning process. As many of these operations are of large scale and any deviation from perfect performance is costly, detergents must be developed to produce clean work in a short time at specified temperatures without adverse effect on the

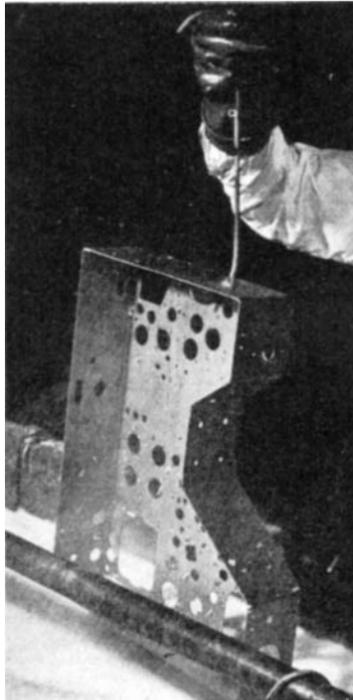


FIG. 6.7. Base plates for television sets are cleaned by hand dipping in an electrolytic cleaning bath of sodium metasilicate solution prior to plating with cadmium.

metal. Most of these operations use silicates (Fig. 6.7). Without elaborating the engineering aspect, it is evident that the processes of this art present requirements very different from those which apply to a textile laundry.

### Soaking

In still cleaning baths for metal, the ideal cleaning process would remove the dirt by floating or sinking without suds, emulsification, or deflocculation of the dirt. In barrel finishing of small metal parts, soap solutions built with silicates are customarily used. They effectively remove solid residues and small quantities of acid which may be carried over from previous

finishing steps in acid solution, they protect against alkaline corrosion of soft metals, and they give clearer and cleaner rinses in cold water, as described by Beaver who illustrates the difference in the luster of glassware washed in pure soap and in built soap.<sup>102</sup>

**Iron Surfaces.** For cleaning iron no question of damaging metal by alkaline solutions applies and high alkalinities are used. If alkalinity were the only requirement, caustic soda would be the cheapest source, but this material by itself may not be satisfactory, either in speed or in quality of work. Cleveland has presented pH values of commercial alkalies in the range of concentrations used in metal cleaning<sup>103</sup> (Fig. 6.8). In practice,

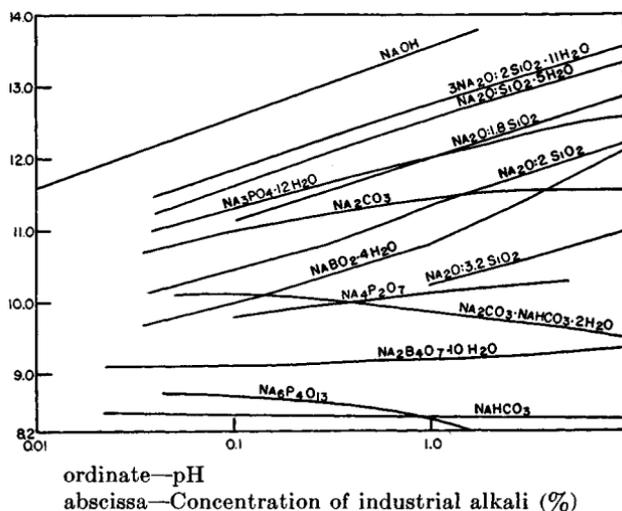


FIG. 6.8. The comparative pH values for the principal industrial alkalies, technical grade, at 20°C, are a useful guide for adequate cleaning coupled with surface protection. (Cleveland)

solutions or readily soluble powders of the silicates are necessary. High alkalinities may be obtained by adding to a caustic soda solution, sodium sesqui- or metasilicate which come quickly to equilibrium. When the colloidal silicate solutions are added to caustic, the colloids come to equilibrium slowly and their valuable properties are available for special purposes.<sup>2</sup> The conductivity of 3 per cent solutions of commercial alkalies (4 ounces per gallon, a concentration frequently used) increases with temperature, another reason for using the solutions hot in cleaning metals which will not be harmed (Fig. 6.9).

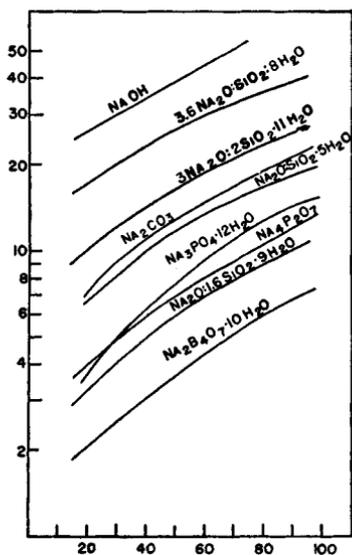
Soaps in electrolytic metal cleaning processes, except as they are produced incidentally by the saponification of fatty materials in the grease to

<sup>102</sup> Beaver, H. L., *Products Finishing*, 4 (6), 40; (8), 34 (1940).

<sup>103</sup> Cleveland, T. K., *Metal Finishing*, 38, 479 (1940).

be removed—for example, in removing buffing compounds, are not as common as in soaking operations.

A large petroleum refinery, washing 2,400 drums per 8-hour shift, sprays them with a solution of sodium metasilicate 5 ounces to the gallon at 82 to 94°C. The cleaning cycle of 3 minutes' duration is entirely automatic, including a 65-second spray of the alkaline solution after stream heating, and followed by hot water rinse. An added reason for using the silicate is that galvanized drums can be processed along with plain iron drums without injury. The metasilicate was adopted after testing other alkalies for speed



ordinate—Conductivity of 3% solution of alkali (amp/sq ft/ft)  
abscissa—Temperature of solution (°C)

FIG. 6.9. Alkaline silicates have a high conductivity in the temperature range used for cleaning. (Cleveland)

and economy. An example of a cleaning job requiring vigorous action is the cleansing of locomotive boilers, which are treated with hot metasilicate solutions to remove grease, oil, and scale residues.

Tank cars, which have been used for the transport of lard by rail, are cleaned with 75 pounds of sodium sesquiosilicate dissolved in 8,000 gallons of water which is boiled in the car. Drum washing to remove oleomargarine, lard, and the like may be done with 2 to 3 ounces per gallon of sodium sesquiosilicate at boiling temperature. Steam-jet machines with metasilicate solutions at from 3 to 9 pounds per 100 U.S. gallons of water, according to the difficulty of the work, leave a clean sanitary surface.

Cleaners for flushing out accumulations of sludge and oil from automobile radiators, thus restoring their efficiency as heat exchangers, are most economically based on sodium metasilicate or a silicate of somewhat

more siliceous ratio, for example,  $\text{Na}_2\text{O}:2\text{SiO}_2$  which comes on the market as a 60°Bé solution. A small addition of sodium or potassium dichromate, which in solution becomes the chromate, adds its inhibiting effect to the protective action inherent in the silicate but is used only where the danger of dermatitis from contact with the chromate in solution may be avoided.<sup>104</sup> If the residue to be removed contains much oil, it is sometimes advantageous to emulsify a solvent for the oil in a silicate solution. A recommended composition is equal parts of sodium metasilicate and kerosene with the addition of 0.5 to 2 per cent by weight of sodium dichromate, which is added to the circulating water in the volume ratio of 1 to 25. The engine is then run for about 30 minutes and the radiator drained, flushed, and refilled. An addition of 0.2 to 0.8 per cent of  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  to the fresh water inhibits the further rusting of the ferrous parts of the cooling system. Small additions of sodium bichromate are also useful here.<sup>105</sup> Similar treatment for the cooling systems of other internal combustion engines is appropriate.

Tall oil, a by-product of the sulfate or kraft process of paper making from resinous wood, yields soaps which are useful in silicate formulation for metal cleaning, as indicated by the following formulae.<sup>106</sup>

*Formula A*

“To remove slushing and shearing compounds and rust preventatives:

Tall oil soap	5%
Sodium orthosilicate	95%

This material acts as a lifter in removing dirt, and is more efficacious than mineral salts or rosin compounds.”

*Formula B*

Tall oil soap	5%
Sodium orthosilicate	50%
Trisodium phosphate	45%

With minor changes, meta- or sesquisilicate may be substituted for orthosilicate in the foregoing formulations.

*Formula D*

Automotive engines	
Tall oil	15%
Sodium metasilicate	80%
Soda ash	5%

used at 4 to 6 ounces per gallon and 80 to 100°C. Rinse.

<sup>104</sup> Snell, C. T., *Chem. Ind.*, **63**, 802 (1948).

<sup>105</sup> Hendrey, W. B., U. S. Pat. 2,104,385 (1938).

<sup>106</sup> Young, C. B. F., Eick, G. H., and Warmack, W., *Soap Sanit. Chemicals*, **25** (12), 40 (1949).

A useful approach to the metal cleaning problem is the devising of lubricants which can be readily removed by silicate solutions. A mineral oil for cold rolling of steel has an addition of 0.2 to 0.5 per cent sulfonated castor oil, 0.5 to 2 per cent tricresyl phosphate, and 0.05 to 0.3 per cent lolol phosphate.<sup>107</sup>

The effect of alkaline degreasing solutions on protective phosphate coatings deposited on iron presents a number of special problems.<sup>108</sup> Sodium carbonate, sodium hydroxide, trisodium phosphate, sodium tetrphosphate, sodium orthosilicate and, at certain concentrations, metasilicate, produce varying degrees of discoloration, while silicates of higher silica-to-alkali ratio are free from this effect. Various emulsion cleaners gave satisfactory results, but were rejected for lack of permanence in storage, or for fire hazards. Hydrated crystalline sodium metasilicate showed no deleterious effect on phosphate finishes at 6 ounces per gallon. The same material, with additions of 5 to 10 per cent nonionic wetting agent at 95 to 98°C, was fully satisfactory as an immersion cleaner for light metals. Tetrasodium pyrophosphate ( $\text{Na}_4\text{P}_2\text{O}_7$ ), sodium tetrphosphate ( $\text{Na}_6\text{P}_4\text{O}_{13}$ ), and ammonia have similar action on some of the coatings.  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  at 6 to 10 ounces per gallon was recorded as the best alkaline immersion cleaner for phosphate coatings, although some additional security could be had from the partial substitution with silicates such as  $\text{Na}_2\text{O} : 2\text{SiO}_2$  or  $\text{Na}_2\text{O} : 3.3\text{SiO}_2$ .

**Nonferrous Metals—Surface Attack.** In cleaning aluminum, copper, tin, zinc, and their alloys, solutions must be formulated with regard to chemical reaction of the metal surface. Sometimes it is desirable to etch the surfaces of these metals to improve the adherence of subsequent coatings but more frequently it is desired to preserve a bright surface unaltered. This requires attention not only to the composition of the cleaning bath but to times and temperatures, a care not required in cleaning iron and steel. It has been stated that if only one alkaline cleaner were available it would be sodium metasilicate because of its adaptability to various processes.

A study by Baker of the conditions in which etching occurs is a useful guide for working out procedures in the cleaning of soft metals.<sup>109</sup> Tin plate at 60°C was subjected to solutions of trisodium phosphate, sodium carbonate, sodium hydroxide, and various silicates, and the results were evaluated by appearance and by loss of weight (Fig. 6.10). Eight-hour immersion in sodium metasilicate up to 0.25 per cent did not impair the bright surface of the tin. The other alkalies all etched the surface at 0.005 per cent as shown in Fig. 6.11 which, by the reflection of diagonal lines,

<sup>107</sup> Kingerley, R. W., U. S. Pat. 2,391,631 (1945).

<sup>108</sup> Newman, S. G., Springfield Armory Technical Report W.O. (630: 12/20/44).

<sup>109</sup> Baker, C. L., *Ind. Eng. Chem.*, **27**, 1358 (1935).

clearly indicates where the metasilicate solution left bright surfaces and when etching took place (Tables 6.4, 6.5).

Caustic soda, soda ash, and trisodium phosphate all attacked aluminum vigorously, the attacks increasing as the concentration increased. Even sodium stearate dissolved considerable aluminum. Sodium metasilicate pentahydrate showed a safe range of concentration between 0.6 and 5 per cent. At concentrations of 0.5 per cent or less this material caused some

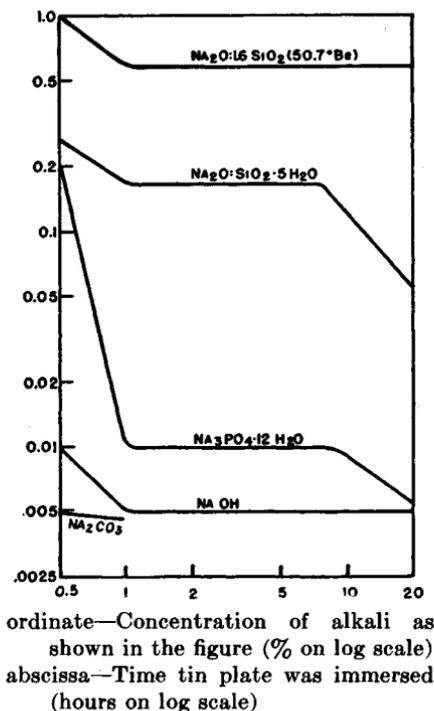


FIG. 6.10. The more siliceous alkalis exhibit a larger safe concentration-time area in which immersed tin plate is not visibly etched at 60°C. (Baker)

darkening and etching, but the loss of metal was very small. At concentrations above 5 per cent it caused etching and considerable loss of metal. More siliceous silicates caused practically no loss of weight at any concentration between 0.005 and 10 per cent but did cause darkening at very low concentrations (less than 0.1 per cent). Silicates more siliceous than those used are known to be excellent inhibitors of corrosion in cleaners for aluminum made of mixed alkaline materials (Table 6.6, Fig. 6.12).

Zinc is more sensitive to alkaline solutions than aluminum, but procedures worked out to yield satisfactory cleaning are detailed below.

The relative effects of the alkalis on pure copper at 60°C were ascer-

tained on the cleanest possible surfaces, which were obtained by preliminary treatment with 3.6 per cent hydrochloric acid to remove oxide films.

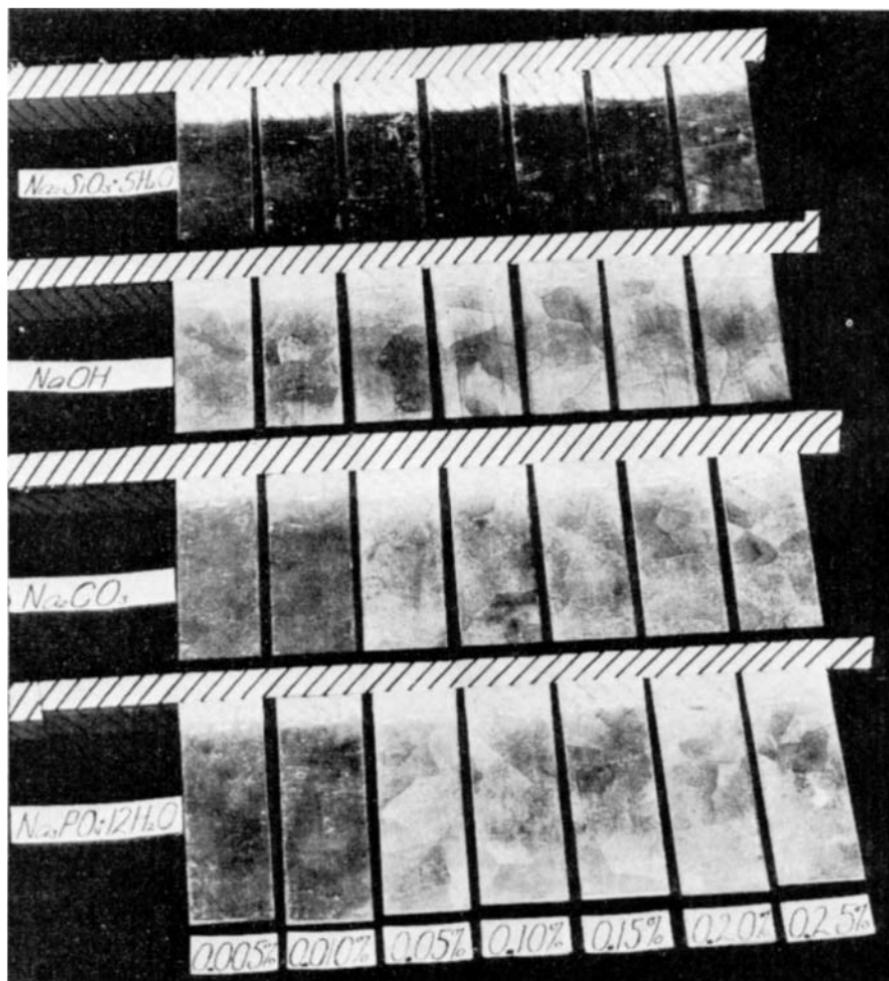


FIG. 6.11. Reflection of the diagonal lines by the tinned strips shows that after 8 hours immersion at 60°C,  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  solutions from 0.005 to 0.25% cause no etching or darkening of the shiny surface. The other alkalis either destroyed or reduced the specular surface. (Baker)

With most of the alkalis a black oxide coating was formed at the lower ranges of concentration. This tended to increase with the concentration of the solution up to the point where thicker films tended to dissolve off, leaving a grayish undercoat. Red oxide was formed with some of the alkalis

at concentrations higher than those which yielded the black oxides. The higher concentrations of the silicates left the metal clean but visibly etched (Figs. 6.13, 6.14; see Table 6.7). The solutions which attacked the copper became colored a greenish-blue. The depth of color roughly corresponded to the extent of attack.

The silicates in general show a greater range of safe concentrations, times, and temperature than other alkalis, and among the silicates the choice of the proper alkali-silica ratio broadens the range much further. The times used in industrial cleaning are so much shorter than those in the foregoing comparison that the silicates are much more available than

TABLE 6.4

Tin plate may be immersed in high concentrations of siliceous silicates for many hours at 60°C without evidence of etching. (Baker)

	% Maximum Concentration Which Did Not Etch at Exposure Time of:							
	0.5 hr	1 hr	1.5 hr	2 hr	3 hr	4 hr	8 hr	24 hr
Alkali (solid)								
Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	0.20	0.01	0.01	0.01	0.01	0.01	0.01	0.005
Na <sub>2</sub> CO <sub>3</sub>	.01	.005	.005	.005	.005	.005	.005	.005
NaOH	.005	.005	.005	.005	.005	.005	.005	.005
Na <sub>2</sub> O:SiO <sub>2</sub> :5H <sub>2</sub> O	.25	.15	.15	.15	.15	.15	.15	.05
Solutions of Sodium Silicate								
Na <sub>2</sub> O:1.6SiO <sub>2</sub> (58.5°Bé)	1.00	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Na <sub>2</sub> O:2.1SiO <sub>2</sub> (59°Bé)	2.50	2.00	1.50	1.50	1.00	.80	.60	.60
Na <sub>2</sub> O:2.5SiO <sub>2</sub> (52.0°Bé)	8.00	8.00	8.00	8.00	8.00	8.00	5.00	5.00
Na <sub>2</sub> O:3.0SiO <sub>2</sub> (47.0°Bé)	50.0	45.0	40.0	35.0	30.0	30.0	30.0	25.0
Na <sub>2</sub> O:3.3SiO <sub>2</sub> (41.0°Bé)	—	—	80.0	60.0	40.0	30.0	30.0	30.0
Na <sub>2</sub> O:4.0SiO <sub>2</sub> (33.5°Bé)								
	(No visible effect at any concentration)							

might at first appear. It will be recognized that peculiarities of individual plants require some adjustment of cleaning procedures.

Sodium metasilicate at high concentrations has been used successfully for stripping enamel from metal with soldered joints without injury to the solder and for stripping chromium plate to reclaim defective pieces. The plating is displaced electrolytically in hot 3 per cent Na<sub>2</sub>SiO<sub>3</sub>·5H<sub>2</sub>O with the piece as anode.<sup>110</sup> The cleaning of printers' halftone plates and the removal of ink from printing machinery are examples of special jobs effectively done by metasilicate solutions.<sup>111</sup> A machine for washing type

<sup>110</sup> Philadelphia Quartz Co., unpublished records.

<sup>111</sup> Kantrowitz, M. S., and Gosnell, E. J., "Detergents For the Printer," GPO-PIA Joint Research Bull. M-1, U. S. Govt. Print. Off., p. 3, (1947).

TABLE 6.5

The weight lost by tin surfaces immersed at 60°C in alkali solutions is a function of concentration and specific alkali, and occurs more rapidly in the first few hours. (Baker)

Concn. of Soln., %	Solids				Solutions					
	Na <sub>2</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	Na <sub>2</sub> CO <sub>3</sub>	NaOH	Na <sub>2</sub> O: SiO <sub>2</sub> : 5H <sub>2</sub> O	Na <sub>2</sub> O: 1.6SiO <sub>2</sub> (58.5°Bé)	Na <sub>2</sub> O: 2.1SiO <sub>2</sub> (59.3°Bé)	Na <sub>2</sub> O: 2.5SiO <sub>2</sub> (52.0°Bé)	Na <sub>2</sub> O: 3.0SiO <sub>2</sub> (47.0°Bé)	Na <sub>2</sub> O: 3.3SiO <sub>2</sub> (41.0°Bé)	Na <sub>2</sub> O: 4.0SiO <sub>2</sub> (33.5°Bé)
<i>Eight Hours</i>										
0.005	0.1	0.2	1.4	0.2						
.01	.1	.3	1.6	.3						
.05	1.3	1.6	1.4	.0						
.10	1.5	1.7	1.3	.1						
.15	1.6	1.8	1.3	.5						
.20	1.7	1.8	1.4	.6						
.25	1.7	1.8	1.6	.8						
<i>Twenty-four Hours</i>										
0.005	0.4	0.2	2.4	0.7						
.010	.5°	.4°	3.5°	.5						
.05	2.3°	2.8°	3.6°	2.2	2.2					
.10	2.7°	2.8°	3.8°	2.4°	2.3	0.2	0.2			
.15	3.1°	3.2°	3.4°	2.6°						
0.20	2.8°	3.0°	3.4°	2.4°	2.5	0.2	0.1			
.25	3.2°	2.8°	3.5°	2.7°						
.30	2.8°	2.7°	3.7°	2.8°	2.0	0.1	0.1			
.40	2.7°	2.8°	5.2°	2.9°	2.4	1.4	.1			
.50	2.6°	2.7°	3.0°	2.6°	2.3	1.6				
0.60	2.9°	2.7°		2.9°	2.4	1.2	0.2			
.80	2.7°	2.9°		2.8°	2.5°	3.2°	.0			
1.00	2.8°	2.4°		2.4°	2.5°	3.5°	.1			
1.50	2.7°	2.4°		2.7°	2.4°	3.1°	.2			
2.00	2.7°				2.8°	3.3°	.2			
2.50	2.9°				2.6°	3.0°	0.1			
3.0					2.7°	3.0°	.0			
3.5						2.8°	1.0			
4.0							0.8	0.2		
4.5							.2	.2		
5.0							1.3	0.2		
6.0							2.1°	.1		
7.0							2.3°	.2		

TABLE 6.5—Continued

Concn. of Soln., %	Solids				Solutions					
	$\text{Na}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$	$\text{Na}_2\text{CO}_3$	NaOH	$\text{Na}_2\text{O} : \text{SiO}_2 : 5\text{H}_2\text{O}$	$\text{Na}_2\text{O} : 1.6\text{SiO}_2$ (58.5°Bé)	$\text{Na}_2\text{O} : 2.1\text{SiO}_2$ (59.3°Bé)	$\text{Na}_2\text{O} : 2.5\text{SiO}_2$ (52.0°Bé)	$\text{Na}_2\text{O} : 3.0\text{SiO}_2$ (47.0 Bé)	$\text{Na}_2\text{O} : 3.3\text{SiO}_2$ (41.0°Bé)	$\text{Na}_2\text{O} : 4.0\text{SiO}_2$ (33.5°Bé)
8.0							2.2°	0.4		
9.0							2.8°	.5		
10.0							2.5°	0.4		
12.5							2.2°	.2		
15.0							2.4°	.5		
17.5								.6		
20.0								.3	0.1	
25.0								1.0	0.0	
30.0								1.7°	.1	0.0
35.0								1.7°	.2°	
40.0								2.1°	.0°	.0
45.0								1.7°	1.6°	
50.0								1.2°	1.7°	.2
55.0									1.6°	
60.0									2.9°	0.4
70.0									1.7°	.2
80.0									3.6°	.2
90.0									1.6°	.3
100.0									0.4°	.2

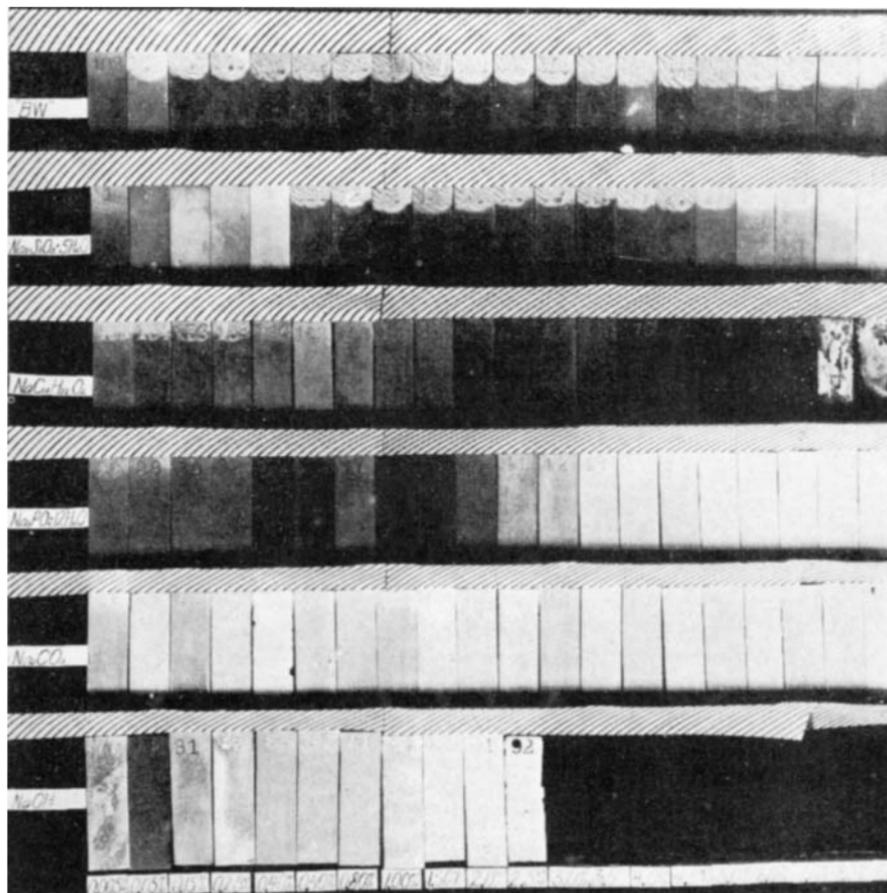
\* Visibly etched.

locked in forms operates successfully with sodium metasilicate,<sup>112</sup> while for cleaning by hand, 20 pounds of metasilicate in 50 gallons of water used hot, works well.<sup>113</sup>

The metal equipment of the food processing industries is well served with sodium metasilicate as a general detergent with appropriate adjustment of temperatures and concentrations to fit the specific work in hand. Aluminum, steel, or glass-lined tanks for the bulk transport and storage of milk may, for example, be effectively cleaned with a solution of 0.6 per cent  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  at 50°C, conditions at which the emulsifying and deflocculating properties of sodium metasilicate are high.<sup>114</sup> Other apparatus requiring cleaning by solvent action calls for higher concentration and temperatures but, with data available from manufacturers, the single reagent

<sup>112</sup> Meehan, J. J., U. S. Pat. 2,010,195 (1935).<sup>113</sup> Bennett, H., "Chemical Formulary," Vol. 2, p. 72, New York, D. Van Nostrand Co., Inc., 1935.<sup>114</sup> Grayson, F., *Food Industries*, 7, 231, 281 (1935).

may be used to dissolve casein and milk albumin, saponify or emulsify fatty materials, and precipitate calcium in a dispersed form which can be



ordinate—"BW";  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ ;  $\text{NaC}_{18}\text{H}_{35}\text{O}_2$ ;  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ ;  $\text{Na}_2\text{CO}_3$ ;  $\text{NaOH}$ .  
 abscissa—Concentration, from left to right: 0.005%; 0.05%; 0.15%; 0.25%; 0.40%;  
 0.60%; 0.80%; 1.00%; 1.50%; 2.0%; 2.5%; 3.0%; 3.5%; 4.0%; 4.5%; 5.0%; 6.0%;  
 7.0%; 8.0%; 10.0%.

FIG. 6.12. Reflection of the diagonal lines in the two top rows shows that neither 0.60 to 4.5%  $\text{Na}_2\text{O}:\text{SiO}_2 \cdot 5\text{H}_2\text{O}$  nor 0.15 to 10% "BW" ( $\text{Na}_2\text{O}:\text{SiO}_2$ , 58.5°Bé) attacked aluminum after 24-hour immersion at 60°C while the other alkalis destroyed the gloss on all and left deposits on some. (Baker)

rinsed away.<sup>115</sup> A mixture recommended for tin and aluminum contains  $\text{Na}_2\text{O}:\text{SiO}_2$  solution, 50 per cent;  $\text{NaOCl}$  solution, 12.4 per cent;

<sup>115</sup> Johnson, J. J., and Roland, C. T., *J. Dairy Sci.*, **23**, 457 (1940).

$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ , 21.6 per cent;  $\text{Na}_3\text{PO}_4$ , 9 per cent; sodium alkyl sulfate, 3.2 per cent; and water, the remainder.<sup>28, 116</sup>

TABLE 6.6

Chemical attack on aluminum by alkalis at 60°C was visible almost immediately where it occurred. Loss in weight in 24 hours was small with silicates. (Baker)

Concn. of Soln., %	Weight Lost, grams per square meter						
	$\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	$\text{Na}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$	$\text{Na}_2\text{CO}_3$	NaOH	$\text{Na}_2\text{O} : \text{SiO}_2 : 5\text{H}_2\text{O}$	$\text{Na}_2\text{O} : 1.6\text{SiO}_2 : 58.5^\circ\text{Bé}$	$\text{Na}_2\text{O} : 2.1\text{SiO}_2 : 59.3^\circ\text{Bé}$
0.005	0.2	0.3 <sup>d</sup>	ce	d	de	0.3 <sup>d</sup>	0.2 <sup>d</sup>
.01	.1	.4 <sup>d</sup>	ce	2.2 <sup>d</sup>	0.2 <sup>de</sup>	.3 <sup>d</sup>	.2 <sup>d</sup>
.05	.3	1.0 <sup>d</sup>	ce	10.6 <sup>d</sup>	.2 <sup>de</sup>	.2 <sup>e</sup>	0
.10	.4	2.3 <sup>d</sup>	ce	24.5 <sup>d</sup>	.2 <sup>de</sup>	.1	0
.15	.3	4.5 <sup>d</sup>	5.3 <sup>de</sup>	36.8 <sup>de</sup>	.2 <sup>de</sup>	.1	0
0.20	0.7	6.0 <sup>d</sup>	ce	43.1 <sup>de</sup>	0.1 <sup>e</sup>	0.1	0.1
.25	.6	7.6 <sup>d</sup>	ce	55.6 <sup>de</sup>	.2 <sup>e</sup>	.1	0
.30	1.2	9.2 <sup>d</sup>	1.0 <sup>ce</sup>	76.4 <sup>e</sup>	.2 <sup>e</sup>	.2	0
.40	1.5 <sup>d</sup>	12.4 <sup>d</sup>	2.4 <sup>ce</sup>	77.4 <sup>de</sup>	.3 <sup>e</sup>	0	0
.50	1.8 <sup>d</sup>	15.0 <sup>de</sup>	32.4 <sup>ce</sup>	68.7 <sup>de</sup>	.1 <sup>e</sup>	0	0
0.60	1.9 <sup>d</sup>	18.2 <sup>de</sup>	12.8 <sup>ce</sup>	93.6 <sup>de</sup>	0.2	0.1	0
.80	2.0 <sup>d</sup>	20.6 <sup>de</sup>	11.5 <sup>ce</sup>	92.3 <sup>ce</sup>	.1	0	0.1
1.00	2.9 <sup>d</sup>	24.1 <sup>de</sup>	20.4 <sup>ce</sup>	250.6 <sup>ce</sup>	0	0.1	.1
1.50	3.8 <sup>d</sup>	31.2 <sup>de</sup>	14.0 <sup>ce</sup>	403.6 <sup>ce</sup>	0	0.1	0
2.00	9.2 <sup>d</sup>	21.2 <sup>de</sup>	44.2 <sup>ce</sup>	478.2 <sup>ce</sup>	0	0	0
2.50		32.4 <sup>de</sup>	30.9 <sup>ce</sup>	697.2 <sup>ce</sup>	0.1	0.1	0
3.00	6.1 <sup>d</sup>	50.4 <sup>de</sup>	22.8 <sup>ce</sup>	all others completely dissolved	.1	0	0
3.50	7.3 <sup>d</sup>	106.3 <sup>e</sup>	24.0 <sup>ce</sup>		0	0	0
4.00	6.3 <sup>d</sup>	120.1 <sup>e</sup>	64.6 <sup>ce</sup>		0	0	0
4.50	7.3 <sup>d</sup>	132.9 <sup>e</sup>	67.4 <sup>ce</sup>		0	0	0
5.00	7.9 <sup>d</sup>	147.6 <sup>e</sup>	51.6 <sup>ce</sup>		0.1	0	0
6.00	8.6 <sup>d</sup>	169.2 <sup>e</sup>	67.1 <sup>ce</sup>	ce	0	0	
7.00	7.6 <sup>d</sup>	202.4 <sup>e</sup>	85.7 <sup>ce</sup>		0	0	
8.00	3.9 <sup>d</sup>	231.9 <sup>e</sup>	118.4 <sup>ce</sup>		ce	0	0
10.00	1.9 <sup>d</sup>	290.9 <sup>e</sup>	162.3 <sup>ce</sup>		131.5 <sup>ce</sup>	0	0

<sup>e</sup> Strip was incrustated; <sup>d</sup> strip was darkened in color; <sup>o</sup> strip was visibly etched.

Restaurants and home kitchens have customarily cleaned silver-plated knives, forks, and spoons by subjecting them to an alkaline solution at boiling temperature in an aluminum container. With sodium metasilicate as the detergent this is not a satisfactory procedure, but the desired results

<sup>116</sup> Mohr, W., and Wullhorst, B., *Molkerei-Ztg. (Hildesheim)*, 50, 2490, 2525 (1936).

are obtained by substituting a tin or tinned plate container for aluminum. As such containers are universally available in restaurants, the practical answer is to use a 1 per cent solution of  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  at  $70^\circ\text{C}$ . The difference in the rate at which the electrolytic action is polarized by the silicate on aluminum and on tin must be part of the explanation because the removal of tarnish is definitely assisted by the potential created by contact of two dissimilar metals in a conducting solution.

In an article reporting favorable experience with crates built of the silicon-aluminum alloy, "silumin", which are used as a substitute for wooden crates in drying sugar beets, the warning is given that they should not be

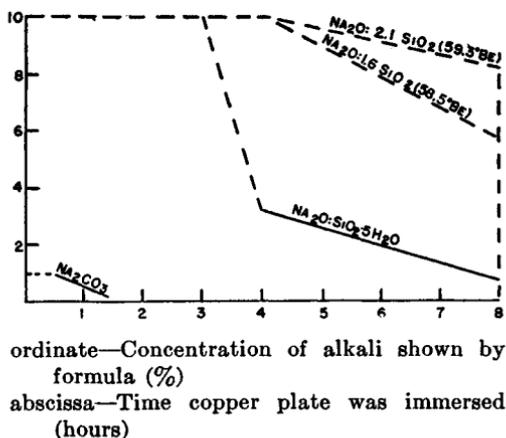


FIG. 6.13. Safe times and concentrations at which alkaline compounds may be used without visibly etching copper at  $60^\circ\text{C}$  lie to the left of and below the limiting lines. (Baker)

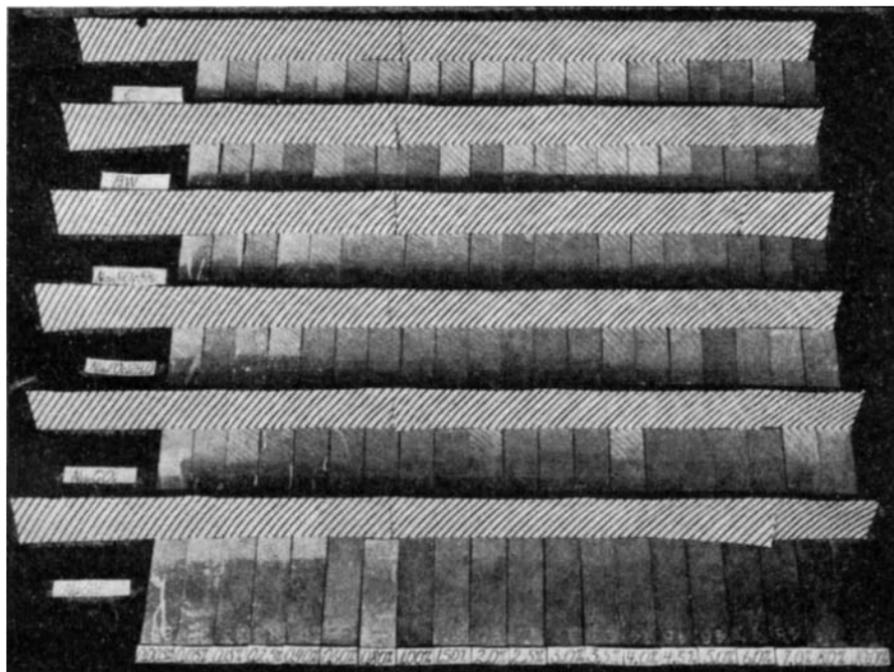
washed in a soda solution alone but that from 1 to 3 per cent of sodium silicate should be added.<sup>117</sup>

**Inhibition of Corrosion. Aluminum.** Mears and Eldredge, in a valuable discussion of the use of inhibitors for protecting aluminum and its alloys, refer to the use of  $\text{Na}_2\text{O}:2\text{SiO}_2$  (17.5 per cent  $\text{H}_2\text{O}$ ) and state that "In alkaline solution, the silicates are the most promising inhibitors" and that in order to inhibit satisfactorily the action on aluminum of hot sodium carbonate solution at cleaning concentrations, 22 per cent by weight of the sodium disilicate should be added to the carbonate or 30 per cent to trisodium phosphate.<sup>118</sup> While their statements are correct, it is misleading, as Stericker has pointed out, to omit reference to the fact that much smaller

<sup>117</sup> Hartl, W., *Listy Cukrovar.* **52**, 171 (1934).

<sup>118</sup> Mears, R. B., and Eldredge, G. G., *Trans. Electrochem. Soc.*, **83**, 403 (1943).

quantities of silicate of higher silica ratio will accomplish the same results.<sup>119</sup> Rohrig found that boiling 5 hours in solutions containing 35 to 160 grams of sodium carbonate per liter destroyed aluminum sheets.<sup>120</sup> The addition of 0.5 gram  $\text{Na}_2\text{O}:3.3\text{SiO}_2$  to any of these solutions gave practically com-



ordinate—"C"; "BW";  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ ;  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ ;  $\text{Na}_2\text{CO}_3$ ;  $\text{NaOH}$ .  
 abscissa—Concentration, from left to right: 0.005%; 0.05%; 0.15%; 0.25%; 0.40%;  
 0.60%; 0.80%; 1.00%; 1.50%; 2.0%; 2.5%; 3.0%; 3.5%; 4.0%; 4.5%; 5.0%; 6.0%;  
 7.0%; 8.0%; 10.0%.

FIG. 6.14. While copper strips were more resistant to 24-hour immersion in alkali solutions (0.005 to 10%) at 60°C than were the other nonferrous metals, the reflections again are more pronounced over a wider concentration range for  $\text{Na}_2\text{O}:\text{SiO}_2 \cdot 5\text{H}_2\text{O}$ ;  $\text{Na}_2\text{O}:2.1\text{SiO}_2$ , 60°Bé "C"; and  $\text{Na}_2\text{O}:1.6\text{SiO}_2$ , 58.5°Bé "BW". (Baker)

plete protection. Thus a maximum of 1.4 per cent of the more siliceous silicate (based on the carbonate) was as effective as 22 per cent of disilicate.

"Since Seligman and Williams first suggested the use of sodium silicates

<sup>119</sup> Stericker, W. (discussion of reference 118), unpublished records, Philadelphia Quartz Co.

<sup>120</sup> Eldredge, G. G., and Mears, R. B., *Ind. Eng. Chem.*, **37**, 736 (1945); Seligman, R., and Williams, P., *J. Inst. Metals*, **28**, 297 (1922); Röhrig, H., *Chem. Ztg.*, **47**, 528 (1923).

TABLE 6.7

The weight loss of copper strips immersed 24 hours in alkali solutions at 60°C is deceptive until the oxide film is removed. There is no simple relation to pH. (Baker)

Concn. of Soln., %	NaOH		Na <sub>2</sub> PO <sub>4</sub> ·12H <sub>2</sub> O		Na <sub>2</sub> CO <sub>3</sub>		Na <sub>2</sub> O:SiO <sub>2</sub> :5H <sub>2</sub> O		Na <sub>2</sub> O:1.6SiO <sub>2</sub> (58.5°Bé)		Na <sub>2</sub> O:2.1SiO <sub>2</sub> (59.3°Bé)	
	A	B	A	B	A	B	A	B	A	B	A	B
0.005	+0.3 <sup>b</sup>	-3.3	-0.5 <sup>v</sup>	-1.1	0.0 <sup>v</sup>	-0.5	-0.6 <sup>v</sup>	-0.8	-0.3 <sup>v</sup>	-0.6	-0.4 <sup>v</sup>	-0.6
.01	+0.4 <sup>b</sup>	-2.7	-0.4 <sup>v</sup>	-0.8	0.0 <sup>v</sup>	-0.2	-0.1 <sup>v</sup>	-0.3	-0.3 <sup>v</sup>	-0.7	-0.3 <sup>v</sup>	-0.4
.05	+0.3 <sup>b</sup>	-3.9	-0.3 <sup>v</sup>	-0.8	+0.1 <sup>v</sup>	-0.3	-0.3 <sup>v</sup>	-0.5	-0.3 <sup>v</sup>	-0.6	-0.3 <sup>v</sup>	-0.5
.10	+0.8 <sup>b</sup>	-4.8	-1.8 <sup>v</sup>	-2.9	+0.1 <sup>v</sup>	-0.2	-0.3 <sup>v</sup>	-0.4	-0.4 <sup>v</sup>	-1.0	-0.1 <sup>v</sup>	-0.4
.15	+0.7 <sup>b</sup>	-4.6	-0.4 <sup>v</sup>	-0.6	+0.0 <sup>v</sup>	-0.4	-0.3 <sup>v</sup>	-0.4	-0.4 <sup>v</sup>	-1.0	-0.2 <sup>v</sup>	-0.5
0.20	+0.5 <sup>b</sup>	-4.3	-0.4 <sup>t</sup>	-0.9	-0.0 <sup>v</sup>	-0.4	-0.4 <sup>v</sup>	-0.9	-0.4 <sup>v</sup>	-0.6	-0.3 <sup>v</sup>	-0.5
.25	+0.9 <sup>b</sup>	-4.9	-0.3 <sup>t</sup>	-0.9	-0.0 <sup>t</sup>	-0.4	-0.4 <sup>v</sup>	-0.6	-0.1 <sup>v</sup>	-0.4	-0.4 <sup>v</sup>	-0.7
.30	+0.8 <sup>b</sup>	-5.4	-0.4 <sup>t</sup>	-1.0	-0.1 <sup>t</sup>	-0.5	-0.4 <sup>v</sup>	-0.6	-0.2 <sup>v</sup>	-0.4	-0.5 <sup>v</sup>	-1.0
.40	+0.8 <sup>b</sup>	-6.1	-0.2 <sup>t</sup>	-1.0	-0.3 <sup>t</sup>	-0.6	-0.5 <sup>v</sup>	-0.9	-0.1 <sup>v</sup>	-0.4	-0.2 <sup>v</sup>	-0.6
.50	+0.9 <sup>b</sup>	-5.8	-0.2 <sup>t</sup>	-1.0	-0.2 <sup>t</sup>	-0.5	-0.4 <sup>v</sup>	-0.5	-0.1 <sup>v</sup>	-0.4	-0.3 <sup>v</sup>	-1.0
0.60	+0.8 <sup>b</sup>	-5.4	-0.4 <sup>t</sup>	-0.8	-0.3 <sup>t</sup>	-0.7	-0.3 <sup>v</sup>	-0.6	-0.1 <sup>v</sup>	-0.5	-0.6 <sup>v</sup>	-1.1
.80	+0.5 <sup>b</sup>	-5.4	-0.1 <sup>t</sup>	-0.9	-0.3 <sup>t</sup>	-0.7	-0.3 <sup>v</sup>	-0.9	-0.1 <sup>v</sup>	-0.5	-0.4 <sup>t</sup>	-1.0
1.00	+0.3 <sup>r</sup>	-6.4	-0.3 <sup>t</sup>	-3.6	-0.4 <sup>t</sup>	-0.9	0.0 <sup>t</sup>	-1.4	-0.1 <sup>v</sup>	-0.7	-1.0 <sup>t</sup>	-1.5
1.50	-1.3 <sup>r</sup>	-6.1	-0.3 <sup>b</sup>	-1.9	-0.2 <sup>b</sup>	-1.5	+0.9 <sup>t</sup>	-2.3	-0.1 <sup>t</sup>	-1.5	-1.3 <sup>t</sup>	-1.7
2.00	+0.2 <sup>r</sup>	-8.5	+0.2 <sup>b</sup>	-4.0	-0.5 <sup>u</sup>	-1.7	+1.3 <sup>t</sup>	-2.4	-0.1 <sup>t</sup>	-1.5	-1.3 <sup>t</sup>	-2.5
2.50	+0.0 <sup>r</sup>	-8.1	+0.1 <sup>b</sup>	-4.0	-0.9 <sup>u</sup>	-1.6	-1.7 <sup>u</sup>	-3.2	-0.2 <sup>t</sup>	-1.7	-1.2 <sup>o</sup>	-1.6
3.00	+0.1 <sup>r</sup>	-7.5	+0.0 <sup>b</sup>	-4.1	+0.2 <sup>u</sup>	-2.5	-2.0 <sup>u</sup>	-2.9	-0.4 <sup>t</sup>	-1.7	-1.4 <sup>t</sup>	-2.0
3.50	-0.2 <sup>r</sup>	-6.9	-0.4 <sup>b</sup>	-3.3	-0.0 <sup>u</sup>	-2.2	-2.2 <sup>u</sup>	-2.9	-0.6 <sup>t</sup>	-1.7	-3.1 <sup>o</sup>	-2.9
4.00	-0.0 <sup>r</sup>	-7.4	-0.1 <sup>b</sup>	-4.5	-0.8 <sup>u</sup>	-2.8	-2.7 <sup>u</sup>	-3.3	-3.2 <sup>o</sup>	-3.6	-3.4 <sup>o</sup>	-3.5
4.50	-0.5 <sup>r</sup>	-5.7	-0.0 <sup>b</sup>	-4.1	-1.3 <sup>u</sup>	-2.5	-2.8 <sup>o</sup>	-3.1	-0.3 <sup>o</sup>	-3.2	-3.3 <sup>o</sup>	-3.5

5.00	-0.5 <sup>r</sup>	-7.1	-0.3 <sup>b</sup>	-4.5	-0.6 <sup>b</sup>	-2.8	-3.0 <sup>e</sup>	-3.1	-2.9 <sup>e</sup>	-3.1	-3.2 <sup>e</sup>	-3.4
6.00	-0.6 <sup>r</sup>	-7.2	-0.1 <sup>b</sup>	-4.4	-0.8 <sup>u</sup>	-2.4	-2.4 <sup>e</sup>	-2.8	-2.8 <sup>e</sup>	-3.1	-3.1 <sup>e</sup>	-3.3
7.00	-0.7 <sup>r</sup>	-5.4	-0.2 <sup>b</sup>	-4.2	-1.1 <sup>u</sup>	-2.2	-2.8 <sup>e</sup>	-3.1	-2.6 <sup>e</sup>	-3.4	-2.8 <sup>e</sup>	-2.9
8.00	-0.6 <sup>r</sup>	-8.6	-0.4 <sup>r</sup>	-3.8	-1.2 <sup>u</sup>	-1.8	-2.2 <sup>e</sup>	-2.5	-2.2 <sup>e</sup>	-2.6	-2.8 <sup>e</sup>	-3.0
10.00	-0.8 <sup>r</sup>	-4.4	-0.3 <sup>r</sup>	-4.8	-1.0 <sup>u</sup>	-2.0	-2.8 <sup>e</sup>	-2.8	-4.0 <sup>e</sup>	-2.3	-3.0 <sup>e</sup>	-3.3
		145.9		63.9		32.2		43.1		37.2		43.4

A = change in weight before removing oxide

B = change in weight after removing oxide

<sup>b</sup> surface coated with black oxide  
<sup>t</sup> surface tarnished

<sup>r</sup> surface coated with red oxide  
<sup>u</sup> tarnished brassy appearance

<sup>e</sup> surface visibly etched  
<sup>v</sup> only slightly tarnished

as inhibitors in alkaline cleaning solutions for aluminum, the suggestion has been widely adopted. It may be stated that it is possible to clean either polished or anodized aluminum, without affecting the dimensions or the surface, with alkaline silicate solutions at approximately the boiling point. Furthermore, cleaning with such solutions prior to anodizing with chromic acid gives a tougher, harder anodic coating than is obtained when the older type of cleaning solutions is used in the preparation. A combination which has been found effective is composed of sodium metasilicate and  $\text{Na}_2\text{O}:3.3\text{SiO}_2$  with a small amount of a wetting agent. This can be used where the aluminum is in contact with other metals.<sup>119</sup>

In 1940, Mears evaluated the components of cleaners for aluminum. "At the present time we are pleased to note that most all of the manufacturers of alkaline detergents which may be used in contact with aluminum are familiar with the inhibiting action of the silicates. This is particularly fortunate, since we do not know of any alkaline cleaners which can be used in contact with aluminum, without risk of attacking it, which do not contain appreciable amounts of silicates.

"Tests which we have made here indicate that about 22 per cent of  $\text{Na}_2\text{O}:2.0\text{SiO}_2$  (17.5 per cent  $\text{H}_2\text{O}$ ) is required in mixture with sodium carbonate so that the resulting solutions will not etch or dull aluminum at elevated temperatures. Similarly about 30 per cent of this silicate is required in mixtures with trisodium phosphate to accomplish the same purpose. Substantial amounts of silicate are also required to inhibit the action of other alkaline materials."<sup>121</sup>

Various workers have reported on cleaners suitable for washing aluminum and the importance of silicates to prevent corrosion by sodium carbonate, oil, or alkaline salts. Thomas, after examining a variety of proprietary cleaners, concluded that about 25 per cent of sodium metasilicate was advisable.<sup>122</sup> Lesser surveyed the field, reporting numerous formulations with smaller quantities, indicating that more siliceous silicates are used.<sup>123</sup> Mitchell uses as a test of the suitability of aluminum cleaners a measurement of hydrogen gas which is generated when aluminum is attacked by alkalis<sup>124</sup> (Fig. 6.15).

Morgan and Lankler have shown that a mixture of 95 per cent metasilicate and 5 per cent synthetic detergent at a concentration of 2 per cent will safely remove mineral oil from an aluminum alloy surface without corrosion at 60°C and 10 minute exposure.<sup>100</sup> Without the wetting agent

<sup>121</sup> Mears, R. B., Aluminum Company of America, private communication, 1940.

<sup>122</sup> Thomas, J. F. J., *Can. J. Research*, **B19**, 153 (1941); Darrin, M., *Ind. Eng. Chem. Anal. Ed.*, **13**, 755 (1941).

<sup>123</sup> Lesser, M. A., *Soap Sanit. Chemicals*, **22** (9), 44 (1946).

<sup>124</sup> Mitchell, R. W., *Metal Ind.* (N. Y.), **28**, 171 (1930).

a 5 per cent solution of sodium metasilicate is necessary to completely remove the oil under these conditions, whereas above 4 per cent, corrosion was evident. Thus by using metasilicate and 5 per cent wetting agent, complete safety is established between corroding and noncorroding concentrations. Of course, a much higher factor of safety is obtainable by using silicate with two or more  $\text{SiO}_2$ 's for each  $\text{Na}_2\text{O}$ , and these also are good cleaners. Where etching was desired, it could be controlled by using orthosilicate with the synthetic (Fig. 6.16).

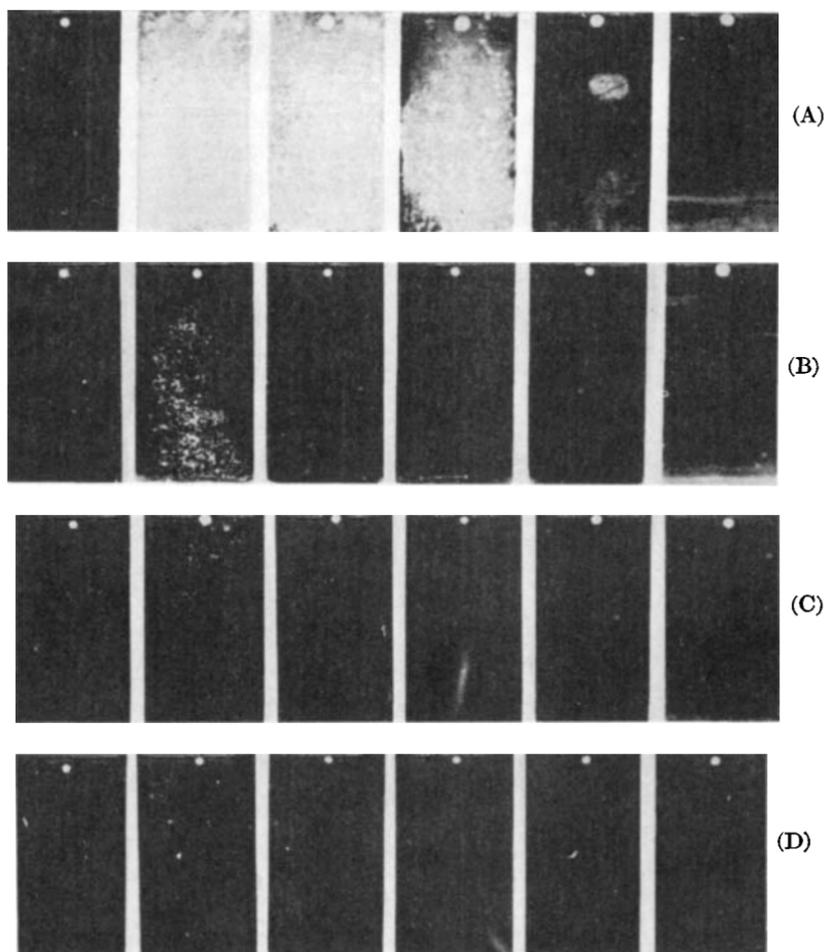
Aluminum surfaces to be prepared for spot welding are first thoroughly cleaned and then treated chemically for oxide removal. When alkaline materials are used for cleaning, silicates are an essential constituent to prevent alkaline attack on the metal. The United States Navy specifies  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ , 48 per cent;  $\text{Na}_2\text{O} : 3.3\text{SiO}_2$  with about 18 per cent of water,



FIG. 6.15. A steel ruler is reflected in the original untreated strip of aluminum and in the unetched strip of aluminum cleaned with 1% solution of sodium metasilicate for 60 minutes at  $100^\circ\text{C}$ . The other alkalis were used under the same conditions. Left to right: prior to cleaning;  $\text{Na}_2\text{CO}_3$ ;  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ ;  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ ;  $\text{NaOH}$ .

48 per cent; and rosin, 4 per cent.<sup>125</sup> Used at 4 ounces per gallon at  $88$  to  $100^\circ\text{C}$  for 5 minutes, it leaves no water break. It is recorded as a good paint remover and satisfactory cleaner with a pH of 11.8 to 12.2. Satisfactory results were obtained from a mixture of the same silicates with sodium metasilicate, 2 ounces per gallon; soluble sodium trisilicate, 2 ounces per gallon; and sodium lauryl sulfate, 1 ounce per gallon of solution at a pH of 11.9. Good results were also obtained from proprietary compositions containing silicate. Sodium metasilicate alone at 2 ounces per gallon, pH 12.8, left a water break and loosened the dirt without completely lifting it, making swabbing necessary. Sodium metasilicate at 2 ounces per gallon plus 1 ounce per gallon sodium lauryl sulfate left no water break but did not eliminate the necessity of swabbing. Sodium metasilicate 2 ounces per gallon plus 0.5 ounce of the soluble trisilicate and 1 ounce sodium lauryl sulfate left no water break and removed most of the dirt from the

<sup>125</sup> U. S. Navy Aeronautical Specification, "Compound; Paint Stripping (Silicate Type)." C-67d (March 4, 1943) and Amendment 2 (October 4, 1945).

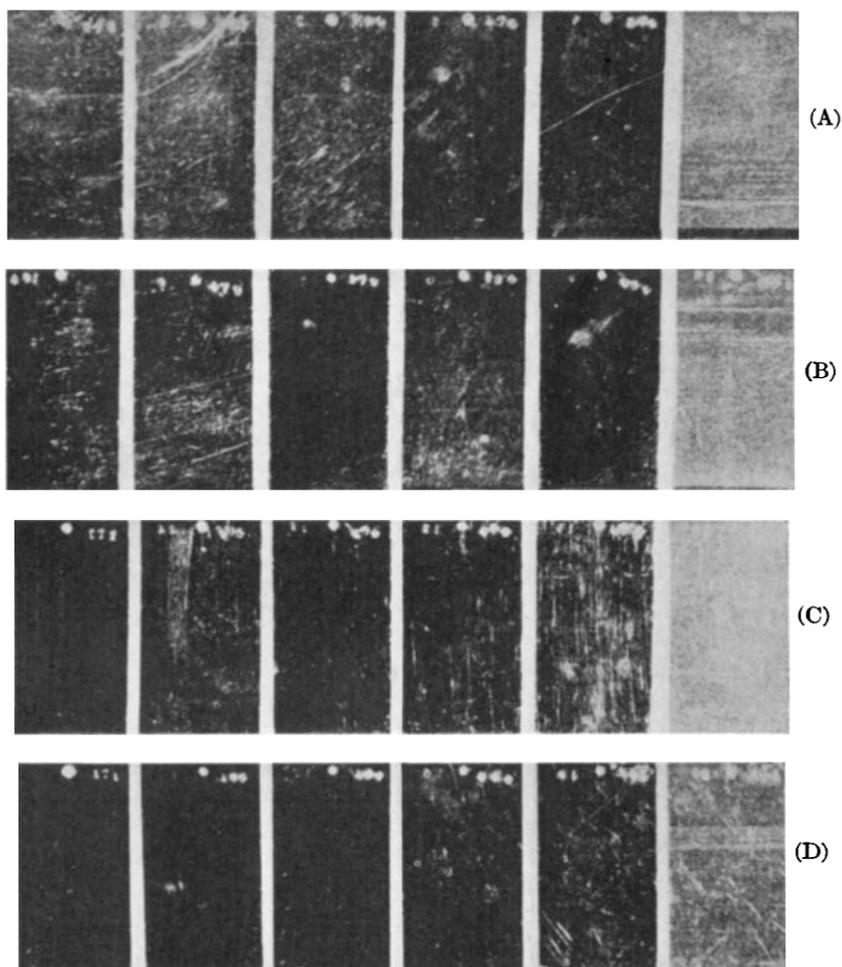


*Courtesy of National Aniline Division,  
Allied Chemical & Dye Corporation*

FIG. 6.16. Fluorescence tests show that mineral oil is completely removed from aluminum by a 2% concentration of 95%  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  and 5% synthetic detergent in 10 minutes at  $60^\circ\text{C}$ . (Morgan and Lankler). Above, ultraviolet light; opposite page, incandescent light. (A)—100%  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ ; (B)—95% A with 5% synthetic detergent; (C)—90% A with 10% synthetic detergent; (D)—80% A with 20% synthetic detergent. Samples from left to right: clean aluminum; 1% cleaner; 2% cleaner; 3% cleaner; 4% cleaner; 5% cleaner.

surface, light swabbing only being necessary.<sup>126</sup> Free rinsing properties

<sup>126</sup> Hess, W. F., Wyant, R. A., and Averbach, B. L., *Welding J.*, **23**, 402S (1944); Progress Report #10, Rensselaer Polytech. Inst.; see also Mullen, H. A., and Boelter, L., *Soc. Automotive Engrs.*, **53** (9), 26 (1945).



(Fig. 6.16 cont'd)

are also necessary so that the cleaner may be entirely washed away before passing through the acid oxide remover. The removal of buffing compounds from metal surfaces which have been polished requires special attention because these compounds are usually based on mixtures of mild abrasive substances with stearic acid. They are applied to the metals by rapidly moving wheels composed of cloth discs on which the compound is placed. The friction developed at the metal surface melts the stearic acid which thus makes a complete contact with the metal surface and penetrates any porosity which may be there. At atmospheric temperatures, the grease film is again solid and requires vigorous detergent action for its removal.

Limitations are imposed by the sensitiveness of soft metals to attack by hot alkaline detergents and by the fact that in strong solutions the stearic acid soaps formed tend to be salted out and to persist as films.<sup>127</sup>

Hazel and Stericker have studied the conditions for removing buffing compounds from zinc, aluminum, steel, and glass surfaces. The test panels were immersed for 10 minutes in an upright position at a temperature of 90°C under standard ASTM procedure.<sup>128</sup> Nonsilicate alkalis which attack aluminum and zinc remove the stearic acid with the help of copious evolution of gas, but are ruled out by their corrosive effect on the metals. High silica silicates are not sufficiently vigorous in action for the purpose, and they may leave films. Sodium metasilicate, at a concentration of 0.184 per cent  $\text{Na}_2\text{O}$ , was not vigorous enough to remove the stearic acid from the zinc surfaces, but concentrations of 0.0148, 0.074, and 0.148 per cent  $\text{Na}_2\text{O}$  removed it from glass, aluminum, and steel, respectively. On aluminum, sodium metasilicate at a concentration of 0.0295 per cent  $\text{Na}_2\text{O}$  showed some attack, but higher concentrations left a specular surface.

At 0.295 per cent  $\text{Na}_2\text{O}$ , zinc was completely cleaned, so also at 0.48 per cent  $\text{Na}_2\text{O}$ ; but from 0.625 upward a residue of salted-out stearic acid soap remained on the surface. There is thus a range of 0.3 to 0.6 per cent  $\text{Na}_2\text{O}$  in which sodium metasilicate will effectively remove stearic acid at 90°C without injury to the metal. A commercial stearic acid having a melting range of 65 to 70°C is the basis of the foregoing findings. A commercial acid of lower melting point, 54 to 57°C, was much more easily removed. "The soap remaining on the panels at 90° in the presence of salting-out concentrations of the cleaners was a liquid crystalline phase. . . . The solubility of the soap depends greatly on the nature of the solution with which it is in equilibrium." Stearic acid was more difficult to remove from zinc than from the other surfaces tested, but it is clear that safe cleaning can be accomplished with sodium metasilicate at 1.3 to 2.5 ounces per U. S. gallon at 90°C (Fig. 6.17).

Greasy residues must be removed from metals used to prepare tinned meats and fish, to clean the pans used in bakeries, and to wash utensils in hotel kitchens. One of the most exacting problems is the cleaning of containers for cooking hams at temperatures high enough to leave residues that are almost charred. Cast aluminum containers are recovered without injury to the metal by soaking in a bath of 8 to 10 pounds of a metasilicate preparation containing an organic surface-active agent in 100 gallons of water. The so-called "ham mold" could be brushed and rinsed clean. Another satisfactory solution is a mixture of metasilicate with  $\text{Na}_2\text{O}:2\text{SiO}_2$  as a solution or soluble powder and an organic detergent.

<sup>127</sup> Hazel, J. F., and Stericker, W., *Ind. Eng. Chem.*, **43**, 919 (1951).

<sup>128</sup> Am. Soc. Testing Materials, Standards. Spec; D930-47T.

**Zinc.** In the manufacture of dry batteries it is important to secure the uniform corrosion of the zinc electrode so that it may be as nearly as possible completely consumed during the working life of the dry cell. Any contamination of the surface with grease or oil tends to uneven reaction and premature failure. Satisfactory cleaning of the zinc plates was accomplished by a mixture of sodium carbonate solution and 42°Bé  $\text{Na}_2\text{O} : 3.3\text{SiO}_2$  at 90°C.<sup>129</sup> The test of the perfection of the cleaning operation consists in quickly dipping the zinc plate in 0.1*N* silver nitrate solution which, if the cleaning is perfect, will produce a uniformly black coating. In the presence of traces of oil the situation is immediately indicated by irregularity in the

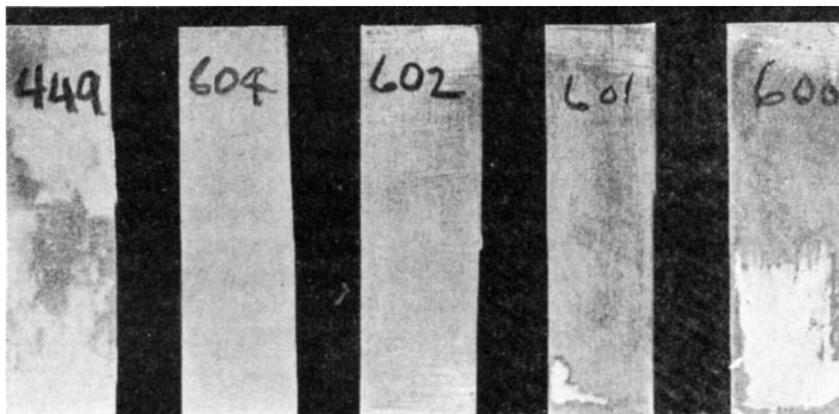


FIG. 6.17. A 10-minute dip in sodium metasilicate (0.074–0.480%  $\text{Na}_2\text{O}$ ) solutions at 90°C was sufficient to remove stearic acid (65–70°C melting range) from aluminum without leaving a deposit. (Hazel and Stericker). 449—0.025%  $\text{Na}_2\text{O}$ ; 604—0.074%  $\text{Na}_2\text{O}$ ; 602—0.480%  $\text{Na}_2\text{O}$ ; 601—0.625%  $\text{Na}_2\text{O}$ ; 600—0.885%  $\text{Na}_2\text{O}$ .

deposition of silver. The test is well adapted to factory control because of its simplicity and speed, and the clearness of its indications.

**Magnesium.** Magnesium is not readily attacked by strong alkali, but complex-ion formers such as the pyro- and polyphosphates rapidly form pits.<sup>130</sup> Sodium silicates reduce the pH at which maximum resistance to alkali is obtained and afford protection against sequestrants, but the mechanism is not clear. Film formation is not a tenable explanation. To protect magnesium alloy against corrosion an oxidizing treatment with potassium dichromate and/or ammonium dichromate is useful, but before such treatment the surfaces must be thoroughly degreased. For this purpose a hot bath containing 5 per cent of a mixture of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ,

<sup>129</sup> Breyer, F. G., and Finkeldey, W. H., U. S. Pat. 1,451,758 (1923).

<sup>130</sup> Hazel, J. F., and Stericker, W. J. *Electrochem. Soc.*, **98**, 273 (1951).

74.5 parts;  $\text{Na}_2\text{SiO}_3$ , 24.7 parts; and sodium oleate, 1 part is said to be best.<sup>131</sup>

*Tin.* Detergent compositions for cleaning tin in alkaline solutions usually contain soluble silicates of ratios between  $\text{Na}_2\text{O}:\text{SiO}_2$  and  $\text{Na}_2\text{O}:2\text{SiO}_2$ , often with the addition of other substances having inhibiting properties such as the following specific solutions; chromates, sulfites, and disulfites of sodium and potassium; and the sodium salt of tetrahydronaphthalene sulfonate.<sup>132</sup> The inhibiting substance may itself be a siliceous silicate.<sup>2</sup> A cleaner which effectively removes multiple coats of silicone resins now replacing grease in baking tins is  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ , 35 to 55 per cent;  $\text{Na}_2\text{CO}_3$ , 22 to 42 per cent; and  $\text{Na}_4\text{B}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ , 18 to 28 per cent.<sup>133</sup> At a concentration of 6 to 12 ounces per gallon of water, this mixture will remove the three or four layered coatings without even spangling the tin surface although the containers may be boiled 6 to 8 hours.

*Additional Components.* The effective ratio of the silica to alkali in a cleaning compound may be increased by the incorporation of acid salts such as disodium hydrogen phosphate, bisulfates, bichromates, or bicarbonates.<sup>134</sup> To reduce the amount of chromate added for inhibiting corrosion of soft metals, the careful use of sodium silicofluoride has been proposed.<sup>135</sup> The avoidance of chromates with their risk of producing dermatitis has been sought by the addition of a long series of water-soluble salts of metals that form insoluble silicates. These appear to exert greater inhibiting effects than would be expected from the change of composition of the silicate in solution, and it seems likely that the protection they afford may be that of colloids which form films more readily than silica in ionic form. Among the compounds suggested to form these insoluble colloidal silicates are soluble barium and strontium salts; mercurous and mercuric salts; and water-soluble compounds of arsenic, antimony, lead, magnesium, and zinc.<sup>136</sup> Perborates used with sodium metasilicate, zinc sulfate, and magnesium sulfate apparently contribute to the inhibiting effect, perhaps by promoting the development of a protective oxide film.<sup>137</sup>

Corrosion inhibiting characteristics may be imparted to various alkaline detergents by the addition of hypochlorites and zinc compounds. Griffith and Hall believe that the inhibiting results may be the consequence of

<sup>131</sup> Sutton, H., and LeBrocq, L. F., *J. Inst. Metals*, **57**, 343 (1935).

<sup>132</sup> Kochs, H. W., U. S. Pat. 1,962,821 (1934); Henkel & Cie. G.m.b.H., British Pat. 415,672 (1934); Campbell, J., and Kerr, R., British Pat. 451,025 (1936).

<sup>133</sup> Reeder, W., and Russ, J. J., U. S. Pat. 2,525,079 (1950).

<sup>134</sup> Comaschi, L. J., U. S. Pat. 2,350,592 (1944); Hart, J. F., U. S. Pat. 2,381,124 (1945).

<sup>135</sup> Metzger, M., and Long, A., U. S. Pat. 2,285,676 (1942).

<sup>136</sup> Schwartz, C., U. S. Pats. 2,303,397-2,303,400 (1942), 2,391,647 (1945); Canadian Pat. 415, 489 (1943). Durgin, C. B., U. S. Pat. 2,037,566 (1936).

<sup>137</sup> Schwartz, C., U. S. Pat. 2,359,587 (1944).

film formation, since the zinc sometimes plates out on metals being cleaned if the concentration is too high.<sup>138</sup> This suggests the possibility of invisible films at lower concentrations. Both alkali metal hypochlorites and alkaline earth metal hypochlorites were included, and the zinc compounds may be either soluble or insoluble. Sodium metasilicate and other alkaline detergents have been used. Examples are given of successful cleaning of zinc, aluminum, and tin ware at concentrations, times, and temperatures such that the untreated alkaline detergent would cause etching.

### Electrolysis Cleaning

The use of the electric current as an aid in cleaning is peculiar to the metal cleaning processes, and most of the solutions used are good conductors.<sup>139</sup> The processes usually demand very short times for the cleaning operation so that polarization of the cells in which the work is used either as anode or cathode is rarely a source of difficulty, but this can be avoided by reversing the current briefly at the end of the operation or by substituting alternating current, with which electrophoretic depositions do not occur. It is, however, advisable to avoid the contact of dissimilar metals to prevent undesirable local reactions. In the case of brasses and bronzes which are composed of more than one alloy phase, the working conditions must be determined by need and often by empirical experiment.

**Steel.** Cleaning strip steel before tinning is an operation which must be done thoroughly and at high speed in a continuous process. It is advisable to eliminate most of the easily removable soil by dilute, hot alkaline solutions supplied as jets or with the aid of brushes, before the final electrolytic cleaning in silicate solutions of about 3 per cent concentration. The conductivity of the  $2\text{Na}_2\text{O}:\text{SiO}_2$  solution is the highest, followed by  $3\text{Na}_2\text{O}:2\text{SiO}_2$  and  $\text{Na}_2\text{O}:\text{SiO}_2$ . (Fig. 6.18). Mixtures of silicates with caustic soda also develop high conductivity and pH. The generation of gas in the electrolytic bath gives mechanical assistance to the removal of dirt. The silicates have good wetting properties and are free rinsing, a strong point in their favor compared with caustic soda without silicate additions<sup>140</sup> (Table 6.8).

Pinner, reporting on the economics of metasilicate cleaning of steel for a direct deposit of nickel, cleaned 16,000 square feet of plating surface per day with an average usage of 2.9 pounds of sodium metasilicate pentahydrate per 100 square feet. This compared with the required 4.4 pounds of the material previously regarded as a standard for good performance and economy.<sup>141</sup>

<sup>138</sup> Griffith, C. L., and Hall, L. A., U. S. Pats. 2,155,045-6 (1939).

<sup>139</sup> Gray, A. G., *Product Finishing*, **15** (6), 54 (1951).

<sup>140</sup> Drake, W. P., *Iron Age*, **141**, 33 (4/21/38); Engel, E., *Iron Age*, **156**, 70 (9/6/45).

<sup>141</sup> Pinner, W. L., "Sodium Metasilicate, A New Industrial Alkali for Use in the Electroplating Industries," Philadelphia, Philadelphia Quartz Co., 1931.