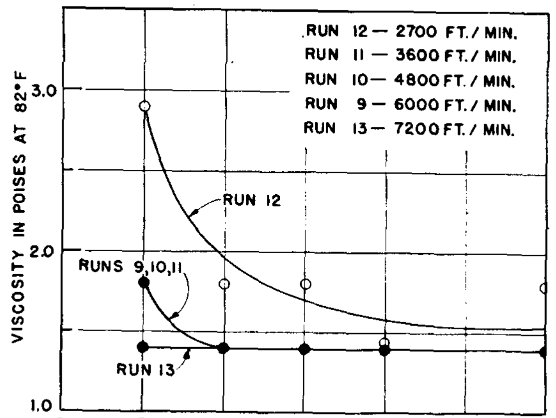

FIG. 20. Effect of peripheral speed upon viscosity of cottonseed slurry.

Disintegration runs 9-13.

due to hardening of the meal particles during prepulverizing.

4. The presence of hulls slightly increased the disintegration, power consumption, and viscosity.

5. The effect of solvents was small; a slightly greater disintegration, power consumption and viscosity being obtained with the heavier solvent.

6. The higher peripheral speeds were the more efficient, the disintegration and power consumption increasing with increase in speed. The higher speeds also caused the limiting value of the slurry viscosity to be reached more quickly owing to the quicker extraction of the oil.

7. In disintegrating the cottonseed meats to less than 80-mesh-particle size, two-thirds of the meats were reduced to less than 300-mesh particle size.

8. The high mechanical strength of pigment glands was confirmed.

Acknowledgment

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Corrosion Tests in Organic Sulfations and Sulfonations

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SULFATION and sulfonation are among the processes used to change the properties of organic materials such as to introduce greater solubility or to make a hydrocarbon more reactive for further synthesis. These processes are used particularly in the preparation of surface-active materials including detergents, emulsifiers, wetting agents, and penetrants from animal and vegetable oils and from fatty alcohols, aromatics, and other hydrocarbons. The agents commonly employed for sulfation or sulfonation are various strengths of SO_3 in water, from 66° Bé sulfuric acid, or even weaker, to strong oleums. The strength of acid used and temperature will depend usually upon the degree of saturation of the hydrocarbon, the location to which the attachment is to be directed and other factors. In some cases chlorosulfonic acid and even bisulfite solutions are used as sulfonating agents.

The selection of corrosion-resisting materials for construction of reactors and for washing and neutralization equipment depends chiefly upon the temperature used and upon the amount of dilution of sulfuric acid which occurs during processing. The purpose of this paper is to present the results of some plant and laboratory corrosion tests in organic sulfations and sulfonations under a variety of operating conditions. This will serve as an indication of the metals and alloys which should be considered for the construction of processing equipment. The information given concerning the test conditions in the plant corrosion tests is that provided by the plant where the tests were made, or as much of it as can be published. Because of the scope and complexity of this field no attempt has been made to deal with the chemistry of the processes referred to except in a general way.

The corrosion tests reported here were made with the spool-type specimen holder illustrated in Fig. 1. This method of testing is substantially in accord with A.S.T.M. Recommended Practice for Conducting Plant Corrosion Tests, A224-41.[1] Briefly, the assembly consists of previously cleaned and weighed specimens of the several metals and alloys to be tested, mounted on the spool-type holder with nonmetallic parts of porcelain to separate and insulate the specimens from each other and from the metallic parts of the holder. Two similar specimens of each material were included on each spool. The complete test assemblies were fastened firmly in place in the desired test locations in operating plant equipment and allowed to remain for sufficient lengths of time to give reliable indications of corrosion behavior. Each of the test specimens used had an exposed area of 0.5 sq. dm.

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[1] A.S.T.M. Standards, Part I, p. 522, 1944.

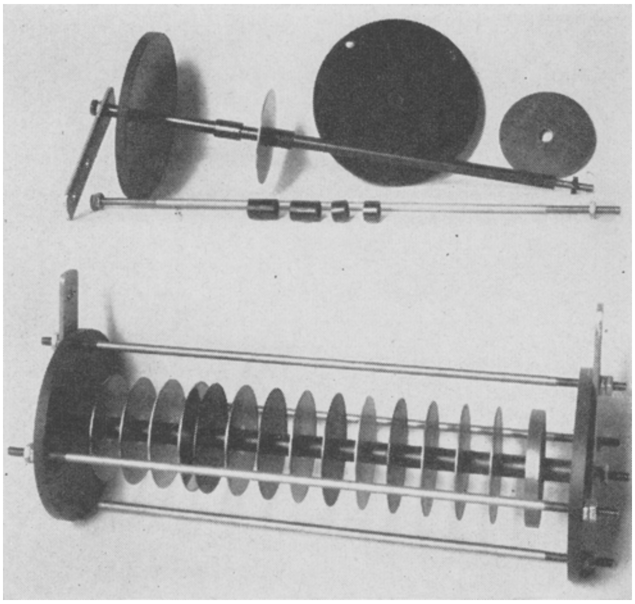

FIG. 1. Spool-type specimen holder used in testing corrosion of metals in plant equipment.

Upon completion of tests, the test spools were removed, dismantled, and the specimens examined, cleaned of all scale and corrosion product, and reweighed. From the weight losses, areas of specimens and duration of exposure, the corrosion rates were calculated in terms of mg. per sq. dm. per day and these rates transposed to inch penetration per year (ipy), the unit used in the accompanying tables. This unit is based upon the assumption of uniform corrosion in practice from one side of the metal only. The rate shown for each material is the average of the two specimens included in each test. In addition, each specimen was examined for cracking, pitting, and other forms of local attack. Where pitting or local attack occured, depth of the five or ten deepest pits was measured microscopically or with a depth gauge. In the accompanying tables maximum depth of pitting is reported where it occurred.

Approximate compositions of the metals and alloys included in one or more of these tests are shown in Table I.

Sulfated Oils

The sulfated oils, long used as wetting agents and penetrants, are made from a variety of animal and vegetable oils including castor, olive, tea seed, corn, peanut, lard, neats foot, and fish oils. They sometimes are referred to as sulfonated oils but more correctly are sulfated oils since the bond is mostly through the oxygen of a sulfate group. A common representative of this class of materials is sulfated castor oil, known as Turkey red oil, used in textile dying. Sulfation of animal and vegetable oils usually is done with 66° Bé sulfuric acid at temperatures from 20 to 60°C. (68 to 140°F.), and with good agitation during reaction. With some of the more highly unsaturated fats, temperatures must be kept in the neighborhood of 10°C.(50°F.). Sulfation usually is done in batches which may require from 6 to 24 hours, depending upon size of batch and nature of the oil. After sulfation, sodium sulfate or sodium chloride solutions are added to salt out the product which is separated, washed with glauber's salt solution, reseparated and finally neutralized with caustic soda, soda ash or ammonia. Frequently, washing and neutralization are done in the sulfation vessel.

The results of a number of plant corrosion tests in the sulfation, washing, and neutralization of oils in operating reactors are summarized in Table II. In Tests 1 to 6 inclusive, sulfation, washing, and neu-

TABLE I

Nominal Compositions of Metals and Alloys Used in Corrosion Tests

Metal or Alloy	Nickel %	Copper %	Chromium %	Iron %	Molybdenum %	Silicon %	Manganese %	Carbon %	Other %
Monel	67	30	....	1.4	....	0.1	1.0	0.15	....
"S" Monel	63	30	....	2	....	4	0.75	0.1	....
Nickel	99.4	0.1	....	0.15	....	0.05	0.2	0.05	....
Inconel	78.5	0.2	14	6.5	....	0.25	0.25	0.08	....
70-30 Copper-Nickel	30	70	....	....	....	....	....	....	....
Copper	....	99.9	....	....	....	....	....	....	....
Bronze (85-5-5-5)	....	85	....	....	....	....	....	....	Pb 5; Sn 5; Zn 5
Red Brass	....	85	....	....	....	....	....	....	Zn 15
Yellow Brass	....	65	....	....	....	....	....	....	Zn 35
Phosphor Bronze	....	96	....	....	....	....	....	....	Sn 3.75; P 0.25
Silicon Bronze	....	96	....	....	....	3	1	....	....
Hastelloy A	57	....	....	20	20	1	2	0.1	....
Hastelloy B	62	....	....	6	30	1	1	0.1	....
Hastelloy C	55	....	15	6	17	1	1	0.1	W 5
Hastelloy D	85	3	....	....	....	10	1	....	Al 1
Illium R	60	3	21	8	5	0.6	1.25	0.1	W 1
Illium G	58	6	22	6	6	0.6	1.25	0.2	....
Durimet 20	29	4	20	Bal.	3	1	....	0.07	....
Alloyco 20	29	4	20	Bal.	3	1	....	0.07	....
Worthite	24	2	20	Bal.	3	3	....	0.07	....
Pioneer Metal	35	....	25	Bal.	5	....	....	0.1	....
18-8 Stainless (Type 302)	9	....	19	Bal.	....	....	1.2	0.20 max.	....
18-8 Stainless (Type 304)	9	....	19	Bal.	....	....	1.2	0.08 max.	....
18-8 Mo Stainless (Type 316)	13	....	18	Bal.	2.25	....	1.5	0.08 max.	....
18-8 Mo Stainless (Type 317)	13	....	18	Bal.	3.25	....	1.5	0.08 max.	....
25-20 Stainless (Type 310)	20	....	25	Bal.	....	....	1.5	0.20 max.	....
25-12 Stainless (Type 309)	13	....	25	Bal.	....	....	1.5	0.20 max.	....
27 Cr Stainless (Type 446)	....	....	27	Bal.	....	....	1	0.35 max.	....
17 Cr Stainless (Type 430)	....	....	17	Bal.	....	....	1	0.12 max.	....
13 Cr Stainless (Type 410)	....	....	13	Bal.	....	....	1	0.15 max.	....
4-6 Cr Iron (Type 502)	....	....	5	Bal.	0.5	....	....	0.10 max.	....
Chemical Lead	....	....	....	....	....	....	....	....	Pb 99.9
Tellurium Lead	....	....	....	....	....	....	....	....	Te .04-.10; Pb Bal.
Antimony Lead	....	....	....	....	....	....	....	....	Pb 94.5; Sb 6
Duriron	....	....	....	Bal.	....	14.5	....	....	....
Ni-Resist Type 3	30	....	3	Bal.	....	1.5	0.6	2.75 max.	....
Ni-Resist Type 1	14.5	6	2	Bal.	....	1.8	1.3	2.8	....
Mild Steel	....	....	....	Bal.	....	0.25	0.45	0.2	....
Cast Iron	....	....	....	Bal.	....	1.8	0.5	3.4	....

TABLE II

Plant Tests in Sulfation of Animal and Vegetable Oils

Sulfations of various vegetable and animal oils with 66° Bé sulfuric acid. Test spool immersed in agitated liquid in sulfation reactors during sulfation, washing, and neutralization, except Tests 7, 8, and 9 involving sulfation only. Acid added was about 20 to 25% by weight of oil in each batch.
Temperature: 20° to 60°C.(68° to 140°F.)

Material	Corrosion Rate, inch penetration per 100 batches (a)						Corrosion Rate, inch per year (b) (c)		
	Test 1 During 16 Batches	Test 2 During 20 Batches	Test 3 During 25 Batches	Test 4 During 14 Batches	Test 5 During 40 Batches	Test 6 During 36 Batches	Test 7 During 70 Days	Test 8 During 7 Days	Test 9 During 20 Days
	Cod Liver Oil	Tallow, Red, Olive, and Castor Oils	Castor and Olive Oils	Neatsfoot and Fish Oils	Castor, Tea Seed, and Olive Oils	Olive and Red Oils	Animal and Vegetable Oils	Vegetable Oils	Peanut and Corn Oils
1. Monel	0.0005	0.0005	0.0008	0.005	0.0006	0.0002	0.0024	0.004	0.005
2. Nickel	0.001	0.0019(p)	0.0010	0.013	0.0010	0.0007	0.0032	0.011	0.010
3. Inconel	....	0.0012	....	0.018	0.0017	0.0004	0.0027	0.012	0.006
4. Hastelloy B	....	....	....	....	....	....	....	....	0.001
5. Hastelloy C	....	....	....	....	....	....	....	0.0005	....
6. Chemical Lead	0.0060	0.012	0.0031	0.011	....	0.0050	0.0019	0.023	0.018
7. Ni-Resist (Type 3)	....	....	....	....	....	....	....	0.015	....
8. Ni-Resist (Type 1)	0.0016	....	0.0016	0.022	0.0050	....	0.0054	0.024	....
9. Copper	....	0.0010(p)	....	....	0.0019	0.0020	....	....	....
10. Mild Steel	....	....	....	....	0.0061	....	....	....	....
11. Cast Iron	0.0070	....	0.039	0.11	....	....	0.0054	....	....
12. *Illium R*	....	....	....	....	....	....	....	0.007	....
13. Durimet 20	....	....	....	....	....	....	....	0.004	....
14. 18-8 Stainless (Type 304)	0.0011	0.0017(p)	0.0027(p)	0.024	0.0010(p)	....	0.0090	0.012	0.008
15. 18-8 Mo Stainless (Type 316)	....	....	....	....	....	....	....	0.011	0.010

(a) Production rates vary considerably at different plants. To standardize the results, corrosion rates in Tests 1 to 6 have been shown in in. penetration per 100 batches. Average production may run 150-250 batches per year. Batches are 12 to 24 hours in duration.

(b) The exact number of batches processed is not known so results of Tests 7, 8, and 9 are shown in inch penetration per year.

(c) Tests 7, 8, and 9 were made during sulfations only without washing and neutralization.

(p) Significant local attack in the form of pitting.

tralization were done in the same vessel. In Tests 7, 8, and 9 sulfation only was carried out. Due to variations in length of batches and other factors, the results of the first six tests have been reduced to a common basis and expressed as "inch penetration per 100 batches." The number of batches carried out per year may vary from about 150 to 250. In Tests 7, 8, and 9 the number of batches was not given so that corrosion rates have been shown as "inch penetration per year." The relative quantities of oil and acid varied, but the proportions used in Tests 3 and 8 probably are typical. In Test 3 each batch required 2,200 pounds of oil and 500 pounds of 66° Bé sulfuric acid and lasted 15 hours. In Test 8 each batch required an average of 4,125 pounds of oil and 1,085 pounds of 66° Bé acid. Corrosion rates in a quick sulfation process, using 98% sulfuric acid and acetic anhydride, are shown in Table III.

TABLE III

Plant Test in Quick Sulfation of Vegetable Oils

Immersed in sulfation reactor in mixture of vegetable oils and 96% sulfuric acid plus acetic anhydride. Sulfation being carried out only half of total exposure time. Exposure to vegetable oil only during balance of time. Agitated 90 r.p.m. under full load.
Temperature: 27°-46°C.(80°-115°F.).
Duration of test: 210 hours.

Material	Corrosion Rate, inch penetration per year
Monel	0.0010
Nickel	0.0029
Inconel	0.0015
Hastelloy C	0.0004
Illium R	0.0013
Chemical Lead	0.032

These test results are indicative of the good performance of Monel in the sulfation of animal and vegetable oils, which has been confirmed by its performance in operating reactors over a period of years. Monel is used for the construction of complete sulfators, linings, heating coils, agitators, pipe, fittings, pumps, and pump rods. Corrosion resistance is favored by the fact that the concentrated acid, when added, is dispersed in the oily media, which provide a somewhat protective film. The ultimate use of most sulfated oils calls for a product of high purity, with minimum discoloration. Users have observed that, in most cases, oils processed in Monel equipment are equivalent in color to those processed in glass. In the case of sulfated olive and tea seed oils there is some indication that nickel sulfating equipment may give better color. Monel also has good resistance to corrosion by the diluted sulfuric acid and the alkalis encountered in washing and neutralization equipment. The results of plant corrosion tests in the washing and neutralization of sulfated vegetable oils are shown in Table IV. The cast nickel-chromium-molybdenum-iron alloys containing silicon and/or copper such as the Durimet alloys, Alloyco 20, and Worthite are used for pumps and valves in sulfation and washing systems since they have suitable resistance to both concentrated and diluted sulfuric acid at the temperatures encountered. Type 1 Ni-Resist and acid resisting bronzes are used to some extent for pumps and valves although their corrosion rates usually are higher than the other materials mentioned.

Chemical lead has been, next to Monel, the material most commonly used for oil sulfation reactors, al-

TABLE IV

Plant Tests in Washing and Neutralization of Sulfated Oils

Test 1: Immersed half-way down in wash tank. Sulfated oil diluted 1 to 1 with water. Neutralized with 10% caustic soda. Agitated. Temperature 40°-60°C.(104°-140°F.). Duration of test 60 days.

Tests 2 and 3: Immersed in wash tank during washing, neutralization and panning. Sulfated vegetable oil mixed with approximately 5% sulfuric acid plus small amounts of sodium chloride and sodium sulfate. Agitated about 640 ft. per minute. Test 2 near bottom of tank in aqueous acid layer. Test 3 half-way up tank, principally in oil-acid mixture. Temperature 50°C.(122°F.). Duration of test 45 days.

Material	Corrosion Rate, inch per year		
	Test 1	Test 2	Test 3
Monel	0.0005	0.0030	0.0032
Nickel	0.0013	0.0044	0.0043
Inconel	0.0008	0.0030	0.0029
Hastelloy B	....	0.0023	0.0030
Hastelloy C	....	0.0003	0.0002
Durimet 20	....	0.0041	0.0043
Ni-Resist (Type 1)	0.006	0.017	0.018
Cast Iron	0.19	0.15	0.12
Chemical Lead	0.009	....	....
18-8 Stainless (Type 304)	0.0035	0.009	0.010
18-8 Mo Stainless (Type 316)	....	0.005	0.007
Bronze	0.0017	....	....

though subject to some attack, particularly by the alkaline solutions used for neutralization. The stainless steels are subject to attack by sulfuric acid solutions in the range of concentrations from about 20% to 80% and consequently are usually not used for oil sulfonation equipment where these concentrations occur. Type 316 stainless steel is used to some extent for washing and neutralization equipment where more dilute acid solutions are encountered.

Nickel-clad, Inconel-clad, and stainless-clad steels are used for the storage of finished sulfated oils. The use of the clad steels for large tanks provides economy as well as protection for the product. The results of some laboratory corrosion tests in several finished sulfated oils are shown in Table V. In view of the fact that these corrosion rates are so low, they have been shown in terms of mg. per sq. dm. per day (mdd) as well as the customary unit of inch penetration per year (ipy).

TABLE V

Laboratory Corrosion Tests in Finished Sulfated Oils

Test 1: In sulfated red oil. Stirred 3 or 4 times a day. Duration 7 days. Room temperature.

Test 2: In sulfated castor oil. Duration 21 days. Room temperature.

Test 3: In sulfated olive oil. Duration 21 days. Room temperature.

Material	Corrosion Rate							
	Test 1				Test 2		Test 3	
	Immersed		Partly Immersed		Immersed		Immersed	
	mdd	ipy	mdd	ipy	mdd	ipy	mdd	ipy
Nickel	1.2	0.0002	3.3	0.0005	0.1	0.00002	0.3	0.00005
Monel	1.2	0.0002	4.3	0.0007	....	....	....	....
Inconel	0.9	0.0002	1.5	0.0003	....	....	....	....

Sulfated Alcohols and Sulfonated Aromatics

A wide variety of detergents and wetting agents are now made by the sulfation of fatty alcohols such as lauryl, myristyl, oleyl, cetyl, and stearyl alcohols, or of fatty esters such as the mono-glycerides, and can be referred to generally as aliphatic or alkyl sulfates. In most cases these are converted to corresponding sodium, potassium, or ammonium salts by treatment with the corresponding alkali for use as detergents. They frequently surpass soap and sulfated oils in wetting out, emulsifying, and detergent properties, do not hydrolyze to alkali in water, and show no tendency to turn rancid in storage. They generally are stable toward acids, alkalies, and salts and are not precipitated by the hardness (Ca. and Mg. ions) present in most natural waters.

Another important group of surface-active agents are those based upon the sulfonation of aromatic hydrocarbons such as benzene and naphthalene. A class of detergents referred to as alkyl aryl sulfonates are prepared by connecting paraffin hydrocarbon groups, such as a keryl or kerosene group, to benzene sulfonic acid and treating the resulting material with alkali. Products of this type are manufactured in petroleum refineries as well as other plants. Benzene sulfonic acid also is prepared as an intermediate product in the synthesis of phenol. Naphthalene sulfonic acids, in addition to serving as a base for wetting agents and detergents, are used for the production of naphthols to serve as dye intermediates.

A considerable number of these sulfations and sulfonations are made with strong sulfuric acid or with oleum at moderate temperatures. Where the sulfuric acid concentration is not allowed to fall below about 80% during the reaction, steel and cast iron reaction equipment generally is used. In some cases where 66° Bé sulfuric acid is used and acid concentrations are likely to fall below 80%, the use of Monel sulfonating equipment would be indicated as shown by the test results in Table VI during sulfonation of naphthalene. These tests unfortunately did not include steel or cast iron specimens for direct comparison. However, in another test, shown in Table VII during sulfonation of phenol with 98% acid at 120°C. (250°F.) and where the acid was diluted with water, mild steel showed a high corrosion rate. Monel, chemical lead, Hastelloy alloys A and B, Alloyco 20, and Illium were observed to have suitable corrosion resistance under these conditions.

TABLE VI

Laboratory Corrosion Tests in Sulfonation of Aromatic Hydrocarbons with Sulfuric Acid

Test 1: Sulfonation of naphthalene to make naphthalene sulfonic acid. Start with 93% sulfuric acid which is diluted with water to about 30% acid concentration at end of sulfonation. Duration of test: 29 hours at sulfonating temperature of 165°C.(330°F.); 792 hours at 30°C.(86°F.) due to plant shutdown. Test spool immersed in liquid. Agitation during sulfonation.

Test 2: Sulfonation of aromatic hydrocarbons with 94% sulfuric acid. Acid concentration at end of sulfonation 80% H_2SO_4. Test specimens immersed in liquid in laboratory sulfonator. Solution agitated. Temperature: 50°C.(122°F.). Duration of test: 24 hours.

Material	Corrosion Rate, inch per year	
	Test 1	Test 2
	Based on 29 hours at 165°C.	
Monel	0.006	0.014
Nickel	0.006	0.022
Inconel	0.012	0.050
18-8 Mo Stainless (Type 316)	1.85	....
25-20 Stainless (Type 310)	2.54	....
Worthite	1.68	....
Durimet 20	0.067	....
Hastelloy B	0.036	....
Hastelloy D	0.015	....
Chemical Lead	0.045	....
Tellurium Lead	0.041	....
Duriron	Gain	....

TABLE VII

Plant Test in Sulfonation of Phenol with 98% Sulfuric Acid

Immersed in sulfonation kettle during 20 batches of 12.5 hours each. Water added during last one-half hour of batch and solution neutralized to pH 3. Make 180 batches per year.

Temperature of sulfonation: 120°C.(248°F.).
Duration of test: 40 days (20 batches).

Material	Corrosion Rate, inch per year, based on 180 batches per year
Monel	0.005
Nickel	0.012
Inconel	0.016
Hastelloy A	0.006
Hastelloy B	0.002
Illium R	0.007
Alloyco 20	0.008
Mild Steel	0.26
Chemical Lead	0.003
18-8 Stainless (Type 304)	0.062
18-8 Mo Stainless (Type 316)	0.14
18-8 Mo Stainless (Type 317)	0.14
25-12 Stainless (Type 309)	0.047
25-20 Stainless (Type 310)	0.040

Where sulfonations are carried out with strong oleums at high temperatures such as 165 to 175°C. (330 to 350°F.), or with weaker sulfuric acid solutions at unusually high temperatures such as 225°C. (440°F.), corrosion rates of all common metals and alloys are likely to be high as indicated by the test results shown in Table VIII. In these cases, sulfonators probably would be made of glass-lined steel or other non-metallic material.

TABLE VIII

Plant Tests in Organic Sulfonations at High Temperatures

Test 1: Sulfonation of pyridine with 65% oleum. Temperature: 165-175°C.(329-347°F.). Duration: 45 hours.

Test 2: Sulfonation of naphthalene with 20% oleum. Temperature 175°C.(347°F.). Duration: 10 hours.

Test 3: Sulfonation of weak organic base under 260 psi, gauge pressure. Mixture composed of 1,000 lb. organic base, 790 lb. 66°Bé sulfuric acid and 2,515 lb. water. Stirred at 35 r.p.m. Temperature: 225°-230°C.(437°-446°F.). Duration of tests: 48 hours and 272 hours.

Material	Corrosion Rate, inch per year			
	Test 1	Test 2	Test 3	
			48-hr. test	272-hr. test
Monel	1.2	0.84	0.16	0.19
"S" Monel	......	0.81	......	......
Nickel	......	1.51	1.48	......
Inconel	0.15	1.67	1.48	......
Hastelloy A	......	0.64	......	......
Hastelloy B	......	....	0.27	0.41
Hastelloy C	0.072	0.77	2.01	......
Hastelloy D	0.38	....	......	......
Illium G	0.15	....	......	......
Illium R	......	....	(x)	......
Worthite	0.038	2.38	......	......
Durimet 20	0.053	....	......	......
Ni-Resist (Type 1)	1.26	....	......	......
Cast Iron	1.45	....	......	......
Duriron	0.059	....	0.38	0.15
Chemical Lead	......	....	0.050	0.094
Antimony Lead	......	....	0.029	0.026
Tellurium Lead	......	....	0.11	0.11
Silicon Bronze	......	....	0.043	0.13
18-8 Stainless (Type 304)	0.12	....	......	......
18-8 Mo Stainless (Type 316)	0.070	....	......	......
25-12 Stainless (Type 309)	0.063	....	......	......
25-20 Stainless (Type 310)	0.11	....	......	......
17 Cr Stainless (Type 430)	0.84	....	......	......
13 Cr Stainless (Type 410)	1.34	....	......	......
4-6 Cr Iron (Type 502)	3.26	....	......	......
Mild Steel	2.12	....	......	......

(x) Corroded entirely away. Original thickness 0.031 inch.

Washing and neutralization of naphthalene sulfonic acid usually can be done in Monel or Type 316 stainless steel equipment as indicated by the test results in Table IX. Considerable Monel and stainless steel equipment is used for the handling of alkyl aryl sulfonates in petroleum refineries and in other plants, both before and after treatment with alkalies. The results of corrosion tests in the storage of a liquid alkyl aryl sulfonate detergent are given in Table X.

TABLE IX

Plant Test in Washing and Neutralization of Naphthalene Sulfonic Acid

Immersed in washing of naphthalene sulfonic acid (containing 50% solids) at pH 1, followed by neutralization with soda ash to pH 3. Agitated at 145 r.p.m.

Temperature: 35°-70°C.(95°-158°F.).
Duration of test: 80 hours.

Material	Corrosion Rate, inch penetration per year
Monel	0.013
Nickel	0.030
Inconel	0.022
Hastelloy A	0.013
Ni-Resist (Type 1)	0.061
Mild Steel	2.2
Cast Iron	4.0
Chemical Lead	0.039
18-8 Stainless (Type 302)	0.040
18-8 Mo Stainless (Type 316)	0.011
Copper	0.020

Inconel and Type 316 stainless steel, either in solid or clad-steel form, are used for the storage and handling of some alkyl sulfate base materials after production and before neutralization. The corrosiveness of these materials will depend upon whether free sulfur dioxide is present in appreciable amount. If so, corrosive conditions may be severe, particularly in the vapor sections of closed storage tanks where sulfur dioxide has an opportunity to accumulate and a sulfurous acid solution to condense. Worthite and the Durimet alloys also are used for pumping these materials. Inconel-clad steel towers are used for the spray-drying of some sodium alkyl sulfate detergents where protection of white color as well as corrosion resistance are factors.

TABLE X

Plant Test in Storage of Liquid Alkyl Aryl Detergent

Composition: 25% active and 10% sodium sulfate. Immersed in liquid phase.

Temperature: 48°-57°C.(115°-135°F.). Duration of test 37 days.

Material	Corrosion Rate	
	mdd	ipy
Monel	0.12	0.00002
Nickel	0.03	<0.00001
Inconel	0.08	0.00001
18-8 Stainless (Type 304)	0.03	<0.00001
18-8 Mo Stainless (Type 316)	0.10	0.00002
18-8 Mo Stainless (Type 317)	0.06	0.00001
Copper	0.45	0.00007
Red Brass	0.42	0.00007
Yellow Brass	0.37	0.00006
Phosphor Bronze	0.36	0.00006
70-30 Copper-Nickel	0.14	0.00002
Chemical Lead	2.4	0.00030
Ni-Resist (Type 1)	0.13	0.00003

< Less than.

TABLE XI

Corrosion Tests in Condensation of Naphthalene Sulfonic Acid with Formaldehyde

Test 1: Test spool immersed in liquid in laboratory reactor. Duration of test: 29 hours at 110°C.(230°F.); 792 hours at 30°C(86°F.) due to plant shut-down. Agitation during elevated temperature operation only.

Test 2: Plant tests in liquid and vapor phases in operating autoclave. Duration of tests: 9 days. Temperature: 115-145°C.(240-293°F.). Pressure: 50 psi.

Material	Corrosion Rate, inch per year		
	Test 1	Test 2	
	Based on 29 hrs. at 110°C.	Liquid	Vapor
Monel	0.007	0.012	0.040
Nickel	0.010	....	0.14
Inconel	0.017	....	0.075
18-8 Mo Stainless (Type 316)	>4.80	....	....
25-20 Stainless (Type 310)	1.10	....	....
Worthite	0.015	....	....
Durimet 20	0.015	....	....
Hastelloy B	0.003	....	....
Hastelloy D	0.006	....	....
Chemical Lead	0.052	....	....
Tellurium Lead	0.053	....	....
Duriron	0.007	....	....

> Greater than. Specimens destroyed by corrosion during test.

TABLE XII

Laboratory Test in Sulfonation of Oleic Acid with Chlorosulfonic Acid

Used 80 parts oleic acid to 20 parts chlorosulfonic acid. Stirred once a week.

Temperature: 20°-45°C.(68°-113°F.).
Duration of test: 42 days.

Material	Corrosion Rate, inch per year	
	Liquid	Vapor
Monel	0.0033	0.0019
Nickel	0.0023	0.0004
Inconel	0.0013	0.0007
18-8 Stainless (Type 304)	0.0021	....
25-20 Stainless (Type 310)	0.0015	0.0013
18-8 Mo Stainless (Type 316)	0.0020	0.0020
17 Cr Steel (Type 430)	0.0035	0.0018
Durimet 20	0.0010	0.0033
Hastelloy B	0.0003	0.0001
Silicon Bronze	0.0063	....
Phosphor Bronze	0.013	....
Chemical Lead	0.037	....
Mild Steel	0.0056	....

Corrosion tests have been made in the condensation of naphthalene sulfonic acid with formaldehyde, with the results shown in Table XI. Monel has shown suitable resistance in this application at 110°C.(230°F.) as indicated in Test 1. However, in Test 2, when operating at 115-145°C.(240-293°F.) under 50 psi. pressure there was evidence that sufficient sulfur dioxide may have collected in the upper part of the vessel to significantly increase the corrosion rate in the vapor phase. A Monel agitator and shaft was used in this reactor, and the shaft showed some increased corrosion in the vapor phase.

TABLE XIII

Laboratory Tests in 99.5% Chlorosulfonic Acid

Half-immersed in liquid in open beakers.
Temperature: Room.
Duration of test: 30 days.

Material	Corrosion Rate		Appearance
	mdd	ipy	
Monel	0.84	0.0001	Greenish discoloration above liquid line
Nickel	Gain		Heavy green discoloration above liquid line
Inconel	0.17	0.00003	No discoloration or attack
18-8 Stainless (Type 304)	0.56	0.0001	Dulling of finish above liquid line

Other Sulfonations

The results of laboratory tests in the sulfonation of oleic acid with chlorosulfonic acid at 20 to 45°C. (68 to 113°F.) are shown in Table XII. It is evident that a good many materials, with the exception of lead, have suitable resistance at this temperature. In view of the laboratory tests in chlorosulfonic acid as shown in Tables XIII and XIV, it is probable that Inconel would be considered a suitable material from the standpoint of product color. No test results are yet available in chlorosulfonic acid sulfonations at higher temperatures although such tests are now in progress. In view of the probable formation of hydrogen chloride, corrosion rates would appear to depend upon amount of water present. Among the wrought materials it would be expected that Hastelloy B, nickel, Monel, and Inconel would have the best corrosion resistance in the order named.

TABLE XIV

Laboratory Tests in Mixture of 50% Chlorosulfonic Acid and 50% Sulfur Trioxide

Exposed in liquid and vapor phases.
No agitation.
Temperature: 10°-29°C.(50°-84°F.).
Duration of test: 145 days.

Material	Corrosion Rate			
	Liquid		Vapor	
	mdd	ipy	mdd	ipy
Monel	0.19	0.00003	0.08	0.00001
Nickel	0.24	0.00004	0.11	0.00002
Inconel	0.06	0.00001	0.05	0.00001
Hastelloy A	1.8	0.0003	0.93	0.0002
Hastelloy B	0.12	0.00002	0.09	0.00002
Mild Steel	1.8	0.0003	0.41	0.00008
Chemical Lead	>380.0	>0.048	5.0	0.0006

> Greater than. Specimens destroyed by corrosion.

In sulfonations with bisulfite solutions, corrosive conditions are likely to be very severe as they are in all hot strong sulfurous acid conditions. Since Hastelloy C normally has the best resistance to such conditions, it would be expected to show best performance and this is confirmed by the test results in Table XV during sulfonation of a tri-basic organic acid with sodium meta-bisulfite. Such cast materials as Illium, Pioneer Metal, and Worthite should be suitable for valves and pumps. Corrosive conditions probably also would prevail during washing of these sulfonates so long as an appreciable concentration of SO_2 remained. At the low temperatures associated with washing Types 316 and 317 stainless steels and lead should be used.

TABLE XV

Plant Test in Sulfonation of Organic Acid with Sodium Meta Bisulfite

Sodium metabisulfite and sulfuric acid added to organic acid at 85°-90°C.(185°-194°F.). Each batch 3 hours. Duration of test, 3 batches or 9 hours. Test spool partially immersed at liquid vapor interface in 50-gallon reactor.

Material	Corrosion Rate, inch per year
Monel	0.14
Nickel	0.17
Inconel	0.049
Hastelloy C	0
Worthite	0.007
Illium R	0.009
Pioneer Metal	0.006
Ni-Resist (Type 1)	0.36
18-8 Stainless (Type 304)	0.11
18-8 Mo Stainless (Type 316)	0.12

Most of the corrosion tests reported here were made in response to questions concerning the corrosion resistance of materials in specific processes. They cover only a limited number of the possible operating conditions which may be encountered in organic sulfonations. Additional tests are being made as the occasion demands and these should help to define more clearly the limiting conditions for the use of the various metals and alloys.

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