TABLE III

	Plants			
	Bay Minette[a]	Jesup	St. Marys	Pensacola
% Rosin acid	42.5	45.0	52.4	46.6
% Fatty acid	48.4	43.0	35.7	42.1
% Ash	....	0.025	0.02 to 0.05	0.025
% Mineral acid	0.011	0.002 to 0.004	0.002 to 0.020	0.002 to 0.009
% Neutrals	2.13	2.0 to 2.7	1.5 to 1.7	1.38
% Unsaponifiable	4.6	7.8	8.4	6.6
% Lignin	0.23	0.09 to 0.16	0.11 to 0.26	0.06 to 0.25
% Moisture[b]	2.1	1.1 to 1.5	1.5 to 1.9	1.5 to 1.7
Acid value	....	169	166	170
Lovibond color[c]	....	35/4.0	35/2.4 to 3.0	35/1.5 to 2.4

[a] Semicontinuous plant.
[b] From centrifuge; 0.6% or less from storage tank.
[c] 5% in benzol, 1 in.

hand-treated. Consequently the reaction time, the treat, and the skimming-off of tall oil are subject to human error. Two washing plants have been installed for a major naval stores producer at two tall oil distillation plants. Briefly the system consists of an AC-VO nozzle-type centrifuge, as used in the continuous tall oil installations, preceded by water washing. Wash water is mixed with the crude tall oil fed to the centrifuge in order to remove the soap, excess mineral acids, and lignin present in most of the batch-produced tall oil. This company has found it imperative that lignin be reduced to a minimum before distilling. From the standpoint of corrosion in their expensive fractionating towers, excess mineral acids must also be reduced to a negligible amount.

This washing system is not required on tall oils produced in the continuous acidulation process, even if they are distilled. For that matter it is not essential for tall oil from batch systems, which are very well controlled.

Summary

The conventional batch process for tall oil production was changed to a semicontinuous one by properly sizing tanks to reaction times and adding a screen and a continuous centrifugation step.

As a further improvement an entirely new, continuous acidulation process has been developed which includes proportioning of reagents, controlled mixing, and degasification, followed by tall oil separation in a special form of nozzle type of centrifuge. Both these processes produce higher quality tall oil at lower cost than the original batch process.

The economy of the process has been improved by modifying the centrifuge to remove fibers, which eliminates a costly and troublesome screening step. Lowest costs are produced by a plant specifically designed to use waste acid from a chlorine dioxide bleaching process.

Acknowledgments

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Corrosion Testing and Corrosion Problems in Processing of Tall Oil

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IT IS OUR INTENT to present information on the corrosion problems encountered in tall oil processing. Some of the information is new, some has been published previously. We shall briefly summarize some of the information published to date, present new plant corrosion test data, and point up areas where empirical corrosion data are lacking or conflicting.

Corrosion test work may be performed in several stages. Laboratory tests using actual or synthesized solutions yield a great deal of information and, in the absence of other means of testing, must be the basis for construction of process equipment.

The next step in corrosion testing frequently will be the pilot-plant stage. Corrosion can be studied by visual observation of corrosion effects on equipment. Samples exposed to the solution can additionally be analyzed by weight loss computed to traditional units for expressing corrosion penetration as inches per year or mils per year.

The ultimate stage for testing would be in the operating plant. Samples exposed to operating conditions of the full-scale plant will yield the most accurate corrosion information. Differences of significance may exist between plant conditions and laboratory or pilot operations, producing inaccurate and sometimes erroneous results. Plant corrosion information comes from examination of equipment after service periods or from special test rods carrying samples of interest as potential construction material. Examination of equipment will yield only qualitative results. Test rods also furnish information of a qualitative nature, and, of greater importance, quantitative

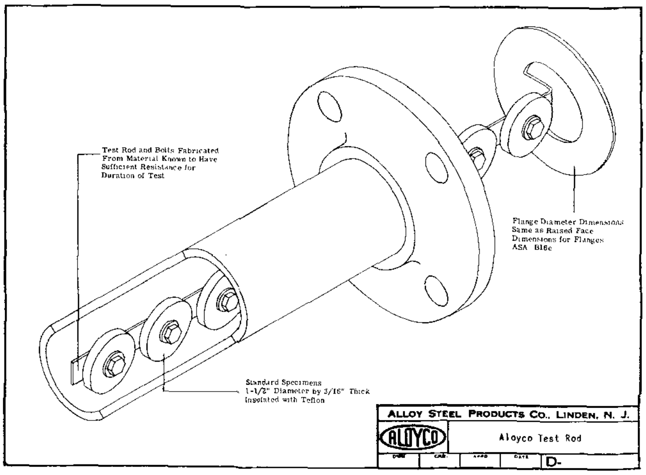

FIG. 1.

data are obtained which can be used for accurate selection of materials.

The type of test rod which we have used in our collaborative plant tests is shown schematically in Figure 1. This rod is designed to be inserted in a flanged process line of any size, 2 in. or larger. The test rod adapter is sized to match the diameter of the raised face flange on the line where the rod is to be installed. The pressure drop is minor and can be tolerated in nearly any operating line. Each rod is custom-built to the proper size and of materials which will withstand the exposure. We normally suggest a minimum exposure time of 60 days. Shorter exposure times may lower the accuracy of the results.

Figure 2 shows test rods constructed and ready for installation. All samples are normally insulated from each other and from the rod-supporting members. When desired, dissimilar materials are coupled together to determine effects from the couple. In other instances some samples may be connected to the rod material and the test rod adapter connected to the piping system to determine effects from dissimilar materials under these conditions. The rod can also be furnished without the flange adapter for installation in a tank or reactor.

Table I shows corrosion test results in a tall oil recovery system. The solution consisted of tall oil and naphtha plus sulfuric acid at a temperature of 200°F. maximum. The solution is noncorrosive to the austenitic stainless steels except 18-8 (304), which shows a low-weight-loss corrosion rate (.0028 in. per year) with some localized attack plus pitting to a depth of .009 in. in a two-month exposure.

TABLE I

Tall Oil Recovery System

Solution: Oil—Naphtha plus sulfuric acid
Temperature: 200°F. maximum
Exposure: 1,440 hrs.

Spec. No.	Alloy	Pen. in./yr.	Remarks
1	Stainless type 316	.0000	No attack
2	Aloyco 20	.0000	No attack
3	Worthite	.0000	No attack
4	Stainless type 304	.0028	Some pitting and localized attack
5	Ampco 18	.0336	Heavy general attack
6	Carbon steel	......	Completely corroded

TABLE II

High Temperature Reactor

Solution: Successive esterifications, amidizations, and sulfurizations of tall oil
Temperature: 300°F. average, 550°F. maximum
Exposure: 421 hrs.

Material	Indicated corrosion rate—inch penetration per year	
	Liquid	Vapor
Monel	0.022	0.012
Nickel	0.038	0.014 [a]
Inconel	0.005	0.0003
18-8S Stainless Steel	0.009	0.0001 [b,c]
18-8Mo Stainless—Type 316	0.0014	0.0001 [c]
Hastelloy B	0.0065	0.006
Hastelloy C	0.0001 [c]	0.0001 [c]
Aloyco 20	0.0006	0.0001 [c]
20% Ni cast iron	0.013	0.016
Ni-resist	0.0062	0.012

[a] Pitting in surface to maximum depth of 0.006 in.
[b] Pitting in surface to maximum depth of 0.002 in.
[c] Less than.

Table II (1) gives the results of plant corrosion test covering successive esterifications, amidizations, and sulfurizations of tall oil. Type 316 is satisfactory for this service. Several other materials are equally suitable but more costly so 316 would be first choice for all classes of equipment.

Laboratory corrosion tests in refined tall oil were reported upon by Teeple (2). These tests were run at various temperatures to determine the effect of temperature on the resistance of the materials. Under the conditions of test, 316 stainless is resistant up to 575°F., but above that temperature the resistance of 316 drops appreciably. La Que and Clarke (3) reported on plant tests of fatty acids from tall oil, giving results both on samples exposed in the liquid and vapor phases. The liquid-phase temperature of test was 530°F., and results show considerably higher rates at this temperature in plant test than were reported for the 545°F.-laboratory tests by Teeple. The specific solution compositions were not given so it is impossible to draw definite conclusions as to the reasons for the variation in corrosion rates reported by these two studies.

We have recently completed evaluation of corrosion test results on samples exposed to solutions at the base of two different tall oil fractionating towers. The exposure temperature was the same in both cases, but the solution conditions were quite different (Tables III and IV).

All of the austenitic stainless steels, except type 304, were resistant to the solution of 20% fatty acids,

TABLE III

Base of Tall Oil Fractionating Tower

Solution: 20% oleic-linoleic acids, 60% rosin acids, and 20% tall oil pitch
Temperature: 265°C.(509°F.)
Exposure: 1,296 hrs.

Spec. No.	Alloy	Pen. I.P.Y.	Remarks
A-1	Stainless type 304	0.1849	Very heavy even corrosion
A-2 [a]	Stainless type 316, 2.2% Mo	0.0001	Very light spotty etch, many very small pits, .001 to .002 in. deep
A-3 [a]	Stainless type 316, 2.5% Mo	0.0001	Same as A-2
A-4	Aloyco 20	0.0000	Bright and clean, no evidence of attack
A-5	Stainless type 317	0.0000	Same as A-4
A-6	Monel	0.0066	Heavily scaled and moderately etched
A-7	Mild steel	......	Completely corroded

[a] Chemical composition of samples A-2 and A-3:

Sample	Heat #	Cr	Ni	Mo	MN	Si	C
A-2	7053	19.32	10.49	2.20	0.52	0.86	.020
A-3	5041	19.33	10.37	2.54	0.55	0.80	.048

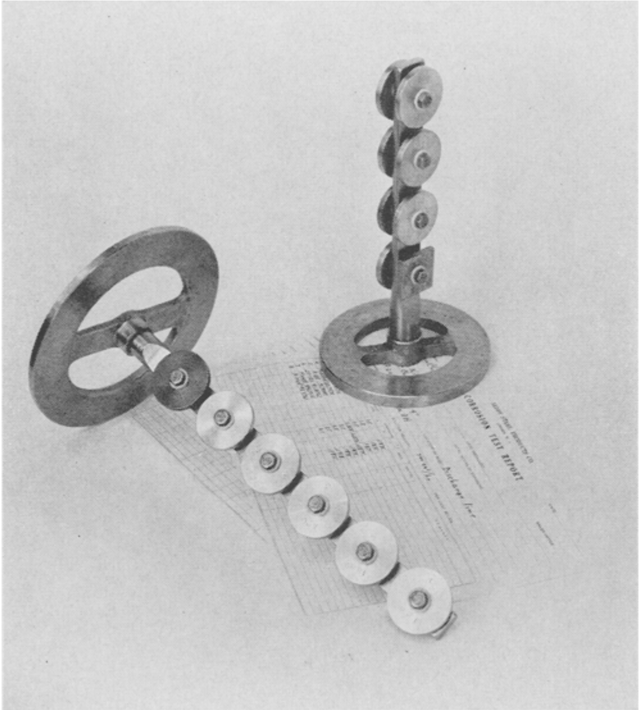

FIG. 2.

60% rosin acids, and 20% tall oil pitch at 509°F. (Table III).

The samples exposed to the solution of 65% fatty acids and 35% rosin acids (Table IV) were heavily attacked except for the 317 alloy sample. The monel sample does not show a high-weight-loss corrosion rate; however selective attack under the metal washer holding the sample and heavy attack at the edges of the specimen would rule out the use of monel. The corrosion rate of 317 alloy would be acceptable for equipment where corrosion allowances can be made. The corrosion rate for 317 alloy is too high for satisfactory use in construction of low-corrosion-tolerance equipment such as valves. Because of this, an additional test rod is presently being exposed to this solution for the purpose of selecting an alloy which would be suitable for equipment such as valves.

These results show the effect of solution composition change on corrosion rate even at the comparatively moderate temperature of 509°F. The corrosion results shown in Tables III and IV demonstrate the very potent effect of solution composition changes on corrosion rate. This appears to be one area where empirical corrosion data are lacking, and additional corrosion work is necessary at the present time.

TABLE IV

Base of Tall Oil Fractionating Tower

Solution: 65% fatty acids, 35% rosin acids, in liquid phase
Temperature: 265°C.(509°F.)
Exposure: 3,216 hrs.

Spec. No.	Alloy	Pen. I.P.Y.	Remarks
B-1	Aloyco 18-8S (304)	......	Completely corroded
B-2 [a]	Aloyco 18-8S Mo, 2.2% Mo (316)	......	Specimen lost
B-3 [a]	Aloyco 18-8S Mo, 2.5% Mo (316)	0.0342	Very heavily etched, somewhat heavier attack adjacent to metal washers
B-4	Aloyco 20	0.0275	Heavy even etch
B-5	Stainless type 317	0.0087	Moderate to heavy etch, slightly heavier attack in area adjacent to metal washer
B-6	Monel	0.0089	Heavy tenacious protective coating, selective attack under metal washer, heavy attack at edges of specimen, where coating was apparently abraded off
B-7	Carbon steel	......	Completely corroded

[a] Chemical composition of samples B-2 and B-3:

Sample	Heat #	Cr	Ni	Mo	MN	Si	C
B-2	7053	19.32	10.49	2.20	0.52	0.86	.020
B-3	5041	19.33	10.37	2.54	0.55	0.80	.048

Type 316 stainless steel is necessary to withstand the corrosive conditions of the tall oil recovery system. Type 304 is not suitable for this service because of the pitting attack of the solution on this alloy. Worthite and Aloyco 20 alloy were also found to be suitable for the service.

Distillation and fractionation of tall oil requires 316 alloy as a minimum. For some conditions, *i.e.*, higher temperature and some solutions, additional alloying is required, for example type 317. In the test results given in Table III, increase of molybdenum content from 2.2% to 2.5% did not eliminate the minor pitting of the 316 alloy. The process conditions which require molybdenum contents in excess of the 2.5% are not clearly outlined on the basis of data presented here. Additional testing would be necessary to determine more accurately the point to which type 316 of 2.5% molybdenum content is usable and where higher molybdenum contents are required.

With an additional increase in temperature (above 575°F. as indicated on laboratory tests), 317 alloy becomes unsuitable for use. Of the materials tested at higher temperature, Hastelloy C and Inconel have the best resistance to attack.

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• *Letter to the Editor*

On the Origin of Stearic Acid in Ruminant Depot Fat

IN 1951 Reiser (1) reported that rumen contents were capable of partially hydrogenating linolenic acid and later (2) explained that the high level of saturated fatty acids in ruminant fat resulted from hydrogenation by rumen bacteria. Similar studies have been made by others (3, 4). Later the evidence (5) was reviewed, and new data were presented to support the hypothesis.

If it should be true that the stearic acid of ruminant depot fat is from hydrogenated C_{18} unsaturated acids of the diet, it should follow that a ruminant animal reared on a ration free of fat would develop depot