

## AN INTERESTING CASE OF BOILER-TUBE CORROSION

By F. LÓPEZ DOMÍNGUEZ and R. FERNÁNDEZ GARCÍA,  
Chief and Associate Chemists, respectively, Insular Experiment Station

In the month of February of the present year, the Insular Experiment Station was informed by the manager of one of the sugar factories of the Island that an unusual corrosion had been taking place in their boiler tubes and that so far they had been unable to find the cause for it, or an appropriate method for its control. They requested, therefore, that the case be investigated by the Station.

Complying with orders of the Director we proceeded in his company to visit the factory, where the following information was obtained:

1. For fourteen years they had been using to feed their boilers, which are of the fire-tube type, water from a stream flownig by the factory, mixed with condensation water from the evaporators, and for the boilers of the locomotives, water from the stream exclusively.

2. The observation was made that there were incrustations left by these waters, and to prevent this they decided to cover the tubes of the factory boilers with graphite paint. This practice was begun in the year 1917.

3. By the end of 1923 on inspecting the factory boiler tubes, some of them were found to be badly corroded; new tubes were then substituted for these corroded tubes.

4. Shortly after the beginning of the 1924 crop a very rapid corrosion of the tubes was noticed. This went to such an extreme that a new set of tubes was ordered from the States. They estimated the expenses incurred on account of this trouble, including the new order for tubes, at \$20,000.

5. The tubes of the locomotive boilers, on the other hand, in which only stream water was used, showed no sign of corrosion but, on the contrary, they were found to be covered with a thick crust of mineral residues. On first consideration of the problem, then it looked as if the corrosion might be due to acidity in the condensation waters, since the water from the stream was capable of forming incrustations. With this idea in mind, we proceeded to take samples of the condensation waters from the evaporators and from the feeding tanks as well as from boilers 1 and 3, the only ones containing water

which had not been changed for the last 24 hours. As additional sources of information we also took samples of the waters from the stream and of the crust found in the tubes of the locomotive boilers.

The water samples from the boilers were of a dark color with a green tinge, and contained black particles in suspension. It was in explanation of this that we were informed that graphite paint had been used in the tubes and that this was the cause of the color of the water.

The samples were brought to the laboratory and the following tests were made:

1. Alpha naphthol tests for sugars in the condensation waters and in the water from the feeding tank. All tests negative.

2. Acidity in 10 cc. of water:

Boiler No. 1.....	9.1 cc. of n/100 Na OH
Boiler No. 3.....	30.5 cc. of n/100 Na OH
Quadruple effect.....	Clean transparent water without traces of oil
Evaporator No. 1.....	0.54 cc. of n/100 Na OH
Evaporator No. 2.....	0.22 cc. of n/100 Na OH
Evaporators Nos. 2, 3, 4 mixed.....	0.35 cc. of n/100 Na OH
Feeding tank.....	0.84 cc. without traces of oil

3. Iron in solution in parts per million:

Boiler No. 1.....	0.216 cc. $Fe_2O_3$
Boiler No. 3.....	0.264 cc. $Fe_2O_3$

4. Analysis of water from the stream:

Loss on ignition.....	102.0 parts per million
Bicarbonates $HCO_3'$ .....	103.1 parts per million
Sulphates $SO_4''$ .....	6.5 parts per million
Chlorides Cl.....	18.7 parts per million
Sodium $Na'$ .....	18.8 parts per million
Calcium $Ca''$ .....	14.7 parts per million
Magnesium $Mg''$ .....	4.1 parts per million
Aluminium $Al_2O_3$ .....	4.0 parts per million
Silica Si $O_2$ .....	34.1 parts per million

5. Incrustation from the locomotive boilers:

Qualitative analysis: Iron, calcium, aluminium, magnesium and silicon present.

The foregoing data show:

1. That there was no sugar going to the boilers in the condensation waters.

2. That the acidity found in the water of the evaporators was too small to account for the trouble observed, inasmuch as the accumulation of acids was avoided by frequently changing the water of the boilers. Notice, however, that the acidity is greater in the feeding tank and greater in evaporator No. 1 than in the rest. This shows that there were acids going into evaporator No. 1 as well as into the feeding tank carried there by the exhaust steam; but in proportion, however, as will be seen later, much lower than those found in the boilers.

3. Boiler No. 3 showed an acidity three times as great as Boiler No. 1, which shows that the cause whatever it might be, was acting with greater intensity in Boiler No. 3. This is confirmed by the figures found for the iron content of the boiler waters, which was higher in the case of the samples taken from Boiler No. 3.

The analysis of the stream water as well as the examination of the locomotive incrustations shows what we already suspected, that this water was not capable of causing corrosion.

It has been proven, then, that the corrosion was not due either to the condensation waters or to the stream water, and we therefore were compelled to give up our first theory that the corrosive agent might be taken to the boilers by the feeding waters. We were then forced to the conclusion that the cause was in the boilers themselves.

Looking then for another explanation of the facts, we remembered that the boiler waters, on being shaken, formed a great deal of foam which stayed for a long a time and had the appearance of soap suds. This gave us the key to the situation. What could be the cause of the foam? There were not enough alkaline salts in solution to account for its formation, as on the contrary the waters were acid. Was there any soap in dissolution? How could the soap get there? There was a possibility. If the paint used in the tubes had been prepared with a vegetable fat, these might very well be partly saponified by the bicarbonates of the stream water. Then we remembered that linseed oil is very frequently used in the preparation of graphite paint. If this was so, we ought to be able to find in the water from the boilers, the products of decomposition of linseed oil and, furthermore, they should be fatty acids capable of dissolving iron under the condition of the boilers. With references to this possible decomposition says Fox, referring to the alterations undergone by linseed oil on being subjected to boiling temperature,<sup>1</sup> "the oxi-

<sup>1</sup>Allen Comm. Organic Analysis. Vol. 11, page 344, Fourth Edition.

dation products are formed from the acids and the glycerol is decomposed into acids of the acrylic series, forming the irritating vapors which always accompany oil boiling. Acetic and formic acids are prominent constituents of these vapors, and carbon dioxide and water are also present." To verify this theory we visited again the factory to get new samples and to obtain more information. On questioning the engineer, we were informed that the graphite paint had been prepared of late, some times with mineral oils and some times with linseed oil. We were also informed that boiler No. 3 had been painted this year when the tubes were changed, and that boiler No. 1 had been painted for the last time the previous year. We were as well informed that the live steam from the boilers on condensing in the low places of the steam pipes, caused corrosion.

We proceeded to take samples of the water from the boiler No. 3 and of the linseed oil and graphite used in the preparation of the paint.

The linseed oil was tested for acidity as follows:

3. cc. of oil were mixed with 300 cc. of water and the mixture shaken at intervals for an hour. At the end of this time 25 cc. of the mixture were titrated with  $n/100$  Na OH after the mixture had been filtered. In the same manner portions of 25 cc. each were titrated two days, four days, and six days later respectively. The results were as follows:

After one hour.....	0.33 cc. N/100 Na OH
Two days after .....	0.73 cc. N/100 Na OH
Four days after .....	1.47 cc. N/100 Na OH
Six days after .....	2.88 cc. N/100 Na OH

The oil as may be seen, contained free acids, which entered in solution almost in direct proportion to the time of contact between the oil and the water. This rather indicates a process of hydrolysis. In the waters of the boilers, tests were made for acetic acid by the acetic-ester method and for formic acid by the reduction of silver nitrate; both tests were positive. As a direct proof we undertook to study the behavior of the linseed oil under the conditions existing in the boilers, duplicating these as far as possible in the laboratory. Accordingly, we heated for 5 hours in an autoclave under 30 pounds pressure in closed bottles the following mixtures:

1. 300 cc. distilled water plus 3 cc. oil
2. 300 cc. distilled water plus 3 cc. oil plus 1 gram graphite
3. 300 cc. distilled water plus 3 cc. oil plus 3 grams iron

4. 300 cc. distilled water plus 3 cc. oil plus 3 grams iron plus 1 graphite
5. 300 cc. stream water plus 3 cc. oil plus 3 grams iron
6. 300 cc. distilled water plus 6 cc. oil

These mixtures were filtered after being taken out of the autoclave and the filtrates were tested for acidity and for iron. In all cases in which iron was added, a positive test was given by the filtrate for this element. The titrations were as follows:

1. 25 cc. filtrate.....	3.59 cc. n/100 Na OH
2. 25 cc. filtrate.....	3.48 cc. n/100 Na OH
3. 25 cc. filtrate.....	3.37 cc. n/100 Na OH
4. 25 cc. filtrate.....	3.70 cc. n/100 Na OH
5. 25 cc. filtrate.....	3.33 cc. n/100 Na OH
6. 25 cc. filtrate.....	6.30 cc. n/100 Na OH

In filtrate No. 6 positive tests were obtained for acetic and formic acids. These new data prove the presence of the products of decomposition of linseed oil in the boiler waters, as positive tests for these products were obtained both in the samples taken from the boilers and in the mixtures prepared and heated under pressure at the laboratory.

It was further proved that the acids formed were capable of dissolving iron, as was seen by the positive tests for this metal obtained in the filtrates of the mixtures containing this element. Notice again that the acidity of flasks 1, 2, 3, and 4 with distilled water and 3cc. of oil each, were far nearly the same, whereas the filtrate from test No. 6 with a double amount of acid contained an acidity which was practically twice as great. In flask No. 5, in which stream water was used, the acidity was much lower, showing that part of the acids had been saponified by the bicarbonates present in the waters. In regard to this it should not be forgotten that boiler No. 3, recently painted, was the one which presented the highest acidity; this may be explained by the fact that it contained more oil than boiler No. 1, which was painted the year before.

The higher acid content of evaporator body No. 1 and of the feeding tank are also explained, as the volatile acids formed in the boilers would pass to the steam pipe and would be carried over by the steam after going through the cylinders of the engines to the *calandria* of the first body of the evaporator. This acidity of the live steam is demonstrated by the corrosion which it produced in the steam pipe and the valves.

The possibility of the exhaust steam pipes carrying vegetable

oils washed from the cylinders as the possible cause of the acidity noticed, did not escape our attention; but upon inquiry from the factory engineer we were assured that all the lubricants used in the factory were of a mineral nature.

Accordingly, we considered it unnecessary to investigate this point further, chiefly when the sample of the condensation waters from the *calandria* of the first body of the evaporator was very clear and did not present any signs of oil. Having satisfied ourselves that the corrosion in this case was due to acids produced by the decomposition of the linseed oil used in the preparation of the paint applied to the boiler tubes, we recommended that as soon as the factory made a stop these tubes should be washed with a boiling solution of caustic soda and in the meantime that lime should be used in the feeding waters to neutralize the acidity in the boilers. This, we were informed, the factory engineer had begun to do. Also that on installing the new tubes the paint should be prepared with a mineral oil. The above discussion may be summarized as follows:

1. Upon testing the stream water and the condensation water, sources from which the feed water was supplied to the boilers, no corrosive agents were formed which could account for the trouble observed. It was evident, then, that the cause was in the boilers themselves.

2. Upon testing the boilers' waters they were found to contain a very high acidity as well as considerable amounts of iron in solution. It was also noticed that they formed a foam which very much resembled soap suds. This led us to believe that the graphite used to cover the boiler tubes had been prepared with a vegetable fat, probably linseed oil.

3. On investigating the kind of acids found in these boiler waters, they were found to be organic acids (acetic and formic). On inquiry from the factory engineer, we were informed that linseed oil had been used.

4. To verify our conclusions we duplicated as much as possible in the laboratory the conditions which we supposed had existed in the boilers, heating under pressure mixtures of water and linseed oil; water, linseed oil and iron; water, linseed oil, iron and graphite. In every case we have obtained the formation of organic acids of the same nature as those found in the boiler waters, and in every

case in which iron was present in the mixture a positive test was obtained for this metal in the filtrates from the solutions.

5. The recommendation was made that the lime be used in the feed water, to neutralize the acidity in the boilers; that the tubes be washed with boiling caustic soda solution to remove the paint, as soon as the factory made a stop, and that when new tubes were installed the paint be prepared with kerosene oil.