

Translation of French original.

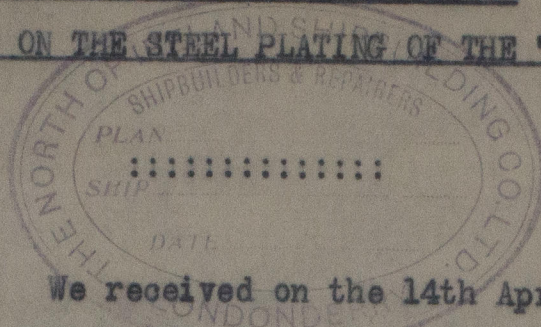
20 Lloyd's

Belfast

A

RESULTS OF THE EXPERIMENTS

CARRIED OUT ON THE STEEL PLATING OF THE "NAUSICAA".



*No photographs enclosed
to Mr. Gifford
Sunderland*

We received on the 14th April, eight circular specimens cut from plates E.8 and E.9, both of which were severely attacked by corrosion.

The position from which the specimens are taken can be seen in photograph 2223/10, dated 23rd of March.

Specimens 1 & 2 are taken from an extensive zone of corrossions in plate E.9.

Specimens 3 & 6 are taken from intact parts (on plates E.9 and E.8 respectively).

Specimens 4 & 5 are taken from the edges of the large zone of corrossions in plate E.8.

Specimens 7 & 8 are of a very deep striated corrosion on plate E.8.

The removal of specimens has been carried out in the cold by drilling and cutting.

The dimensions of these specimens were about 18 m/m diameter by 14 m/m thick, with an approximate weight of 30 grammes each.

Two series of experiments were carried out; chemical tests and physico-chemical tests; as about 50 grammes of metal were required for each of the former tests, the specimens were divided up as follows:-

ANALYSIS A:-

About 2/3 of specimen 1, and the whole of specimen 2.

ANALYSIS B:-

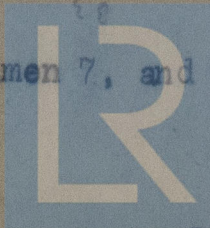
About 2/3 of specimen 3, and the whole of specimen 6.

ANALYSIS C:-

About 2/3 of specimen 4, and the whole of specimen 5.

ANALYSIS D:-

About 2/3 of specimen 7, and the whole of specimen 8.



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W518 - 0 226 (1/10)

The cutting of specimens 1, 3, 4 & 7 was done perpendicular to the face of the plates.

There were left then for the physico-chemical tests only, 4 small pieces, each of about 10 grammes, whose form made it very difficult to state the number of micrographic markings; for these specimens the side which was in the tank was marked by means of a centre punch.

The metal was examined in its rough state without treatment.

I CHEMICAL TESTS.

The chemical analysis was carried out as follows:-

TEST FOR SILICON:- By adding a mixture of sulphuric acid and Nitric acid, and by evaporating.

TEST FOR PHOSPHORUS:- In addition to those for silicon, precipitation by a molybdenum solution and carried on to a pyrophosphormolybdate.

TEST FOR MANGANESE:- Oxidation to the peroxide and titration to arsenious acid.

TEST FOR SULPHUR:- Formation of Barium sulphate.

TEST FOR ARSENIC:- Precipitation by sulphuretted hydrogen.

An analysis for the presence of carbon could not be tried on account of the scarcity of the metal.

The following are the results of these analysis:-

<u>ANALYSIS</u>	<u>A.</u>	<u>B.</u>	<u>C.</u>	<u>D.</u>
Silicon	0.01	0.01	0.01	0.008
Phosphorus	0.019	0.027	0.03	0.03
Manganese	0.46	0.45	0.46	0.46
Sulphur	0.008	0.005	0.009	test unreliable.
Arsenic	traces	traces	traces	traces.

The specimens shew great similarity in their composition; the constituents point to, a priori, insufficient deoxidation; although the analysis are normal, it must not

be forgotten that, on the one hand, these analyses give only the mean constituent, and do not shew the possible segregations, that is to say, the local distributions of the constituents or impurities; and on the other hand, it must be remembered that no tests have been made for oxides.

II PHYSICO-CHEMICAL TESTS

Different examinations, under the Chatelier metallographic microscope, of the four pieces of specimens 1, 3, 4 & 7 (polished and cleaned following the cutting) have led to the following conclusions:-

Cleaning alone with any chemical tests:-

Impurities, to a slight extent, of some non-metallic substance, are visible in the four specimens; they are almost all together in a band covering half of the polished surface, a band parallel to the direction of the lamina, and in the middle of the depth of the plate.

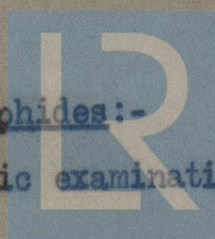
Examination of the normal structure of the steel:-

The usual reaction with an alcoholic solution of picric acid (4%) for one minute shewed the steel to be of ordinary formation, with about 0.2% of carbon; the structure of the steel is almost normal at the sides of the plate (Fig. 1), but in the middle could be seen isolated alignments of iron compounds in the direction of the laminae; the greyish matter, mentioned in the previous examination, was to be found in these segregations of iron compounds.

Such alignments always point to the presence of impurities.

Tests for the presence of sulphides:-

The micrographic examination on Baumann paper



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W 518-0226 (3/10)

(by the application on the polished surface, for 3 minutes, of a sheet of bromide photographic paper which had been dipped in a dilute solution of sulphuric acid (about 3%) revealed the presence of sulphides. (Fig 3). The sulphides with silver bromide and sulphuric acid gave a black precipitate of silver sulphide. It was obvious that the four specimens contained sulphur impurities collected together for the most part in the middle region already spoken of; specimen 7 shewed very clear alignments parallel to the lamina; the three other contained less, but even in No. 3, right in the intact zone, were grains of sulphides scattered through the metal.

In speaking of these tests (Fig. 3), it should be noted that none of the obvious lines of corrosion (even in specimen 7, the most seriously attacked) touch this central zone of impurities.

In fig. 4 can be seen, without much enlargement, some of these marks of sulphides brought out by the Baumann test.

The micrographic examination of the sulphides by a dilute solution of oxalic acid (about 0.2%) for 30 seconds, clearly identified them as ferrous and manganese sulphides (Fig. 5 to 10); the more important groups of these are found in lines parallel to the laminae (Fig. 5 to 9) the others, not nearly so large, are spread over different parts as shewn in fig 10.

Tests for the presence of Oxides:-

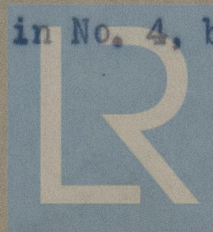
An examination by the Ghatellier Dupuy copper test gave, on all the specimens, lines, parallel to the line of the laminae, on which there was no copper deposit; on washing with ammonia and dissolving any copper deposited outside these lines, the latter were seen to stand out very brilliantly, and to be right on the most deeply corroded parts; in the photograph these brilliant lines appear black

on account of the lighting. (See figure 4).

Recent research (1919) by M.H. Le Chatelier, carried out following a controversy with Stead, prove definitely that this non-deposit of copper in certain parts is characteristic of a metal holding in solution ferrous oxide in a proportion of between 0.01 & 0.2% (the copper is deposited outside these regions). Finally it has been established that the contrast was all the more striking if the amount of oxide present was in the neighbourhood of 0.1 to 0.2%, and that the bringing together of the oxide was facilitated by the presence of phosphides in solution; the clearness of the micrographies shew clearly what is the case here: there can be seen the white bands rich in ferrous oxide, orientating in the direction of the laminae and shewing up on the black background of the deeply corroded iron, and interspersed with small white spots corresponding to perlite; at the edges of the ^{plates the} proportion of oxide is on the other hand very small (Fig. 14)

The photograph of the specimens after this test (Fig. 11) compared with those after the Baumann (Fig. 3) shew clearly that the stronger lines of sulphides coincide with the more oxidized parts: (it should be noted, when reading these photographs that for the same specimen the photos are reversed in these two cases; the negative having been placed directly on the metal specimen for the oxides, and on the bromide paper for the sulphides) photograph No. 12 shows this quite clearly; but while the sulphides can be seen as impurities of relatively small dimensions, the oxides appear in characteristic lines grouped together and covering the central part of the plate.

Finally these phenomena are seen in all four specimens, very clearly in No. 4, but even more so in No. 7.



These micrographic results corroborate then the chemical analysis; we have here a metal insufficiently de-oxidized; the oxide in solution at the moment of solidification has become concentrated in the central part of the ingot, thus following the well known phenomenon of liquation; the laminae have arranged themselves in form examined, that central part of the ingot being found in the central part of the plate; moreover the presence of this oxide in large quantity has led to the concentration of the sulphides and perhaps of the phosphide and the breaking up into groups of the iron compounds.

CONCLUSIONS.

I The plates experimented on, strongly oxidized in their central portion, but having slightly less than 0.01% of dissolved oxide at their outsides, also, and containing moreover sulphurous impurities are extremely subject to corrosion; they produce in the presence of sea water an electrochemical reaction, a fact which has been testified to recently for the couple, steel-iron sulphide, in a paper of Mr. Robert Stumper read before the Academie des Sciences by Mr. H. Le Chatelier on 3rd April 1923.

These results explain very well the corrosions observed on the edges and corners of the plates, as well as those at the joints of the rivets, the galvanic contact being produced here in a perfect manner.

These plates are bad all over, even in those parts still intact, and it is to be feared that any plates rolled from this smelting or similar smeltings will be subject to corrosion. It is possible on the other hand that some intact plates of the ship were rolled from quite good smeltings.

It must be said that protection by paint in such a case is quite illusionary; in the first place it has been seen that the corrosions which received at Antwerp a fresh coat of paint have already at the end of 2 months brought out lines of

oxides; in the second place the paint can disappear locally on account of its bad quality, rubbing or fouling, of ship's side or removal by impure waters. It is therefore absolutely necessary in such work to make sure of the good quality of the steel, especially in oil Tankers, which are more liable perhaps to the disappearance of the paint than other ships.

II. The corrosions, up to the 23rd March, had not reached the central part of the plates, by far the most impure region. It is evident that when this part is reached, the corrosion will proceed with a much greater intensity.

III The results obtained point to the insufficiency of Lloyd's tests.

IV Another examination, when the ship is next in dry dock is certainly necessary; the photographs of the shell and the impressions in lead will make it possible to follow the progress of the corrosion. Finally it would be very useful to obtain specimens of about 1 metre by 1 metre from the intact and from the corroded plates so that the experiments may be carried on even further, although they are very conclusive so far.

CARRIED OUT AT PARIS, 21st JUNE 1923.

(SGD) LEON GUILLET.

Director of the Ecole Centrale des Arts et
Manufactures.

Professor at the Conservatoire National des Arts
et Metiers.

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W518-P226(7/10)

"NAUSICAA" REPORT.

Description of Prints.

Fig. 1
X75

Specimen No. 3. Edge of plate reacted on by an alcoholic solution of picric acid (4%); white (ferrite) and black perlite; alignments of laminae; structure almost of normal steel with 0.2% of carbon.

Fig. 2.
X75

Same specimen - Centre of plate.

Same test as above.

Abnormal segregation of iron compounds into strips in the direction of the lamina; some impurities of greyish non-metallic substances very clear, (in particular a large impurity right in the middle of the photograph).

Fig. 3.

Baumann Reaction - Actual size - the dark parts are the regions containing sulphides.

Fig. 4.
X50

Specimen 7 - Middle of the plate.

Micrography after Baumann reaction.

Lines of black sulphide impurities in the direction of the laminae.

Fig. 5.
X.200

Specimen 7. - Middle of plate.

Without any chemical test.

Grey non-metallic impurities in the lines of the laminae.



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WS18

0226(8/10)

Fig. 6.
X200

Same part as previous photo.

Reaction for 30 seconds with a dilute solution of oxalic acid (.2%)

Heterogeneous colouring from the impurities; impurities form a mixed solution of black manganese sulphide and ferrous sulphide of a lighter tint.

Fig. 7.
X50.

Same part as previous two, but not so enlarged.

Same reaction. Lines of sulphide impurities in the direction of the laminae, some of the impurities being diluted outside the principal band.

Fig. 8.
X200.

Specimen No. 1. Middle of plate.

Without any chemical test.

Sulphide impurities in the direction of the laminae.

Fig. 9.
X500

Same part as above more enlarged. Reaction for 30 secs. with a diluted oxalic acid solution (.2%)

Same result as fig. 6.

Fig. 10.
X75.

Specimen No. 7.

Region situated at about $\frac{1}{4}$ depth of the plate.

Reaction for 30 secs. with a diluted oxalic acid solution (.2%)

Scattered sulphide impurities.

Fig. 11.

Test by the Chatelier Durprey reaction; wash with ammonia. Actual size.

The black lines are the brilliant oxidized and non-reacted regions and shown black

518-0226(9/10)

in the photo.

Fig. 12.
X50

Specimen No. 7. Middle of plate, same part as Fig. 7.

After above reaction.

Very clear bands of white ferrous oxide in the direction of the laminae black background of (ferrite) with small white patches of perlite; in the central part grey sulphide impurities as in fig. 7 are visible.

Fig. 13.
X50.

Specimen No. 1. Middle of plate.

Same reaction as above.

Very clear segregations of white oxide orientating along the lines of the laminae; grey sulphide impurities in the central band; black background of ferrite with small white patches of perlite.

Fig. 14.
X50.

Specimen No. 1. Edge of plate. Same reaction as above. Some small lines of white oxides; black background of ferrite with small white patches of perlite.

Fig. 15.
X50.

Specimen No. 4. Middle of plate.

Same reaction as above.

Bands of white oxide at about half the depth; black background of ferrite with white patches of perlite.



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W518-0226(10/10)