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No. 408

DURALUMIN AND ITS CORROSION

By Lieut. Comdr. Wm. Nelson, (CC), U.S.N.

From "Aviation," November 1, 1926

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS.

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DURALUMIN AND ITS CORROSION.*

By Lieut. Comdr. Wm. Nelson, (CC), U.S.N.

The corrosion of duralumin is real, and it is perhaps the most important factor extant that prevents its wholesale employment in general engineering where light weight is an advantage. According to the early advocates of this metal, duralumin was classed with the fine metals in its ability to remain bright and cheerful in the face of corroding influences. Engineers, impressed with the many other advantages of this aluminum alloy, took to it readily and made extensive applications, particularly as a structural material for aircraft. As the products of duralumin were put into use and service, reports began coming back to the designers that rapid deterioration of the metal due to certain corroding mediums was taking place.

Complicity of Corrosion Problem

During the fifteen years that duralumin has been known, much discussion has taken place and many divergent views have been expressed on the question of the susceptibility of duralumin to corrosion. That this should be the case in view of our experiences with rusting in steel seems odd; but when the records show that on the one hand duralumin structures have been

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used for years in airships with very slight corrosion and on the other hand intensive corrosion has taken place in similar structures within a few months, we can realize that varying results cause varying opinions. However, a judicious investigation of these results brings out the all-important factor that variations in the conditions of exposure are practically entirely responsible for the apparent inconsistencies. This should not be construed to mean that the type and degree of exposure is the only variable, for that is hardly the case; but, where widely different results between two duralumin structures occur, the differences can, as a rule, be traced to the corroding mediums.

The corrosion in duralumin has been compared with rusting in steel and failure in other aluminum alloys. It is hardly practicable to compare duralumin and steel corrossions. Our experience with steel in structures has been with relatively thick sections where a little rust has not materially affected the strength. Our experience with this aluminum alloy as a structural material has been with very thin sections where a little corrosion has gone a long way. However, in a salt atmosphere, rust on steel and oxide on duralumin appear after approximately the same time of exposure, but from then on the corrosion in each is manifestly different.

The latitude allowed in comparing deterioration in aluminum alloys is great because the amount of corrosion in these metals is usually determined by a visual inspection. The loss of weight

method is not readily applicable. The loss of strength method is not usually employed.

To state that duralumin is not subject to corrosion is entirely misleading. It is better to say that all duralumins corrode more or less, depending on the factors controlling, and these factors are usually outside influences.

First Evidences

The types of corrosion ordinarily found in duralumin can be classified more or less by degrees or by stages. No effort will be made here to describe the many types, but the usual first evidence is a gray white powder deposit much like dust on the surface of the alloy. It goes from this, if the exposure is continued, through various stages until it reaches a point where the metal breaks up in a scaly sort of mass such as deteriorated zinc.

A type of corrosion which may or may not be related to those mentioned, and one that is difficult to contend with, is inter-crystalline corrosion. Its presence cannot be readily detected without the use of a microscope, but it does manifest itself by embrittlement of the material. This type of corrosion can be described as consisting of fissures or cracks between the crystals outlining very distinctly the crystals making up the duralumin. They extend in from the surface as a rule and are not found all along the surface. Polishing and etching of specimens

are necessary to get a certain indication that this type of corrosion exists in piece of duralumin.

It is not known at what stage of duralumin corrosion that intercrystalline corrosion becomes important but where surface corrosion has reached the pitting stage tests for intercrystalline embrittlement should be made. The surface corrosion on a sheet of metal as measured by the eye is no true measure of the intercrystalline corrosion that may exist.

Factors Governing Corrosion

The factors that generally govern the amount of corrosion which will take place in duralumin can be given as follows:

1. The chemical composition of the alloy;
2. The physical condition of the alloy;
3. The corroding medium including its composition, temperature condition, etc.;
4. The time of exposure; and
5. The presence of other metals.

The chemical composition of duralumin includes magnesium, aluminum, manganese, iron, copper and silicon. They have been named in the order in which they appear in the electrochemical series. A large spread exists, and it can be readily understood when consideration is given to the elements themselves and the combinations they make with each other that a great variety of electrolytic actions are possible and probable when duralumin is placed in an electrolyte. These electrolytic actions will

vary with variations in the chemical composition and the net result will undoubtedly be corrosion to suit. So far, in the development of duralumin, the chemical compositions have been dictated by the physical properties desired, so it is not likely that much can be done in the direction of corrosion control by control of elements for the present. It might be well to note that magnesium, in its usual forms, is particularly susceptible to rapid deterioration in a corroding atmosphere. It is not believed that iron or silicon play any important role in this respect.

Cold rolling and working the material, produce the same results as far as corrosion is concerned. In general, hard-worked aluminum will appear more corroded than annealed material subjected to the same conditions. Duralumin which has been moderately hard-rolled, however, shows a very low rate of reduction in physical properties when subjected to corroding influences compared to the reduction obtaining in heat-treated material. Nevertheless, it is believed that severely hard-rolled material is very susceptible to corrosion. These variations in the ability of this material to withstand the action of a certain medium might be explained by changes in the potential of the alloy, by differences in the oxide films on the surfaces, or by changes in the solubility of the alloying constituents.

Welds made in duralumin by torch seem to be particularly susceptible to corrosion. Sometimes the concentrated corrosion

takes place a short distance away from the weld and at other times right in the weld. This may be due to differences in the composition of the metals or it may be due to the welding fluxes. Either riveting or special protection to welds will have to be resorted to in seams if the localized attacks are to be avoided.

Scratching or abrading the surface of the metal tends to cause localized attacks in these places. This is undoubtedly due to the fact that recesses formed by such scratching afford a convenient rest for corroding liquids. It may be enhanced also by the rupture of the oxide film on the surface of the duralumin. A noteworthy consideration in this connection is the greater resistance to corrosion obtained by highly polishing the surface of the metal.

Corroding Mediums

The corroding mediums are perhaps the most important of the factors in the deterioration of aluminum alloys. Practically all degrees of corrosion can be attained by varying the medium to which the material is subjected; but those encountered in ordinary practice will be the only ones discussed here. These can be classified in a general way as follows:

1. Ordinary inland atmospheres;
2. Salt atmospheres;
3. Fresh and salt water;
4. Liquid fuels;
5. Acids;
6. Alkalies.

When an aluminum alloy is exposed to the air, a thin transparent film of aluminum oxide forms on the surface. This film is practically ever-present after duralumin leaves the mill unless it is purposely removed by chemical or mechanical means. It undoubtedly acts in a measure as a protective coating but is easily broken by abrasion when the material is put into use. Outside of forming the aluminum oxide film, ordinary atmospheres relatively free of moisture and contaminating gases have little or no effect on duralumin. Atmospheres which are heavy with moisture such as fog, rain, etc., cause a very slow deterioration of duralumin which in a majority of the cases does not require special attention. The great difficulty with such a proposition is that moisture will get into the structure in places and stand for long periods and will cause localized attacks. The oxide film is not water-tight and cannot form a protective coating against most corroding mediums although it will last for long periods in ordinary atmospheres.

Corrosion from Salt Atmosphere

Salt atmospheres such as are encountered at sea and near the seacoast cause a relatively rapid corrosion of duralumin when compared to that caused by ordinary atmospheres. The reduction in the physical properties of duralumin exposed to salt atmospheres is not as great as that produced by salt water; but since most structures which are liable to be subjected to salt

atmospheres will also meet salt spray and salt water, the corrosion is worthy of note and protective means should be provided.

In considering the effect of water on duralumin, a solution or a chemical reaction or an electrolytic action might be effected, or it is possible that combinations of these may result. To attribute the corrosion of duralumin to one or the other is difficult. However, duralumin in ordinary tap water corrodes in spots below the water line and rather evenly at the water line. The corrosion at the water level is usually more rapid than that which takes place below that level. This may be due in part to the gas and liquid condition existing at that point. Salt water or sea water is particularly active on duralumin. In the ordinary service of aircraft it is believed that this is the most difficult corroding medium to contend with. The corrosion of duralumin in sea water will run from two to ten times as much as is the case in tap water. The chloride solutions are much more active in corroding aluminum alloys than the sulphates, nitrates, and practically all the other common salt solutions. Sodium and calcium chloride solutions are used for inducing corrosion and the effect of placing duralumin in intermittent or continuous contact with these solutions is to cause corrosion which reduces the physical properties of the material considerably and rapidly. This may manifest itself as intercrystalline corrosion in addition to producing surface corrosion.

Effects of Fuel

Fuels such as gasoline, alcohol, etc., attack duralumin slightly if any water is present in the fuel. The degree of the corrosion is not sufficient, however, to make any special provision against it inside of fuel tanks, etc. Some of the special preparations (picric acid) used in fuels to increase their efficiency may corrode duralumin to a serious extent. The avoiding of fuel dopes with an acid base seems to be the only alternative.

Practically all of the acids attack duralumin. Hydrochloric acid is very active on this metal causing pitting. Nitric and sulphuric acids attack duralumin rather uniformly leaving a slightly etched surface. Other acids such as acetic, picric, oxalic, oleic are slow in their actions on duralumin but do corrode sufficiently to warrant special measures to prevent contact. Battery acids spilled on duralumin structures in service have been known to completely destroy the structures affected.

The alkalies are perhaps the most active in their action on duralumin. They cause a more or less uniform attack and reduce the original proportions of the metal very rapidly. A satin finish can be produced on duralumin with facility by dipping it in a hot lye solution. Cleaning compounds containing alkalies are a source of danger to duralumin in service.

Some special materials which are used on duralumin from time to time under varying circumstances may or may not cause actions which are intensive enough to warrant special attention depending

somewhat on the circumstances. Duralumin left in carbon tetrachloride for relatively long periods will show signs of corrosion. Although sodium and potassium nitrate solutions do not cause embrittlement in the way chloride solutions do they leave strong evidences of a uniform corrosion. Ammonia causes a uniform attack on duralumin. Iodine and bromine attack duralumin.

The time element in considering any corrosive action is important also. It cannot be definitely stated that the amount of corrosion in duralumin is directly proportional to the time. This is due to the fact that the first products of corrosion tend to protect the metal in a measure, so that the usual result is rapid action in the beginning with a slowing up as the corrosion proceeds. However, in most cases in service the amount of corrosion necessary to produce a protection is so great that the structure is impaired; so for all practical purposes the amount can be assumed to be directly proportional to the time element.

Contact Corrosion

Placing other metals in contact with duralumin causes complications. The most violent corrosion is obtained by placing duralumin in contact with copper or any of its alloys in a salt atmosphere. The copper alloy seems to be affected very little, if at all, whereas the duralumin disintegrates completely in a relatively short time. The corrosion that takes place in case of steel and duralumin contact is not as violent as in the case

of copper and duralumin, which is fortunate in a way since most installations do require a combination of high strength alloy steel with duralumin.

Steel and iron rivets placed in a duralumin structure and subjected to a salt spray have resulted in localized attack to the duralumin in the vicinity of the rivets, and the rivets have rusted more than that ordinarily obtained. Another case worthy of note was where a steel casting on a duralumin sheet subjected to a salt atmosphere resulted in practically complete failure of the plate. The data on these combinations indicate that the amount of corrosion is dependent on the corroding medium and that the aluminum alloy will usually suffer in any medium which is active.

Galvanized steel placed in contact with duralumin in a corroding medium usually causes the galvanizing to soften up and break down. The duralumin on the other hand seems to maintain its original condition until the galvanizing has completely failed.

Aluminum is a strong electropositive metal and it can be expected that aluminum alloys will corrode rapidly when placed in contact with other metals provided an electrolyte is furnished. This contact corrosion is particularly important when platings on duralumin are considered. Any break in the surface of a plating of a dissimilar metal causes very rapid action when the specimen is subjected to a corroding medium. That is one reason for

the failure of platings as protective coatings on duralumin.

Induced Corrosion

In recent years a great deal of attention has been given in laboratories to inducing corrosion in metals. Duralumin is no exception and considerable data is available on the subject of duralumin in salt sprays and other mediums. These tests, in addition to giving data on duralumin, are also used to test the relative values of protective coatings and other special matters connected with corrosion.

Duralumin can be tested by exposing it to the same elements to which it will be exposed in service, but the time taken to induce corrosion in this way is too long for ordinary use. Salt sprays, intermittent immersion in salt solutions and intermittent immersion in other mediums are the usual means for producing corrosion in a relatively short time and represent in a way what will happen to material exposed in service.

The spray and alternate immersion are approximately equally effective in producing corrosion. The advantages of one over the other are centered on other factors.

Corroding Solutions

The corroding solutions used in spray and alternate immersion methods are:

1. Sodium chloride solutions;
2. Calcium chloride solutions;
3. Sodium chloride - hydrogen peroxide solutions;
4. Hydrogen peroxide solutions.

The losses in physical properties of duralumin corroded by induced corrosion are of importance. There are many factors that influence the rapidity of the action in the various solutions and various means used for inducing corrosion, and as a consequence the results obtained are applicable only to the particular investigations being performed.

The aluminum products of corrosion are exceedingly difficult to remove. Their removal is necessary for examination of specimens in the laboratory and for refinishing the surface in service. The laboratory method for removing products of corrosion and salts consists of immersing the specimen in a weak solution of nitric acid until the surface appears relatively clean. This same method has been used in service where the size of the parts and the disassembly of the parts permitted it. As a rule, though, this method cannot be used in service because it requires disassembly. Other procedures are therefore necessary. Where the corrosion is scattered over flat surfaces, the use of a putty knife or equivalent is believed to be as effective

as any means known. Over rivet heads and similar irregular surfaces wire brushing produces the best results. After scraping or brushing the dust left should be blown off or wiped off with a dry rag. Efforts have been made to find a more satisfactory way to clean corroded duralumin but without material success. Water and most of the usual liquid chemicals aggravate the condition rather than assist the project. Pickling in nitric acid, scraping, and brushing must be relied upon to produce as good results as can be expected.

Conclusion

It appears that all duralumin will corrode to some extent in service if left unprotected. The difference in the amounts of corrosion under various circumstances is not great enough to warrant the omission of any measure tending to reduce the susceptibility of the metal to corrosion in service. Salt water is the most common of the corroding media with which we have to contend in using duralumin in aircraft and ships. Due consideration to these factors during the design, construction and maintenance of these craft is necessary to get the maximum life.



Fig.1 Severe intercrystalline corrosion magnified to 100X.



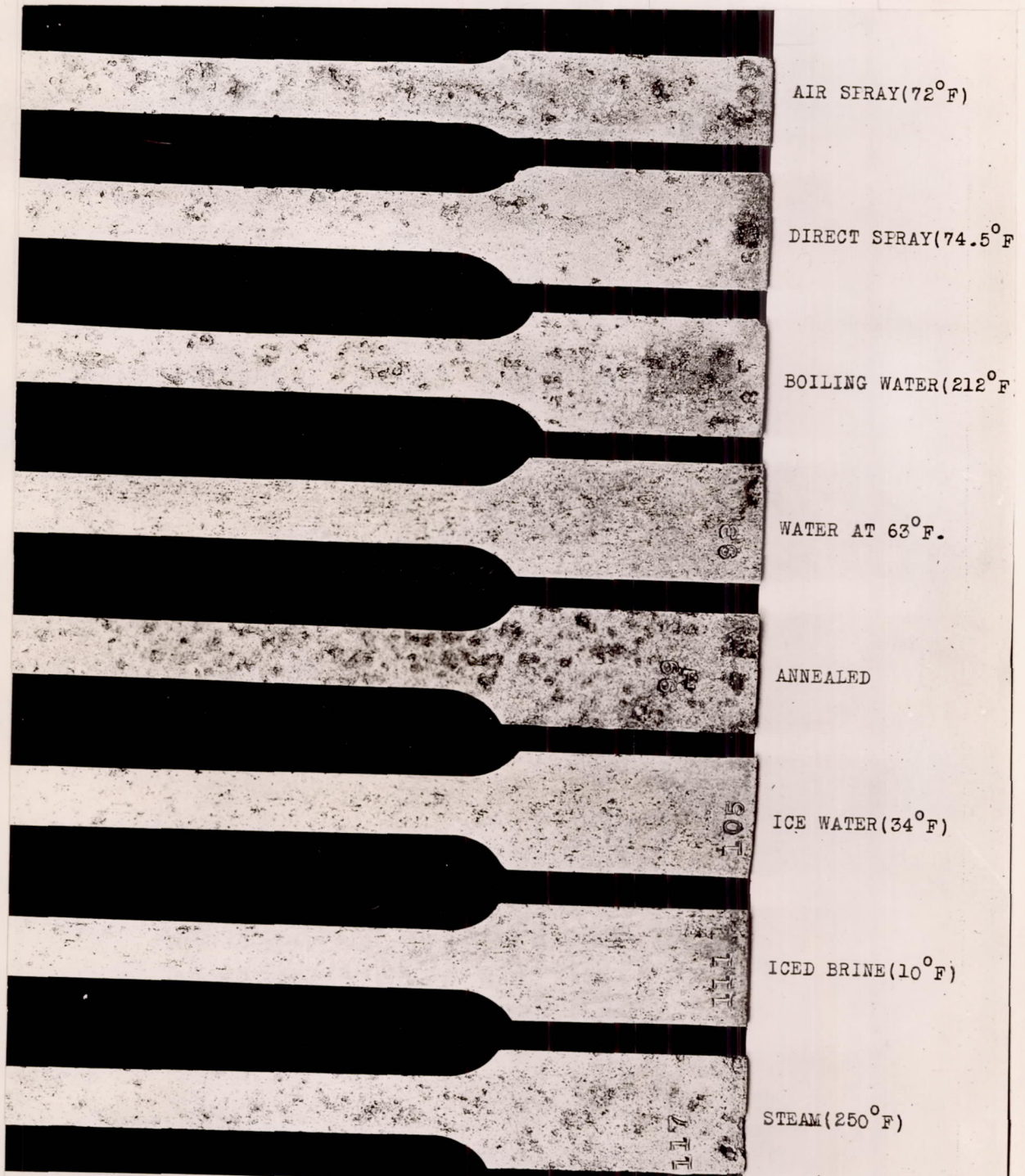
Fig.2 Intercrystalline corrosion in duralumin as brought out by etching.



View of edges of 1/8" thick quenched duralumin tensile test specimens after 60 days in salt water spray corrosion, and cleaning in 10% HNO₃. Quenching mediums are indicated.

- Air Spray (72° F)
- Direct Spray (74.5° F)
- Boiling Water (212° F)
- Water at 63° F.
- Annealed
- Ice Water (34° F)
- Iced Brine (10° F)
- Steam (250° F)

Fig.4



1/16" THICK QUENCHED DURALUMIN AFTER 60 DAYS IN SALT WATER
SPRAY CORROSION TEST AND REMOVAL OF PRODUCTS OF CORROSION

QUENCHING MEDIUMS ARE INDICATED

Fig.3

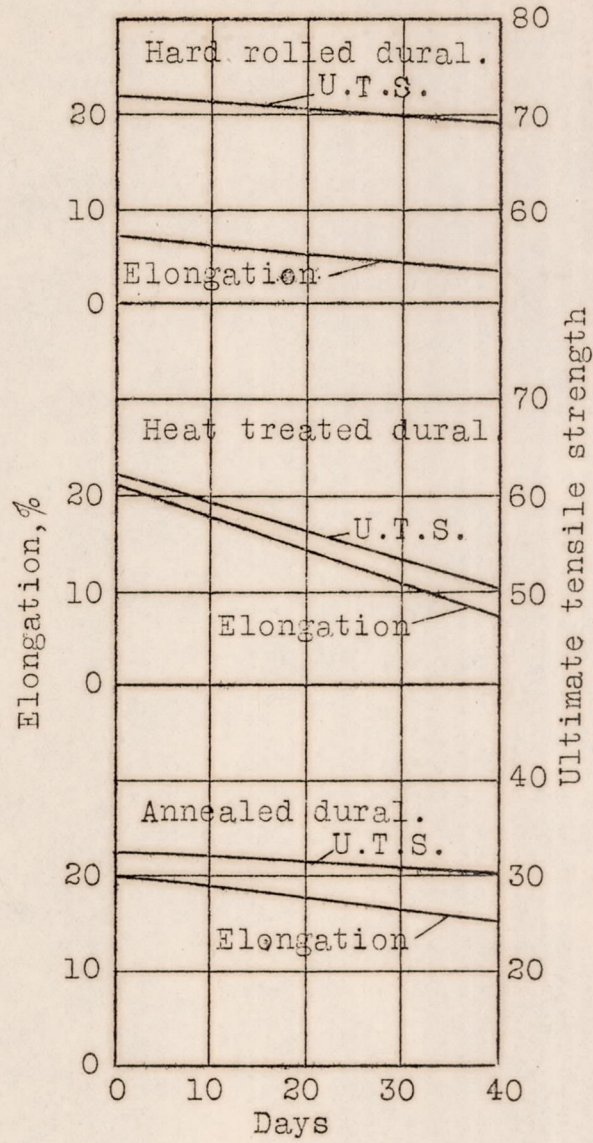


Fig.5 Losses in properties by corrosion in normal solution CACl_2 spray.

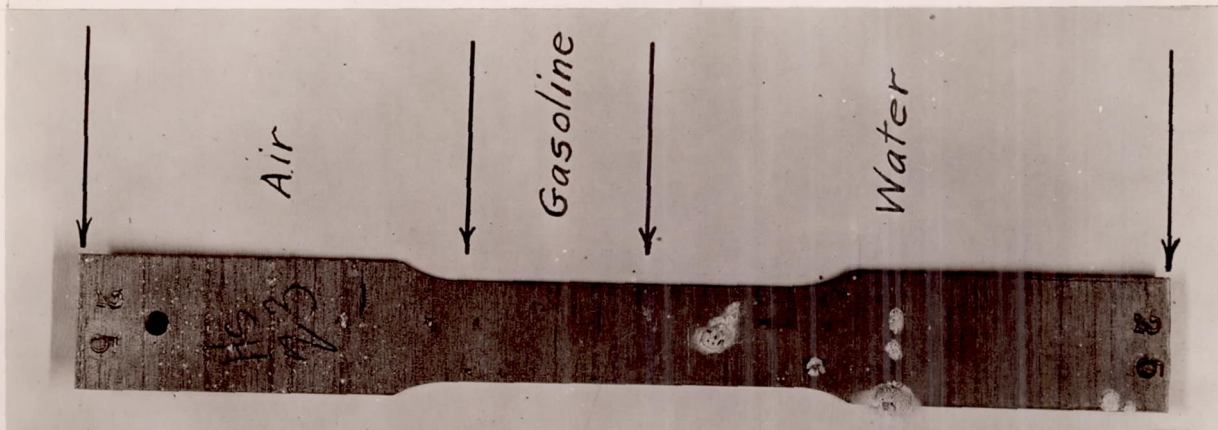


Fig. 6 Corrosion on duralumin due to presence of water in fuel.

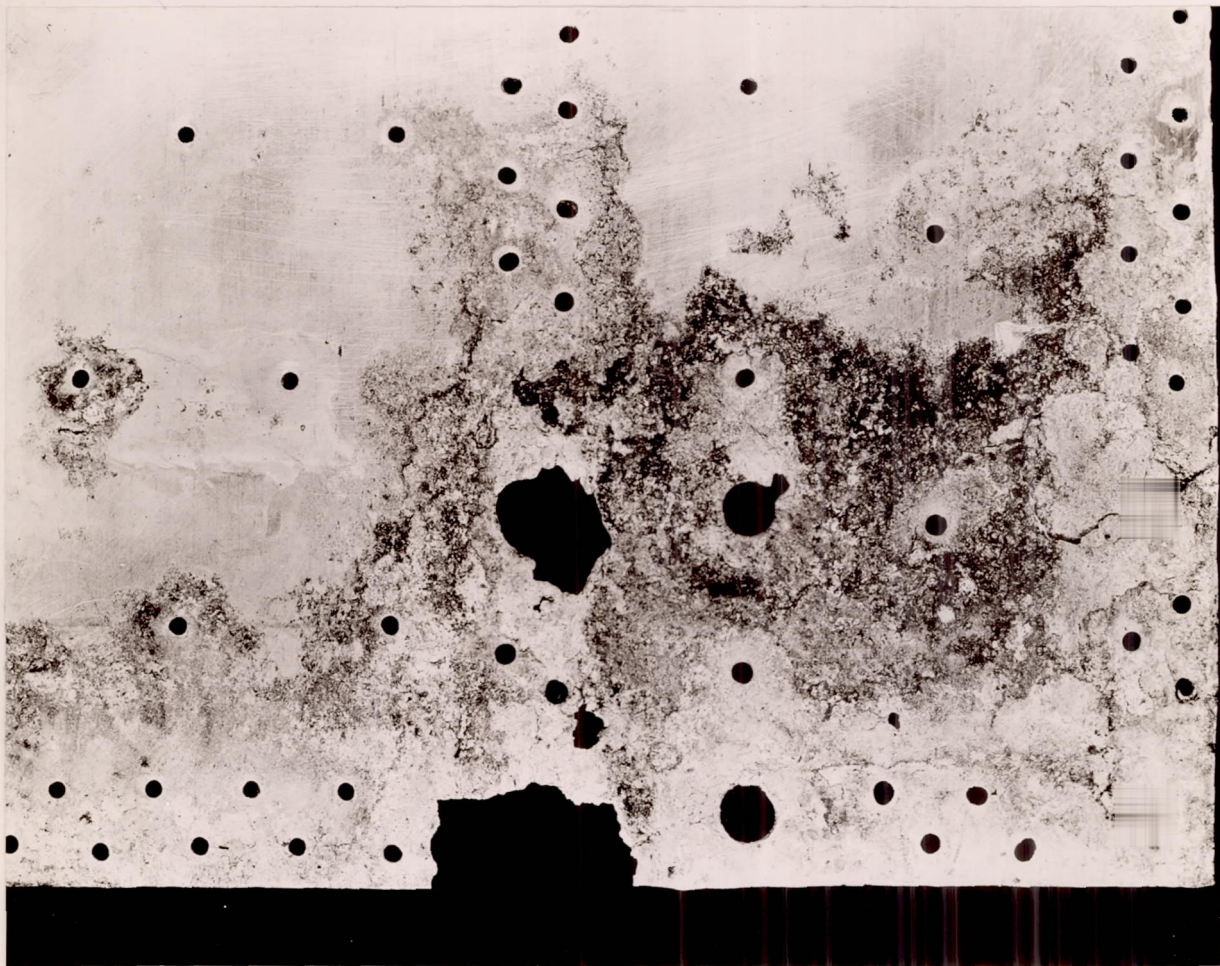


Fig. 7 Duralumin sheet in the wake of a steel forging after a short service at sea.