TECHNICAL NOTES

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

No. 285

CORROSION EMBRITTLEMENT OF DURALUMIN
IV.    THE USE OF PROTECTIVE COATINGS

By Henry S. Rawdon
Bureau of Standards

Washington
April, 1928

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS.

TECHNICAL NOTE NO. 285.

CORROSION EMBRITTLEMENT OF DURALUMIN.

IV.   THE USE OF PROTECTIVE COATINGS.

By Henry S. Rawdon.


Light aluminum alloys of the duralumin type, that is, high-strength wrought alloys whose properties can be improved decidedly by heat treatment are of very great importance, especially in the form of sheet and tubes, for aircraft construction.  The permanence of such materials when exposed to corrosive conditions such as may obtain in aircraft service should be known, however, with a high degree of certainty and precautionary measures taken to guard against any possible serious deterioration in service.  To obtain reliable information along this line an investigation, the results of which form the basis of this series of reports (Reference 1), has been carried out at the Bureau of Standards in cooperation with the National Advisory Committee for Aeronautics, Bureau of Aeronautics of the Navy Department, and Army Air Corps.  The leading manufacturers have also participated in the investigation by furnishing practically all of the materials needed.  The investigation, which was started in the latter part of 1925, is still in progress and final and complete answers have not been reached on all points concerning the permanence of duralumin in service.  The informa-

tion which has been obtained, however, is of very considerable
value to both manufacturers and users of aircraft and its publi-
cation at this time would seem to be warranted although possibly
some of the statements made may be modified slightly in the light
of future results.

## I.   Introduction

It has been shown in a previous report (Reference 1 - N.A.C.A.
Technical Note No. 284) that the resistance of duralumin sheet to
corrosion, especially of the intercrystalline type, can be very
greatly improved by proper treatment of the alloy.  It does not
follow, however, that the use of protective coatings can be en-
tirely dispensed with.  Corrosion of the more familiar type,
that is, by surface roughening or pitting, apparently may occur
regardless of the previous treatment which the alloy may have
received.  So, for this reason, if for no other, surface protec-
tion of duralumin parts will always be considered desirable in
order to ensure long life to the material.  The methods used for
protecting the surface will, of course, differ according to the
conditions which may be expected to occur in service, thus, for
example, the type of coating required for protecting parts fre-
quently, if not constantly, in contact with sea water, as in
seaplane floats, must of necessity be quite different from one
which would be found satisfactory for airplane parts subjected
only to atmospheric conditions far removed from the ocean.  The

physical nature of a coating, aside from its imperviousness to corrosive agencies, is also of importance, especially its ability to withstand a considerable amount of deformation without the coating cracking or flaking from the base.

No attempt was made in this investigation to study the relative merits of the multitudinous coatings which have been proposed for use on aircraft. Since the investigation was primarily concerned with the subject of the intercrystalline corrosion of sheet duralumin, the coating methods and other protective treatments studied were confined largely to those which have already come into rather wide commercial usage and the tests were made with the aim of showing the effectiveness of these protective measures against corrosive attack of this type. In addition, a few protective methods which seemed to offer very distinct advantages over some of those already in use were included. The real value of any protective means used to combat corrosion can be determined fully only by service. The results of accelerated corrosion laboratory tests are of value to the extent to which they indicate what the behavior in service may be expected to be like. The results given in this report must be considered in this light and the final and complete answer can only be given when the results of the weather exposure tests, which form part of the complete investigation and which are now under way, are available. These results will form the subject of a subsequent report.

## II.  Types of Coatings and Test Methods
### 1.  Classes of Coatings

The different types of protective coatings used on duralumin may be conveniently grouped into the following classes:

a) <u>Varnish</u> type of coatings.  These coatings are non-metallic in their nature and are applied by brushing, dipping or spraying.  Spar varnish, which is used in both the plain and the aluminum pigmented condition is undoubtedly the best known coating of this type.  Coatings of a bitumastic nature and of sodium silicate as well as those having a rubber base may also be placed in this category.  The behavior of a good many coatings of this type when used on sheet duralumin in weather exposure tests in a sea atmosphere, the tests being carried out in cooperation with the Bureau of Aeronautics, has been reported by Gardner (Reference 2).  The observations were confined almost entirely to an inspection of the change in the appearance and character of the coatings after six months' exposure to the weather.  No determinations of the change in the strength characteristics of the underlying metal were made.

b) <u>Oxide films</u>.- The corrosion resistance of an aluminum alloy may be greatly improved by the formation of an oxide film over the surface.  This is done by chemical treatment, usually of the finished article, and the method of treatment is often electrochemical in its nature.  The protection afforded by such

oxide coatings, which at the best are only very thin, can be greatly improved by the use of a supplementary grease or oil film.

c) Metallic coatings.- Of the various metallic coatings which might be used on duralumin, those of aluminum would seem from theoretical considerations, to be most suitable. A considerable amount of work has been done by other investigators on the use of zinc and cadmium coatings deposited by electroplating. Such coating methods, however, have not proved nearly so useful in service as some of those of the preceding types and are not used commercially to any appreciable extent at present. In this investigation, the use of aluminum as a coating has been given special consideration. Such a coating cannot be deposited by electrolytic deposition, however.

## 2.   Test Method

In the tests relating to coatings, the same general method as has been described in the preceding reports (Reference 1 - N.A.C.A. Technical Notes Nos. 283 and 284) was followed, that is, full-size tension specimens of the sheet material, after being coated as desired, were corroded and the tensile properties of the corroded bars then determined. One shortcoming in the method of testing used is that the accelerated corrosion test does not, in some cases, include those factors which are most potent in causing deterioration of some coatings. This is particularly true of varnishes. On the other hand, the method usually employed for the testing of coatings of the paint

and varnish type would induce very little, if any, corrosion of the underlying duralumin base unless the tests were continued for a very long period after the coating has been broken down. The intermittent immersion method which was used does, however, simulate in many ways the most severe service conditions which aircraft materials are called upon to withstand, for example, the conditions to which seaplane floats are subjected.

At the time the first tests on coated specimens were made, the entire investigation had not progressed far enough to show how the susceptibility of duralumin to intercrystalline attack can in large measure be controlled by the method of heat treatment. The test results of the A and B materials, coated in the same manner, differed considerably as is shown in Figure 1. The results obtained with the 'B' material which, in the "as received" condition, was much more susceptible to attack than the 'A,' are more indicative of the relative value of the applied coatings, that is, in showing what the useful life of the coating is before the "breakdown" is so serious that the underlying metal is seriously attacked.

For the later tests, especially the weather-exposure tests, sheet material which had deliberately been made susceptible to attack by quenching in hot water was used. With such specimens, a corrosive attack of the metal can be expected to occur within a relatively short time following the breakdown of the coating and thus shorten very materially the period necessary for a positive test of the coating.

### III.  Coatings of the Varnish Type

Most of the tests on coatings of this kind were carried out
upon tension bars coated in accordance with current practice in
aircraft construction.  Specimens representative of the three
coatings in common usage,  (a) plain spar varnish,  (b) the same
varnish pigmented with aluminum powder, and  (c) a coating of a
bitumastic base, were coated at the Naval Aircraft Factory.

Testing of the three kinds of coated specimens for 40 days
in the "salt spray," both sodium chloride and calcium chloride
being used, failed to show any marked difference in the proper-
ties of the three coatings.  As is shown in Figure 1, for these
conditions, each of the coatings gave perfect protection to the
duralumin beneath for this length of time.  When tested for 40
days by the intermittent immersion method in $\frac{N}{4}$ $CaCl_2$ solution
(approximately 1.5 per cent by weight) the results, especially
for the material having the lower corrosion resistance, showed
that some corrosive attack of the metal had occurred.  The re-
sults for the three different coatings, however, did not differ
enough among themselves to warrant any conclusions as to their
relative merits.  When oxidizing solutions were used, the break-
down of the coating, as indicated by the corrosive attack upon
the underlying metal, was unmistakable.  The degree of protection
afforded by the bitumastic coating was somewhat better than that
of the other two.  The aluminum-pigmented spar varnish was found
to be somewhat inferior in its protection, under the conditions

used, to the plain varnish, which is in opposition to usual ex-
perience in service under atmospheric exposure.  Thus, a recom-
mendation for the use of any one of these three types of coating
in preference to the others on the basis of these results, would
not be warranted.  "Failure" of the coating, resulting in the
corrosive attack of the underlying metal, usually was revealed
by the formation of "blisters" as the coating was loosened from
the base.   The blisters varied in size, some of the largest
ones being approximately $\frac{1}{2}$ inch in diameter.  The aluminum-
pigmented varnish showed the greatest propensity to form these
"blisters," this being especially true for the hydrogen peroxide
and the hydrogen peroxide-sodium chloride solutions.

The blisters beneath the coating were filled with gas.
The results of analysis of the gas collected from the blisters
which formed under an aluminum-pigmented coating indicated that
it contained approximately 20 per cent of oxygen, 9 per cent
of hydrogen, and the remainder, nitrogen, with traces of carbon
dioxide and carbon monoxide.

In brief, it may be said that on the basis of the results
obtained with these three types of coatings, it would seem that
neither of the spar varnish coatings, plain or pigmented, is
satisfactory for duralumin parts which are in direct contact
with sea water for a great deal of the time.

The difference in the behavior in atmospheric service of
spar varnish coatings, both plain and pigmented with powdered

aluminum, is indicated by the results of a series of tests
(Reference 3) carried out to show the permeability of such coat-
ings to water vapor. Varnish films of three compositions 8,
30, and 50-gallon varnish, (8, 30, or 50 gallons, respectively,
of tung oil to 100 pounds rosin) both in the plain and the
aluminum-pigmented condition (2 pounds aluminum per gallon)
which were formed on a supporting network of 100-mesh sieve wire
cloth, were exposed to the atmosphere. The specimens which were
exposed on one of the Bureau of Standards buildings were inclined
45 degrees to the horizontal and faced south.

The permeability of the films to water vapor was determined
in the following manner: The varnish film, on its supporting
network, was fastened over a small glass Petrie dish containing
calcium chloride, the initial weight determined, and also the
weight after 20 hours' exposure in air saturated with moisture
and 1 hour's conditioning in an atmosphere of 32 per cent rela-
tive humidity, 30°C. This was done at the end of each successive
exposure period. The initial permeability of the coating, that
is, before any exposure to the weather, was also determined.
The results obtained for 43 weeks' exposure are given in Figure 2.
The "30-gallon" varnish may be considered as representative of a
spar varnish of very good commercial grade; a "short oil" varnish
represented by the "8-gallon" varnish is not intended for out-of-
doors service. This is borne out by the very short life shown
by this material in the permeability tests. The greatly increased
life of coatings of this same grade of varnish by pigmenting it

with aluminum powder serves as a striking illustration of the
relative value of these two types of varnishes for atmospheric
service.  The results obtained for the plain "30-gallon" varnish
indicate that the breakdown of this coating was under way after
approximately 40 weeks' exposure.  As judged by the behavior of
the "8-gallon varnish" films, the aluminum-pigmented "30-gallon
varnish" films, as well as those of the "long oil" varnish, may
be expected to show high resistance to penetration of moisture
for many months to come.

Bitumastic coatings, pigmented with aluminum powder, are
used to some extent in actual service.  A number of specimens
representative of the pigmented and of the plain bitumastic
coatings were prepared by the Naval Aircraft Factory for the
tests reported here.  The results obtained by means of a severely
corrosive solution (sodium chloride and hydrogen peroxide solu-
tion) are summarized in Figure 3.  These results indicate no
pronounced difference in the degree of protection given by these
two coatings when corroded under the conditions used.  Blister-
ing and some flaking of both types of coating occurred after
prolonged attack.  A preliminary oxidizing treatment of the
metal surface, either by the anodic treatment or by immersion
in a dilute nitric acid solution, before the bitumastic coating
is applied is, on the basis of these test results, not to be
recommended.  Especially is this true for the nitric acid treat-
ment.  Very good protection was shown by the pigmented bitumastic

coatings on specimens which had previously received anodic oxidation but not with the plain bitumastic coatings used under the same conditions.  The advantage to be gained by pigmenting bitumastic coatings is probably of the same general nature as that shown by the tests on plain and pigmented varnish (Fig. 2), that is, the retardation of the deleterious action of sunlight and other atmospheric agencies.

Sodium-silicate coatings have been found very satisfactory for aluminum alloy castings for some types of service (Reference 4), but such coatings have not been used to any extent on sheet material.  Corrosion tests were carried out on a number of tension bars which were coated for the investigation in the laboratories of the Army Air Corps at McCook Field, Dayton, Ohio, where this method of coating has received most attention.  The specimens after cleaning were immersed in a sodium silicate solution (1.1 sp. gr.) for 30 minutes, air dried for 10 minutes, then "baked," the temperature being held at $230^\circ F$ ($110^\circ C$) for 10 minutes, then raised to $280-300^\circ F$ ($140-150^\circ C$) and maintained for 30 minutes.  The results obtained in the tension tests of corroded specimens, which are summarized in Figure 3, indicated that for mild corrosive conditions, such as a solution of hydrogen peroxide in water, the sodium silicate coating gave very good protection.  Under severe corrosive conditions, such as a solution of sodium chloride and hydrogen peroxide, the coating was quickly broken down.

A recent coating method which has shown promise of being
very useful for duralumin consists in the use of a special alum-
inum-pigmented rubber cement, applied to the surface in the form
of a solution.  This type of rubber cement, "Vulcalock," which
is said to consist largely of a rubber isomer, produced by an
acid treatment from ordinary rubber in hydrocarbon solvents,
has the property of clinging tightly even to a polished metal
surface, so that very good adhesion can be secured without pre-
liminary roughening of the surface.  The presence of traces of
oil on the metal surface to be coated does not appear to pre-
vent adhesion as would be the case with varnishes.  As received,
the cement contains no aluminum powder.  This may either be in-
corporated into the cement, before it is applied to the surface
by brushing, or it may be dusted on to the "tacky" rubber sur-
face and then brushed down.  Duralumin sheet panels coated with
this type of rubber coating, both in the plain and the aluminum-
pigmented condition, were exposed to the accelerated weathering
test employed in the testing of paints and varnishes.  (The
number of 24-hour cycles, each cycle including successive ex-
posure to ozonized air, "rain" spray, ultra violet radiation,
and refrigeration, required for breakdown of the coating, is
taken as a measure of the life of the coating.)  Specimens coat-
ed with the plain ("non-aluminized") rubber cement coating were
removed at the end of three days as "failed," but specimens with
the aluminum-pigmented rubber coating are still in very good

condition after approximately seven months' exposure to the accelerated weathering test.

Because of the marked effect of the aluminum powder in protecting the coating from deterioration, it should be pointed out that poor service results obtained in the past with plain rubber coatings should not be taken as evidence against the usefulness of the combination of special cement and aluminum powder here suggested.

This type of coating appears to be especially applicable for those parts where flaking of the ordinary type of varnish coatings would occur in a relatively short time as a result of vibration, flexure or similar conditions, as has been shown by the results of tests now in progress in which specimens are corroded while being subjected to repeated flexure.

## IV.   Oxidation and Other Surface Treatments

The condition of the surface is a factor of very considerable importance in determining the rate at which a corrosive attack of sheet duralumin proceeds, particularly during its early stages.  Specimens which are polished, as a rule, show a greater corrosion-resistance than do specimens of the same material in the "as rolled" condition.  When mild corrosive reagents are used the advantage of polishing is more pronounced than when severe ones are used.  From a comparison of the results obtained on specimens polished by buffing with those polished

by hand in a manner similar to that used in the preparation of
metallographic sections, it appears that at least part of the
superior corrosion resistance shown by polished surfaces should
be attributed to the grease which is present in ordinary buffing
compounds.

## 2.  Surface Oxidation

It has long been known that an oxidized aluminum surface
resists corrosion better than a "fresh" surface does.  The same
is true of a number of other metals.  A commercial method for
the protection of duralumin and other aluminum alloys based
upon this fact is that commonly known as the "anodic treatment"
(Reference 5).  The method consists in using the material to be
treated as the anode of a suitable electrolytic cell.  A solution
of chromic acid is generally used as the electrolyte.  In pre-
paring the specimens for the tests described below, the sheet
steel container functioned as the cathode.  By means of a second
or outer container through which either hot or cold water could
be passed as desired, the temperature of the entire unit was
maintained at approximately $40^{\circ}C$, and the treatment was allowed
to continue for one hour.  The voltage applied, which initially
was quite low, was increased to approximately 40 volts in 15 min-
utes and finally to 50 volts just before the end of the "run."
This treatment is essentially that described in the reference
cited above.  In order to avoid "contact" difficulties, the
junction between the duralumin specimen to be treated and the

connecting wire must be exceptionally well protected from the
solution, or, preferably, the junction should be above the solu-
tion.  In the treatment of the tension bars this was done by al-
lowing one corner of the bar to project above the solution, and
in other cases, by using a narrow "tail" of metal which projected
above the solution level and which was sheared off after the
treatment had been finished.

A slight loss of weight ordinarily occurs as a result of
the anodic oxidation treatment.  This varies slightly in differ-
ent materials, perhaps depending upon the previous heat treat-
ment, and was found to range from .001 to .004 oz./sq.ft. (ap-
proximately).  The tensile properties are affected only to a
slight degree by the treatment; sometimes the elongation is
found to be lowered slightly but no general conclusion in this
respect is warranted.  The results in Figure 4 illustrate the
magnitude of the change in the tensile properties.  In the com-
mercial use of the anodic oxidation process as a means for pro-
tecting duralumin against corrosion, a supplementary treatment
whereby a thin grease film is formed over the entire surface is
recommended.  Lanoline has generally been used for this purpose.
In the results reported here the lanoline, when used, was usual-
ly applied as a solution in benzene, the amount of the grease
used in the film being very small (approximately .05 to .10 oz./
sq.ft.).  In addition to the very uniform distribution of the
grease film formed in this manner, the use of such a solution

has another very distinct advantage in that it penetrates into all crevices in riveted parts and the like, in which corrosion, if it occurred at all, would be expected to occur sooner than elsewhere on the specimen. The solution can be applied by dipping, brushing, or spraying. Spraying with an atomizing nozzle that will produce a very fine mist would appear a promising method for the initial application and periodic re-greasing of the framework of an airship, for example.

The results of tension tests of duralumin specimens which had been given the anodic oxidation treatment previous to being used in accelerated corrosion tests of the kind already described showed that the oxide film, even without greasing, afforded a very considerable degree of protection against intercrystalline corrosion when a mildly corrosive solution such as dilute hydrogen peroxide solution was used. This is shown in Figure 4. With a severely corrosive reagent, such as the solution containing both sodium chloride and hydrogen peroxide, the results showed that the protective oxide film was broken down, although there was some indication that the attack had been retarded appreciably in the early part of the exposure period.

The oxide film has a smooth surface and may, indeed, be formed so smooth that it is almost glass-like in appearance. Severe bending or other deformation causes no flaking of the film but does result in microscopic fissures through which corrosive agencies gain ready access. This is shown by the results

of the corrosion tests made on treated specimens which were per-
manently stretched prior to corrosion (Fig. 4).

The use of grease on specimens which have received the
anodic oxidation treatment increases the corrosion-resistance
of such material many-fold.  As already mentioned, lanoline is
generally used for this purpose.  Other greases or oils may be
used, however, apparently with equally good results as is shown
by the data summarized in Figure 4.  The oxide coating is neces-
sary, however, to serve as a "body" for holding the grease film.
Specimens to which a film of grease was applied directly on the
untreated surface were found to be almost as readily attacked
by the sodium chloride-hydrogen peroxide solution as were com-
panion ungreased specimens and as were also similar specimens
which had been given the anodic oxidation treatment but no greas-
ing.  The combination of the anodic oxidation and a greasing
treatment, however, gave almost complete protection under the
same severe corrosive conditions.  As compared with lanoline,
commercial slushing grease, castor oil and lard oil were found
to give essentially the same degree of protection (Fig. 4).
However, if a relatively thick grease coating, e.g., slushing
grease, is used and particularly if aluminum powder is used with
it so as to give it "body" and also a more resistant surface
(as in the method which has been used in practice by C. W. Hall
even upon duralumin surfaces not anodically treated), a very
high degree of protection of duralumin sheet against corrosion

can be secured.   Information on the further behavior of this
type of coating is being sought through the weather-exposure
tests now under way, the results of which will form the basis
of another report.

The examination of the microstructure of the corroded spec-
imens, the results of which are summarized in Figure 5, serves
also to demonstrate the degree and the nature of the corrosive
attack which occurred in spite of the "protective" coating on
the surface.

A simpler method for the production of an oxide film on
duralumin or other aluminum alloys consists in immersion in
dilute nitric acid.   Presumably, comparable results may be ob-
tained by means of other oxidizing solutions.   The surface film
produced by dilute nitric acid is more "open" in its appear-
ance than is that produced by anodic oxidation.   Under severely
corrosive conditions, it affords no protection whatsoever but
against mild corrosion attack it does protect to some extent,
as is indicated by the results in Figure 6.

Another method for the surface treatment of aluminum and
its alloys which is usually referred to by the name of its orig-
inator (Reference 6), consists in immersion in a hot solution,
the composition of which may be varied considerably according
to the published description of the method.   The process is de-
cidedly empirical in its nature but the solutions usually con-
tain a chromium salt and a dichromate together with some carbon-

ate (sodium or potassium).  Other substances, the purpose of
which is not at all clear, may be present in some of the differ-
ent solutions.  The appearance of the finish produced by this
treatment varies somewhat with the alloy and especially with the
initial character of the surface treated, that is, the degree
of polish, freedom from oxide films and the like.  The coating
is of a pleasing iridescent gray color and often has a smooth
glasslike finish.  The tensile properties of heat-treated sheet
duralumin are not affected to any extent by heating for 30 min-
utes or so at $100^{\circ}$C but, as explained in a previous report, such
a heat treatment, in itself, would be expected to result in a
somewhat lower corrosion resistance.  The results summarized in
Figure 7, clearly show that this treatment gives some protection
against mild corrosion, for example,  N/10 sodium chloride solu-
tions (approximately .5 per cent by weight).  When corroded with
a more concentrated solution of sodium chloride, a normal solu-
tion (approximately 5.8 per cent by weight; sea water contains
about 3.3 per cent NaCl), the treated specimens were attacked
to approximately the same degree as untreated specimens except
that, in the early stages of the attack, the coating retarded
the corrosion somewhat.  The "grease-holding" properties of this
type of coating are not nearly so good as the oxide coatings
produced by the anodic treatment and in general the coatings
would be recommended, on the basis of the laboratory tests, only
for very mild service.

## V.  Metallic Coatings

From theoretical considerations, such as that of solution
potential, it would be concluded that aluminum is the most
suitable metal to use for coating duralumin or other aluminum-
base alloys if a metallic coating is desired.  As has been
pointed out in earlier reports in this series of technical notes,
unalloyed aluminum is not subject to the intercrystalline type
of corrosion.  An aluminum coating in such intimate contact
with the duralumin that it becomes a part of the sheet itself,
adds structural strength to compensate for the added weight,
whereas other types of coatings do not.  This is the only coat-
ing metal which was used in this investigation.  Electro-
deposition as a coating method is not at all practicable in the
case of aluminum coatings.  The most convenient and dependable
means for the application of aluminum coatings to specimens
for use in the laboratory study of the problem is the metal
spraying method.  It is not to be inferred, however, that this
method is good only for the laboratory.  For certain phases of
the problem of the protection of duralumin against corrosion,
the metal spraying process is particularly well adapted, al-
though in the case of sheets and the products fabricated from
sheets, a special coated sheet referred to below as "Alclad"
(aluminum-clad) is now used commercially.  This product may be
regarded as the logical commercial development which embodies

the principles which were established as a result of the tests carried out on specimens coated by spraying them with aluminum.

A sprayed-metal coating adheres to the base in a mechanical way only, as a paint does; there is no alloying of the base metal with the coating metal.  It is necessary therefore, in order to secure good adhesion, that the surface to be coated be given a preliminary treatment of some sort.  Usually this consists in a slight roughening, sand-blasting being used for the purpose.  This is one obstacle to the ready application of the metal spraying method for the coating of duralumin sheet.  The mechanical properties of the sheet are affected decidedly by the sand blasting and in the case of very thin material, the method would probably not be feasible at all.  In the case of sheet of the thickness used for most of the tests of this investigation (14-gauge), however, although the sand blasting had a pronounced hardening effect upon the material, as is shown by Figure 8.  This effect could be entirely removed by heat treating the material afterwards.  This was done after the aluminum coating had been sprayed on to the test specimens.

A very distinct advantage of the metal spraying process as a coating method is the range of coating thickness that can be readily and easily obtained.  For the tests reported here, the average weight of coating applied was .0042 oz. per sq.ft. of surface (.0028 to .0056).

In preparing the metal-sprayed specimens for the early

tests, aluminum wire of two different compositions was used;
one of good commercial grade (Cu, .10%;  Fe, .20%;  Si, .13%;
Sn, Ni, Mn, Zn, Cr, Ca, Mg, not detected) and the other of high
purity (Cu .08,  Fe .05,  Si .03,  other elements listed above,
not detected).  No essential difference in the behavior of the
coated specimens was shown by the corrosion tests carried out
and in the later tests, the coating was done with only the com-
mercial grade of wire.  Experiments with the metal spraying
process, made in connection with other investigations, have in-
dicated the advantage to be gained in using an inert gas for
spraying instead of compressed air, the coating being denser
and apparently more impervious.  In the tests which were made
on duralumin test bars sprayed according to these two methods,
however, no marked difference was noted in the behavior of the
two sets of specimens coated in these two ways when subjected to
very severe corrosion  ($NaCl + H_2O_2$).  Hence, the commercial
type of gas-heated metal spray gun using compressed air, should
be suitable for spraying aluminum for the purpose under discus-
sion.  In one case only, and then only after a prolonged attack
(21 days), was any sure indication obtained of a "breakdown" of
the aluminum coating during corrosion.  In all other cases, as
shown by the results in Figure 8, complete protection was ob-
tained, the differences in the tensile properties of the coated
specimens after corrosion being of the same order of magnitude
as those which would be shown by a series of uncorroded specimens.

Sprayed-aluminum coatings are not damaged very easily by deforma-
tion such as cold rolling or stretching. Sprayed specimens
which were corroded after being cold-rolled or stretched (4 per
cent) showed a resistance to corrosion which in all essential
respects was no lower than that of sprayed specimens which had
not been deformed prior to testing (Fig. 8). The ability of
the aluminum coating, whether sprayed or as "Alclad" to be
scratched or dented without baring the duralumin gives such
coatings marked advantages when rough usage is to be expected.

Sprayed specimens which were given a grease film (lanoline)
withstood perfectly very severe corrosion attack for 40 days.
Except for very severe prolonged attack, the greasing treatment
would not seem to be necessary, however, for coatings of this
type.

## "A l c l a d"

This material, which is now commercially available in sheet
form, has already been described (Reference 7). Its development
resulted from the same considerations that prompted the use of
sprayed-aluminum coatings in the laboratory corrosion tests sum-
marized above. Details of the method of manufacture have not
been published as yet, but this information is not needed for a
full appreciation of the superior properties of this type of
sheet material. It probably differs little in principle from the
method commonly used for the production of such materials as

"copper-clad" steel.  In its finished condition, "Alclad" consists of a sheet of duralumin (or other high-strength aluminum alloy sheet may be used), each surface of which is covered by a coating of aluminum which, as a result of the rolling of the coated slab together with the annealings intermediate between rollings, has become firmly alloyed to the underlying duralumin and forms an integral part of the finished sheet.  No buckling, or separation of the coating and base, occurs upon bending the sheet, even if the deformation is very severe.  The relative thickness of the aluminum coating as shown in Figure 9, which depicts a cross section of a sheet of this material, is quite representative of material of the thickness used in the tests (14-gauge).

While the initial strength of the triplex sheet is, of course, slightly less than one of the same thickness consisting of duralumin alone, the comparison should not be made on the basis of initial strength only.  A comparison made between an unprotected duralumin sheet and an "alclad" sheet, in which the unprotected one had begun to suffer appreciably from intercrystalline corrosion after say, a year's exposure in service, would show little difference on the score of strength but a great superiority for the protected sheet on the score of ductility and freedom from brittleness.

From the results summarized in Figure 9, it will be seen that this material shows an exceptionally high degree of resistance even to prolonged corrosion under severe corrosive condi-

tions.  Ordinarily, no precaution need be taken to guard against corrosion of the cut edges of "Alclad" sheet.  However, if the material has been heat-treated by quenching in hot water, it appears that the cut edges must be protected.  Tests of specimens of "Alclad" sheet which had been quenched in hot water gave results very much inferior to those obtained with the same material which had been quenched in cold water.  Microscopic examination showed that corrosion had occurred where the duralumin base was exposed along the cut edges of the specimen.  Without question, the lower tensile properties obtained under such conditions are to be attributed to this, since no failure whatever of the coating itself was detected in any case.

## VI.  Summary

1.  Although the corrosion resistance of sheet duralumin can be greatly improved by suitable heat treatment, protection of the surface is still necessary if long life under varied service conditions is to be ensured.  On many points concerning the service behavior of the coatings, information which can be gained only from the weather-exposure tests now under way is necessary before final conclusions can be drawn.

2.  The coatings used for this purpose may be conveniently grouped into three classes: the varnish type of coatings, which are nonmetallic in their nature and are applied by brushing,

spraying or dipping; the oxide type produced by a chemical
treatment of the metal whereby the surface metal is converted
into a film of oxide or some similar compound; and metallic coat-
ings, of which aluminum appears to be the most promising.

3.    The test method used was similar to that described in
previous reports and consisted in the corrosion of full-size
tension bars which had been coated in the desired manner, the
effectiveness of the coating being shown by the results obtained
when the bars were tested in tension after being corroded.  In
order to obtain by this method the most definite and rapid indi-
cations as to the relative merits of any given coating for use
on duralumin, the duralumin sheet used should be in such a con-
dition as to be, in the uncoated state, readily susceptible to
intercrystalline corrosive attack by the solution used.

4.    Specimens were prepared at the Naval Aircraft Factory
representative of the three most commonly used coatings of the
varnish type, viz., plain spar varnish, spar varnish pigmented
with aluminum powder and bitumastic coatings.  Tests by the
"spray" corrosion test and by intermittent immersion failed to
show any pronounced differences in the three coatings.  All
showed high resistance.  Oxidizing solutions caused a breakdown
of the coatings, the bitumastic being most resistant.  Failure
of all the coatings of this type in immersion tests usually oc-
curred by "blistering" of the coating.  By determination of the

progressive changes in the relative permeability to moisture of coatings of plain and of aluminum-pigmented spar varnish coatings, as a result of weather exposure, the pronounced advantage to be gained by the use of aluminum powder in such coatings for atmospheric service was clearly indicated.

No pronounced difference in the behavior of plain bitumastic and aluminum-pigmented bitumastic coatings for severe corrosive conditions was shown by the tests carried out. Sodium silicate coatings when used on sheet duralumin are suitable only for mild corrosive conditions. The baking treatment which this coating method necessitates would be expected to lower somewhat the general corrosion-resistance of the uncoated material. Rubber coatings when pigmented with aluminum powder gave results in laboratory tests indicating their decided usefulness as a means of protecting sheet duralumin.

5.   The character of the surface, especially the degree of polish, has a noticeable effect upon the rate of corrosive attack provided the attack is a mild one. Much of this effect should evidently be attributed to the grease incorporated into the polished surface from the buffing compound used.

6.   Oxide coatings can readily be produced on duralumin and other aluminum alloys by the "anodic" method, the material to be treated being made the anode of an electrolytic cell with a solution of chromic acid as the electrolyte. Such coatings when

greased showed very superior protective properties, even under
very severe corrosive conditions. For this protection to con-
tinue in actual service, the grease film must remain intact.
Re-greasing will be necessary from time to time. Exposure tests
with different re-greasing schedules are under way. The oxide
film is necessary in order to "hold" the grease; simple greasing
of the surface, except in the case of a very heavy coating used
together with aluminum powder, failed to protect duralumin under
the same conditions for which the "anodic" oxide coatings plus
a grease film gave perfect protection. Coatings produced by
anodic oxidation unless greased cannot be relied upon except for
very mild corrosive attack. Oxide coatings produced by prolonged
immersion in dilute nitric acid are decidedly inferior to those
produced by anodic oxidation. Likewise, the coatings produced
the Jirotka method of immersion in a hot solution of a chromium
salt, and a dichromate together with other additions, failed to
protect duralumin sheet except under mild corrosive conditions.

7. Aluminum coatings can be readily applied to sheet dura-
lumin by metal spraying. In order to obtain good adhesion, the
surface must be roughened before being sprayed, which is usually
done by sand blasting. The changes induced by this treatment
would prohibit the use of this method on very thin sheet. On
sheet of the thickness used for the tests, 14-gauge, the ill
effects of sand blasting were readily removed by heat treating

after spraying.  Aluminum-sprayed coatings showed a very high
degree of protection against very severely corrosive conditions
even when the coated sheet, before corrosion, had been subjected
to deformation by cold rolling or by stretching.

8.  The advantages of aluminum coatings as a means of pro-
tecting duralumin against severe corrosion, shown by the results
of the tests with metal sprayed coatings, have been embodied in
the development of "Alclad," an aluminum-coated duralumin sheet
now commercially available.  In order to obtain the highest de-
gree of protection, however, this material should be heat-
treated by quenching in cold water.  If hot water quenching is
used in heat treating it, corrosion of the underlying duralumin
along the cut edges may be expected to occur.

9.  It will be noted that the newer coating methods which
appear most promising on the basis of the evidence so far obtain-
able, (a) metallic aluminum, (b) oil or grease over the anodic
coating (with frequent re-oiling for thin oil coats or with
aluminum powder over heavy coats), (c) tight-clinging rubber
cement carrying, or covered by, aluminum powder, – do not readily
crack, flake nor bare the duralumin beneath, on weathering and
vibration, which is in marked contrast to the ordinary "alumi-
nized" varnish or bitumastic coatings.  Those coatings, whose
behavior is known from service experience will, of course, con-
tinue to find use.  The newer coatings, except the "aluminized"

rubber which is, as yet, used only to a limited extent, are also
beginning to come into commercial use and their suitability
should soon be better understood.  The metallic aluminum coatings
will stand quite severe abuse, such as scratching or denting
without baring the duralumin.  The flexible oil or rubber coat-
ings can, of course, be scratched through, but will withstand
far more abuse than a weathered varnish-type coating.

Any of the flexible coatings may be applied over the alumi-
num coating, to give added protection for severe service.  It
would appear that seaplane floats made of "Alclad" and coated
with aluminized rubber cement deserve service tests.

The choice among these various coatings or combinations of
coatings will have to be made on the basis of the particular
conditions to be met in service and on the weight that can be
allowed in order to secure protection.  Exposure tests and serv-
ice tests will be required to tell just what combination gives
the best results for any particular case.

As soon as the exposure tests have progressed sufficiently
to give enough definite information to warrant it, the results
will be reported in another technical note in this series.

# References

1.  Rawdon, Henry S. : Corrosion Embrittlement of Duralumin.
                        I. Practical Aspects of the Problem.
                        N.A.C.A. Technical Note No. 282 (1928).

                        Corrosion Embrittlement to Duralumin.
                        II. Accelerated Corrosion Tests and the
                        Behavior of High-Strength Aluminum Alloys
                        of Different Compositions. N.A.C.A.
                        Technical Note No. 283. (1928)

                        Corrosion Embrittlement of Duralumin.
                        III. Effect of the Previous Treatment of
                        Sheet Material on the Susceptibility to
                        this Type of Corrosion. N.A.C.A. Tech-
                        nical Note No. 284. (1928)

2.  Gardner, H. A.    : Protective Coatings for Duralumin and
                        Similar Light Weight Alloys for Exposed
                        Construction. Published by Henry A.
                        Gardner Laboratory, Washington, D.C. (1926)

3.  Hickson, E. F.    : Tests by - Paint and Varnish Section,
                        Bureau of Standards.

4.  Daniels, S.
        and           : Treatment of Aluminum Castings with Water
    Zimmerman, A. C.    Glass. U.S. Army specification (Air
                        Service) No. 57-72-3, 1927. U.S. Patent
                        1,540,766, 1925.

5.  Bengough, G. D.
        and           : Protection of Aluminum and Its Alloys
    Sutton, H.          against Corrosion by Anodic Oxidation.
                        "Engineering," 122, p.274, 1926.
                        U. R. Evans, Corrosion of Metals, p.185,
                        1923, British Patents 223,994 and
                        223,995, 1923.

6.  Jirotka, B.       : Coatings on Aluminum and Aluminum Alloys.
                        U.S. Patent 1,607,676, 1926.

7.  Dix, E. H.        : "Alclad" A New Corrosion-Resistant Product.
                        National Advisory Committee for Aeronau-
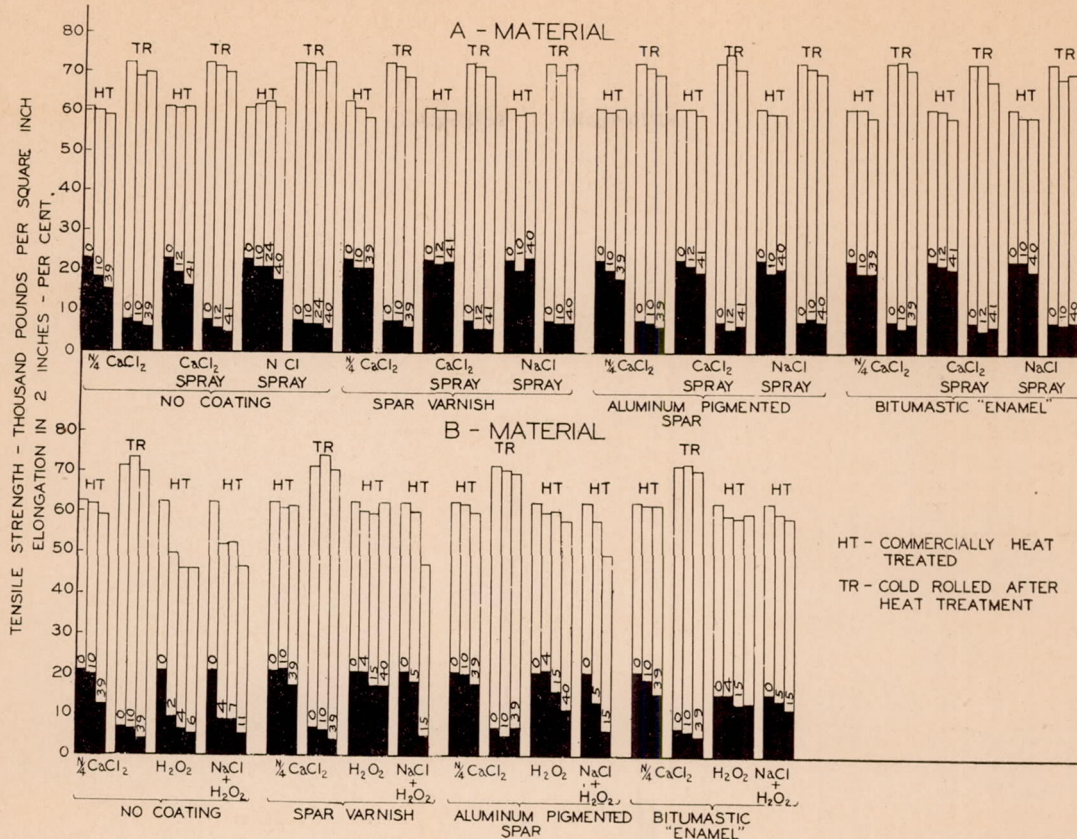                        tice Technical Note No. 259. (1927)

**Fig. 1**

Corrosion tests of sheet duralumin protected by means of coatings of the varnish type. Unless indicated otherwise here and elsewhere tests were made by the intermittent immersion method. 14-gage sheet material was used here and elsewhere. The height of the unshaded rectangle shows the ultimate tensil strength and that of the shaded portion the elongation ( 2 inch gage length ).   The latter value is by far the more significant one.
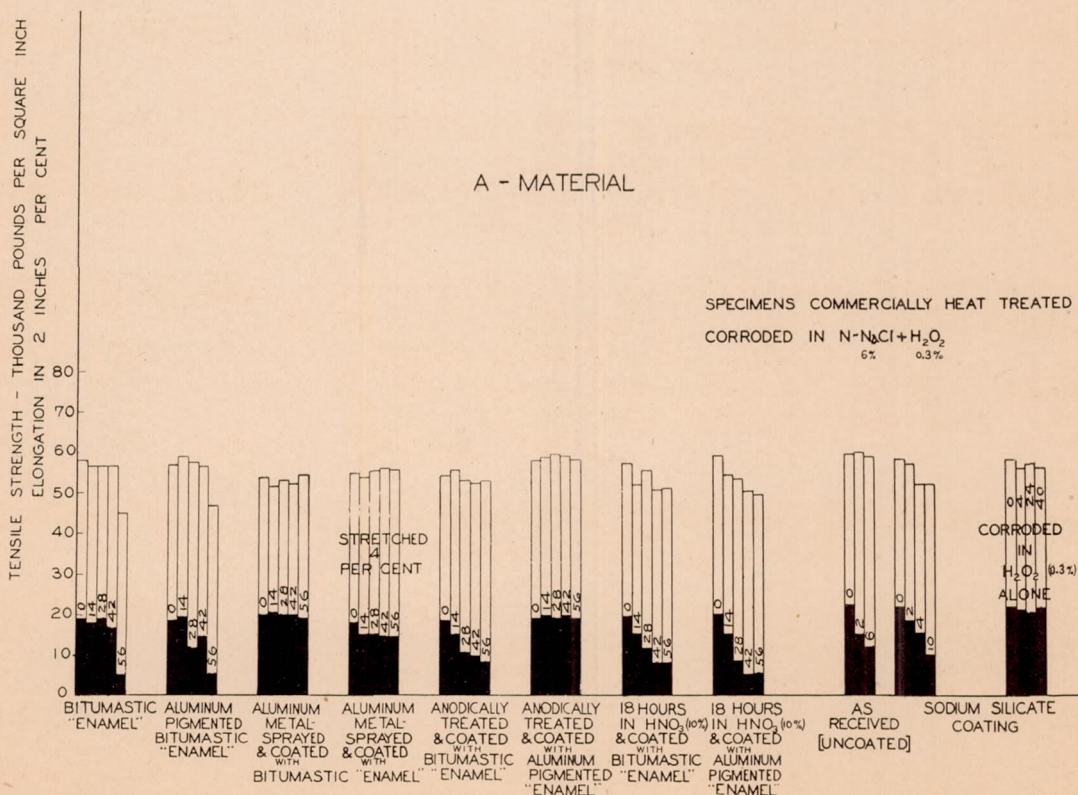
HT – COMMERCIALLY HEAT TREATED

TR – COLD ROLLED AFTER HEAT TREATMENT

A – MATERIAL

B – MATERIAL

A – MATERIAL

SPECIMENS COMMERCIALLY HEAT TREATED

CORRODED IN N–NaCl + H₂O₂

Fig. 3   Protection afforded sheet duralumin by bitumastic coatings and sodium silicate coatings.
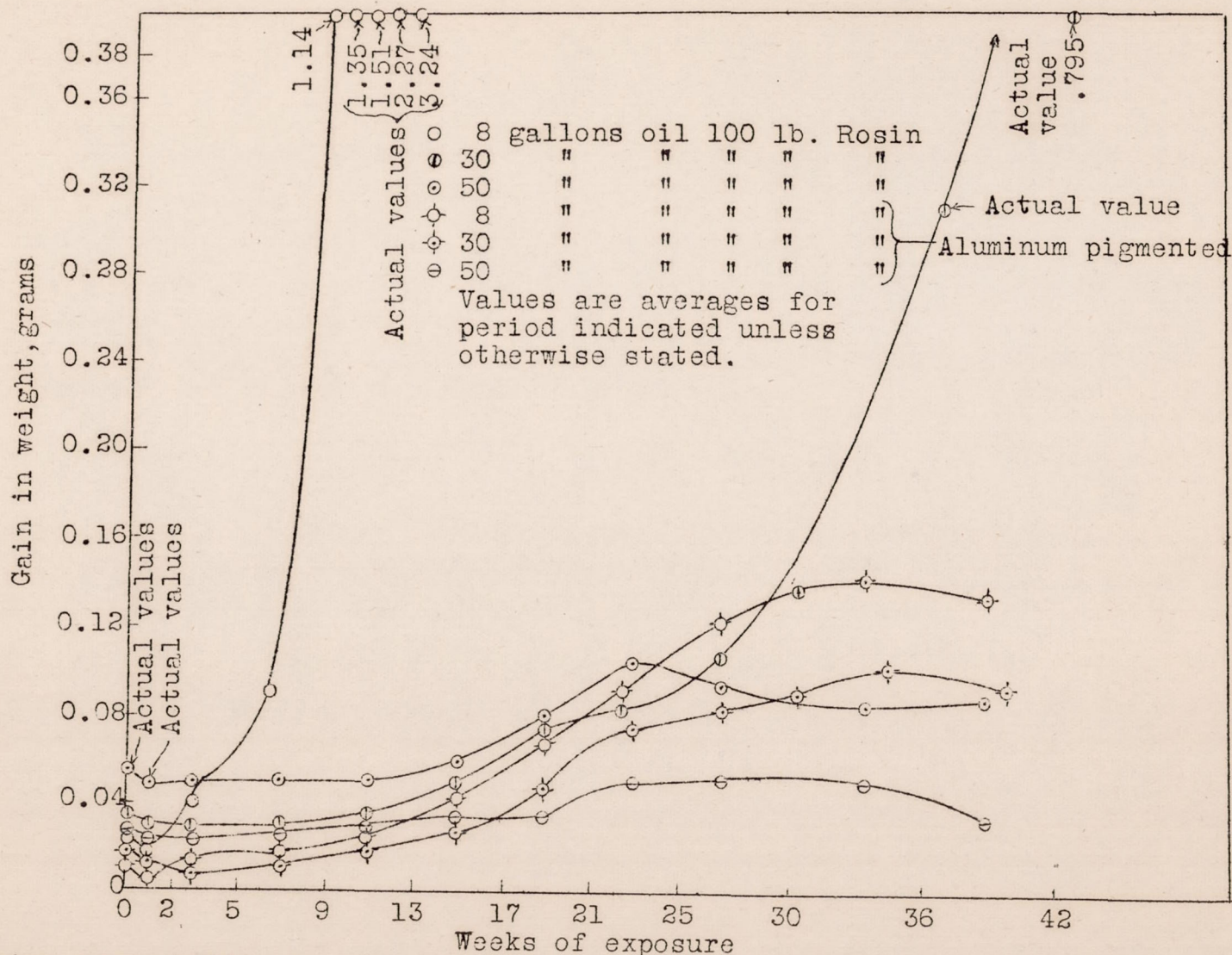
Fig.2 Relative permeability to atmospheric moisture of plain and pigmented varnish coatings. The permeability was determined after each week's exposure, only averages are given above. Note the decided improvement in the "short oil" varnish (8 Gallon) which resulted from the pigment.
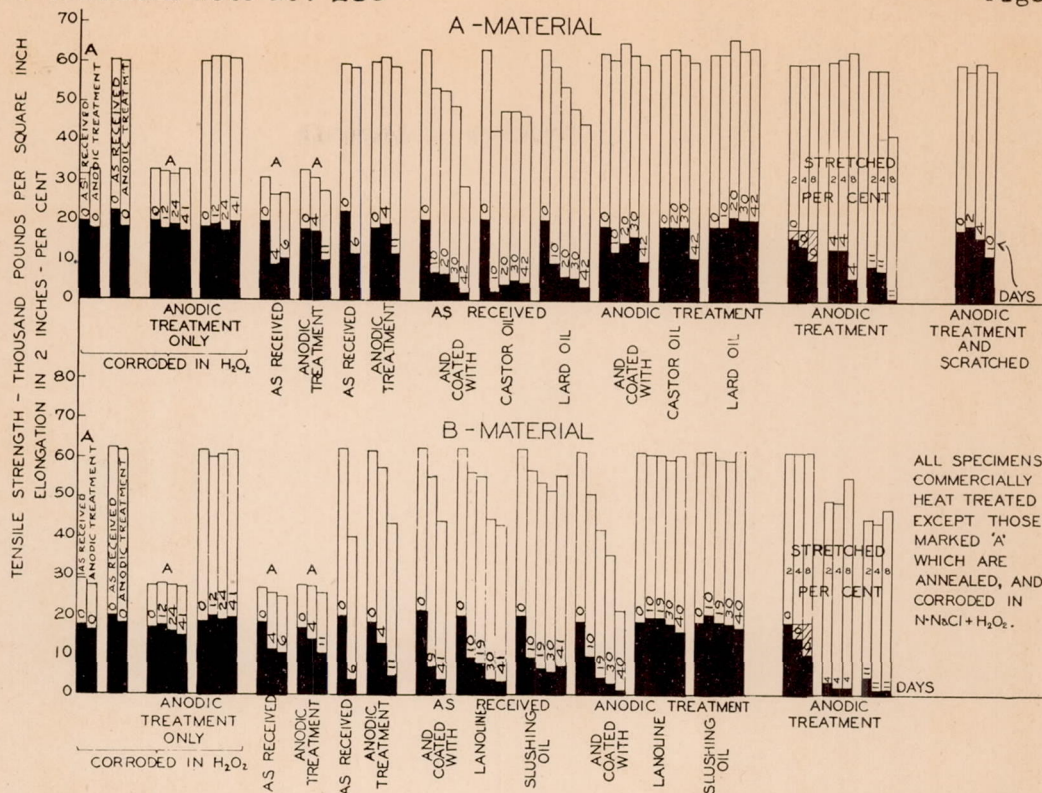
Fig.2

Fig.4  Protection afforded sheet duralumin by oxide coatings produced by anodic oxidation together with various supplementary greasing treatments.
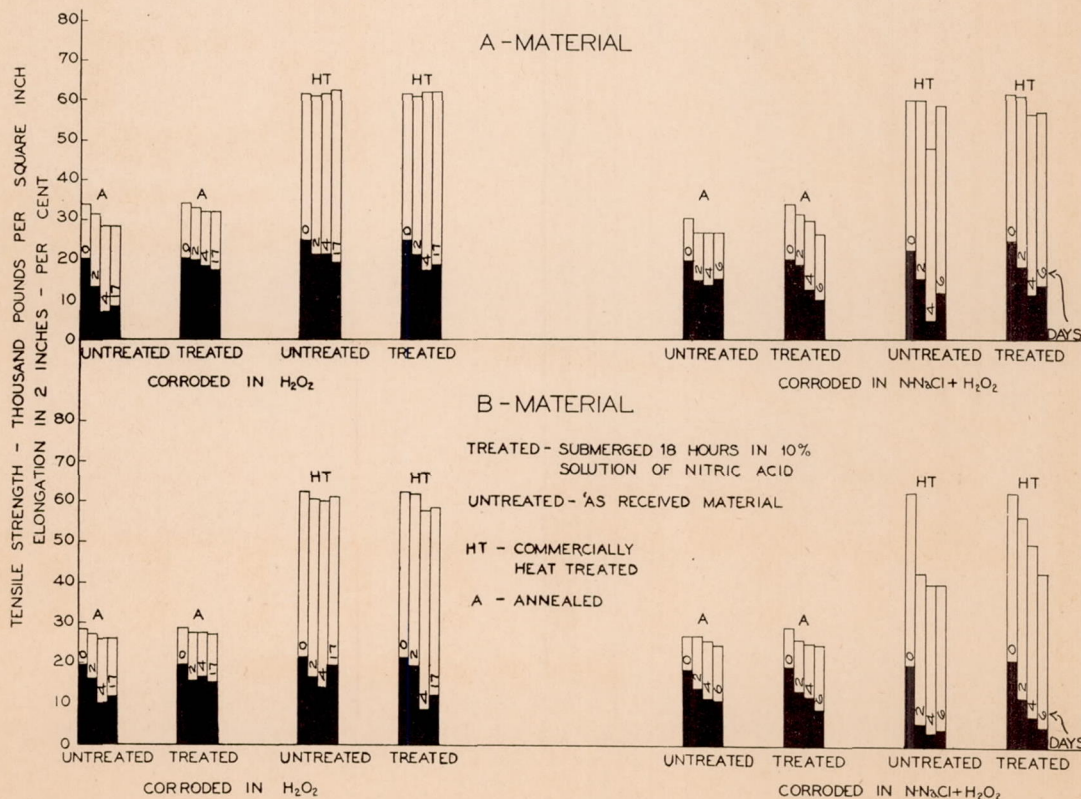


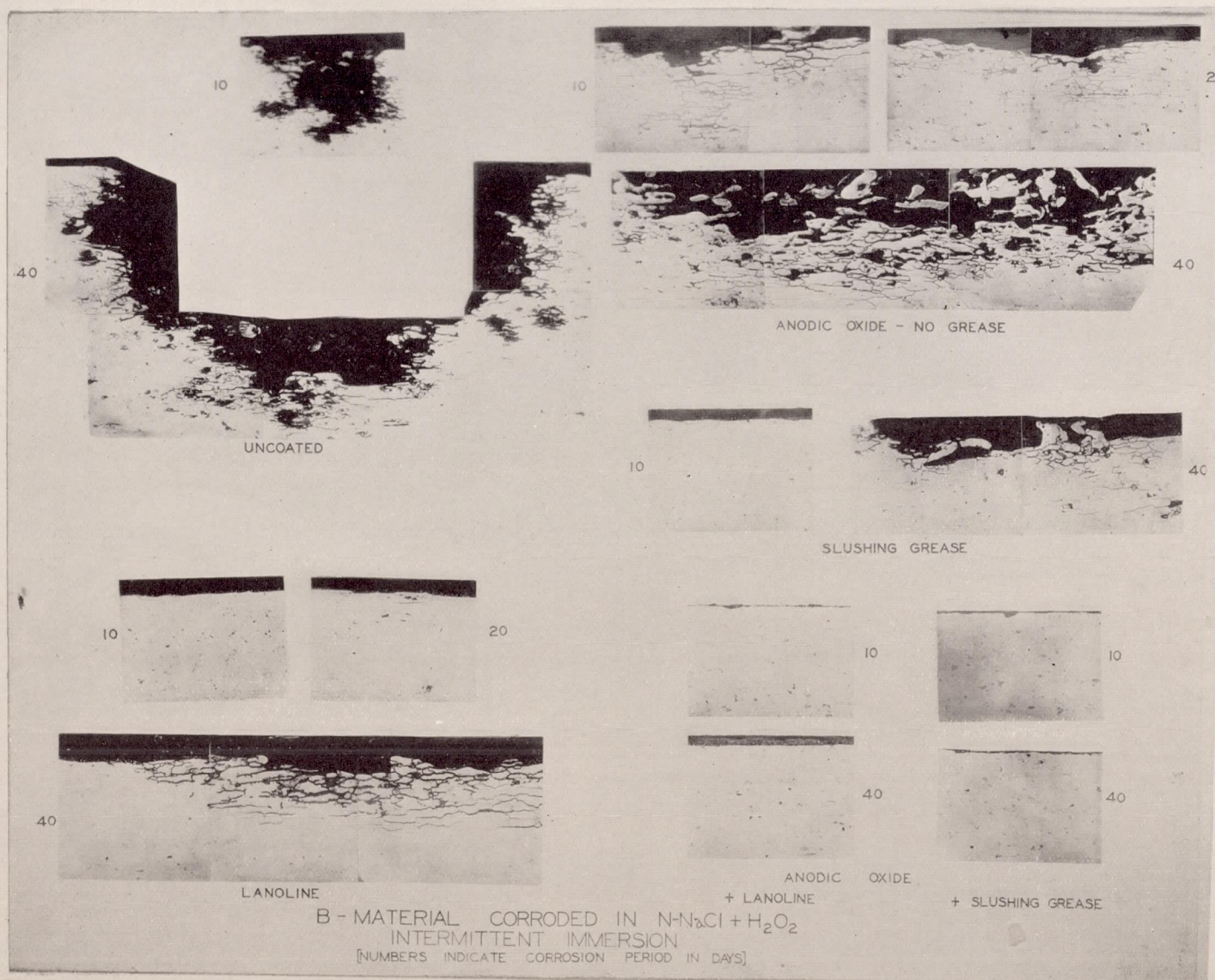Fig.6  Degree of protection afforded sheet duralumin by oxide coatings produced by dilute nitric acid.

Fig. 5

UNCOATED

ANODIC OXIDE – NO GREASE

SLUSHING GREASE

LANOLINE

ANODIC OXIDE
+ LANOLINE          + SLUSHING GREASE

B – MATERIAL CORRODED IN N-N₂Cl + H₂O₂
INTERMITTENT IMMERSION
[NUMBERS INDICATE CORROSION PERIOD IN DAYS]

Fig. 5   Micrographs to supplement Figure 4.   Original magnification x 250, reduced to x 70 (approx.)

Fig. 7 Degree of protection afforded sheet duralumin by "oxide" coatings produced by immersion in in hot solutions containing chromium salts

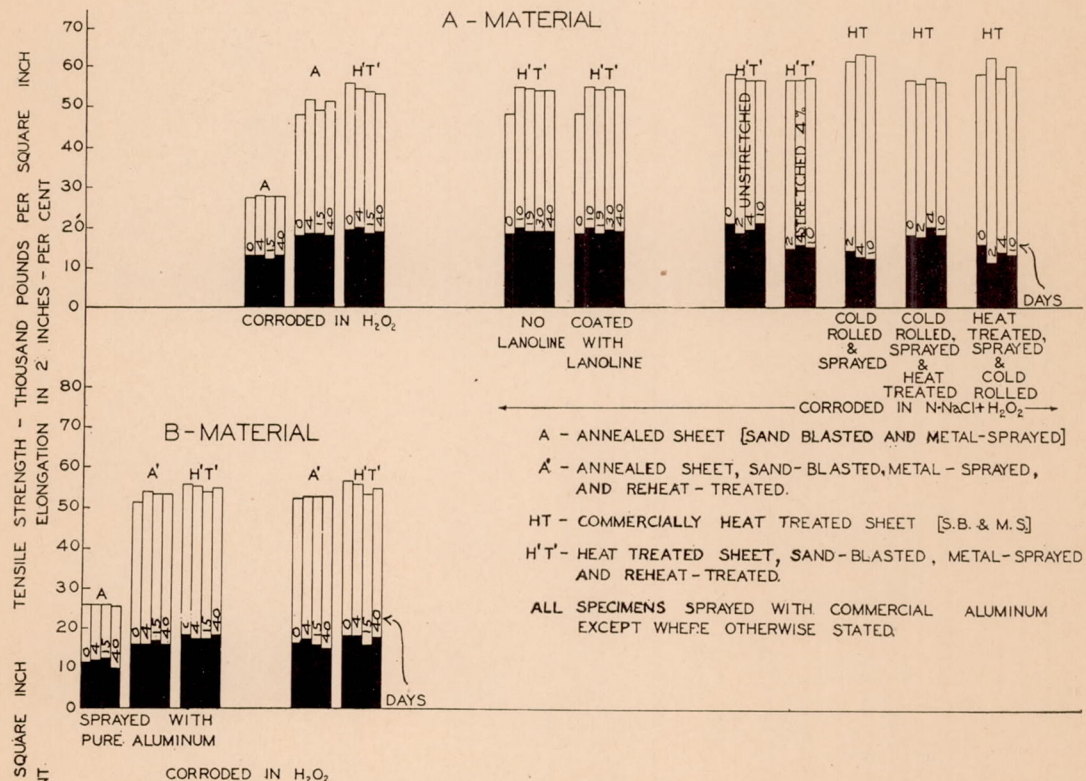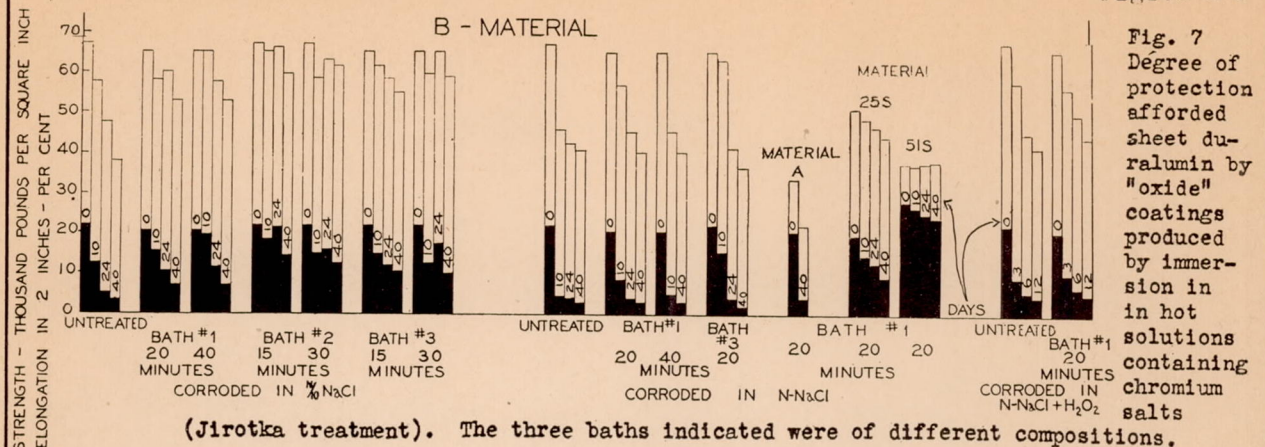(Jirotka treatment).  The three baths indicated were of different compositions.
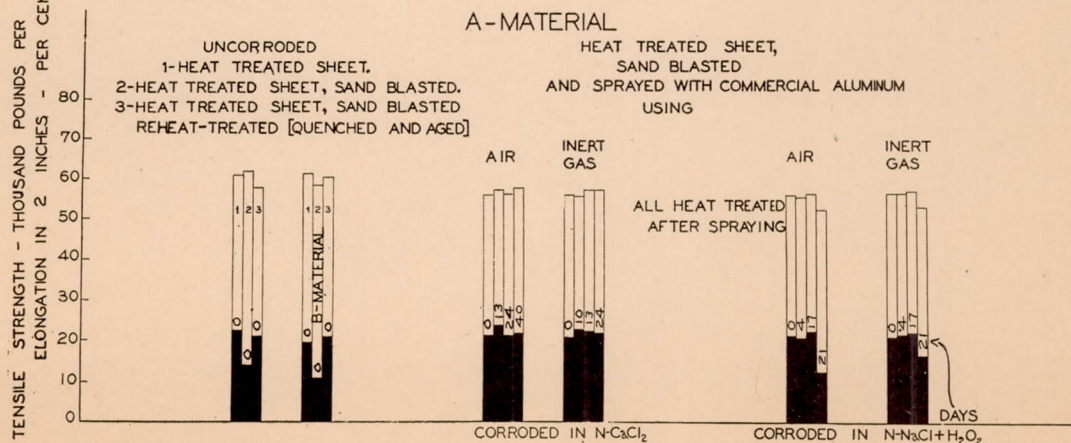


Fig.8  Protection afforded sheet duralumin by sprayed-metal (aluminum) coatings; average weight of coating .0042 oz./ sq.ft.
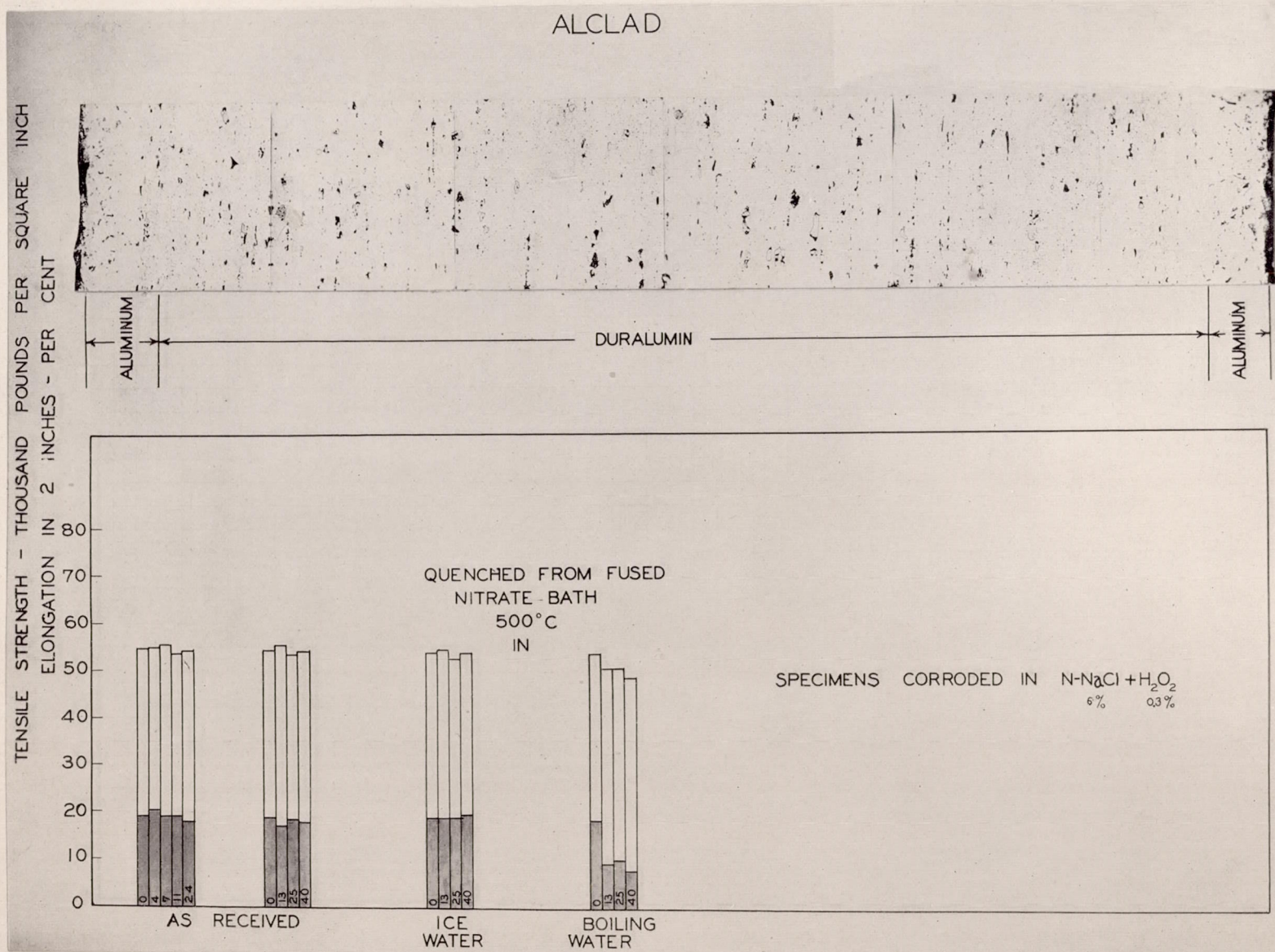
Fig. 9    Structure of "Alclad" sheet and its behavior when corroded.

Fig. 9