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CORROSION EMBRITTLEMENT OF DURALUMIN
IV. THE USE OF PROTECTIVE COATINGS

By Henry S. Rawdon
Bureau of Standards

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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 publication 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 entirely 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 protection 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 frequently, 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) Varnish type of coatings. These coatings are nonmetallic 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) Oxide films.- 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 properties 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 results 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 breakdown 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 experience in service under atmospheric exposure. Thus, a recommendation 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 coatings 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 relative 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 solution) 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. Blistering 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 treatment. 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 coatings 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°F (110°C) for 10 minutes, then raised to 280-300°F (140-150°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 dularumin consists in the use of a special aluminum-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 preliminary roughening of the surface. The presence of traces of oil on the metal surface to be coated does not appear to prevent adhesion as would be the case with varnishes. As received, the cement contains no aluminum powder. This may either be incorporated into the cement, before it is applied to the surface by brushing, or it may be dusted on to the "tacky" rubber surface 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 exposure 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 coated 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 preparing 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°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 minutes 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 solution. In the treatment of the tension bars this was done by allowing 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 different materials, perhaps depending upon the previous heat treatment, and was found to range from .001 to .004 oz./sq.ft. (approximately). 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 commercial use of the anodic oxidation process as a means for protecting 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 usually 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 permanently 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 necessary, 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 companion ungreased specimens and as were also similar specimens which had been given the anodic oxidation treatment but no greasing. 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 specimens, 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 obtained by means of other oxidizing solutions. The surface film produced by dilute nitric acid is more "open" in its appearance 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 originator (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 decidedly empirical in its nature but the solutions usually contain 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 different 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 minutes or so at 100°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 solutions (approximately .5 per cent by weight). When corroded with a more concentrated solution of sodium chloride, a normal solution (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 coating metal which was used in this investigation. Electrodeposition 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, although 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 commercial grade of wire. Experiments with the metal spraying process, made in connection with other investigations, have indicated 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 discussion. 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 obtained, 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 deformation 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 summarized 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 coatings, 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 indications as to the relative merits of any given coating for use on duralumin, the duralumin sheet used should be in such a condition 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 occurred 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 continue 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 duralumin 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 protecting 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 degree 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 obtainable, (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 "aluminized" varnish or bitumastic coatings. Those coatings, whose behavior is known from service experience will, of course, continue 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 coatings 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 aluminum 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 service 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.

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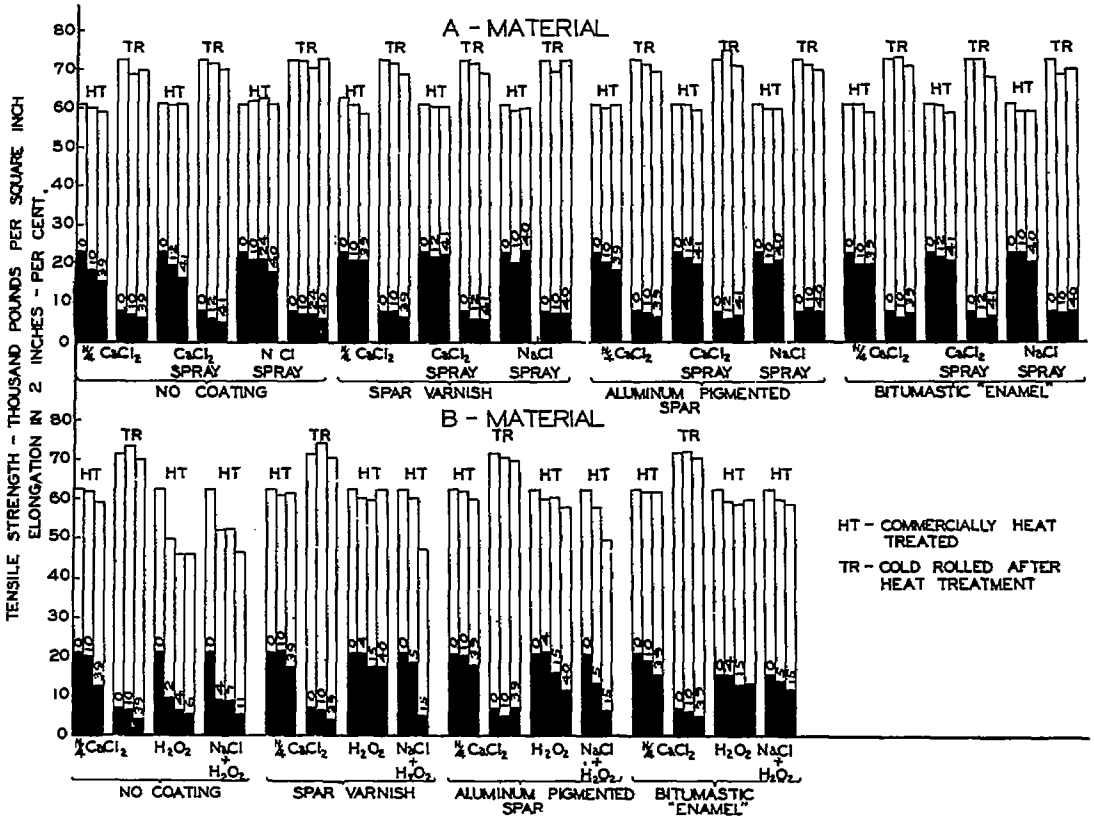

Fig. 1 Corrosion tests of sheet duralumin protected by means of coatings of the varnish type. Unless indicated otherwise here and elsewhere tests were made by the intermittent immersion method. 14-gage sheet material was used here and elsewhere. The height of the unshaded rectangle shows the ultimate tensil strength and that of the shaded portion the elongation (2 inch gage length). The latter value is by far the more significant one.

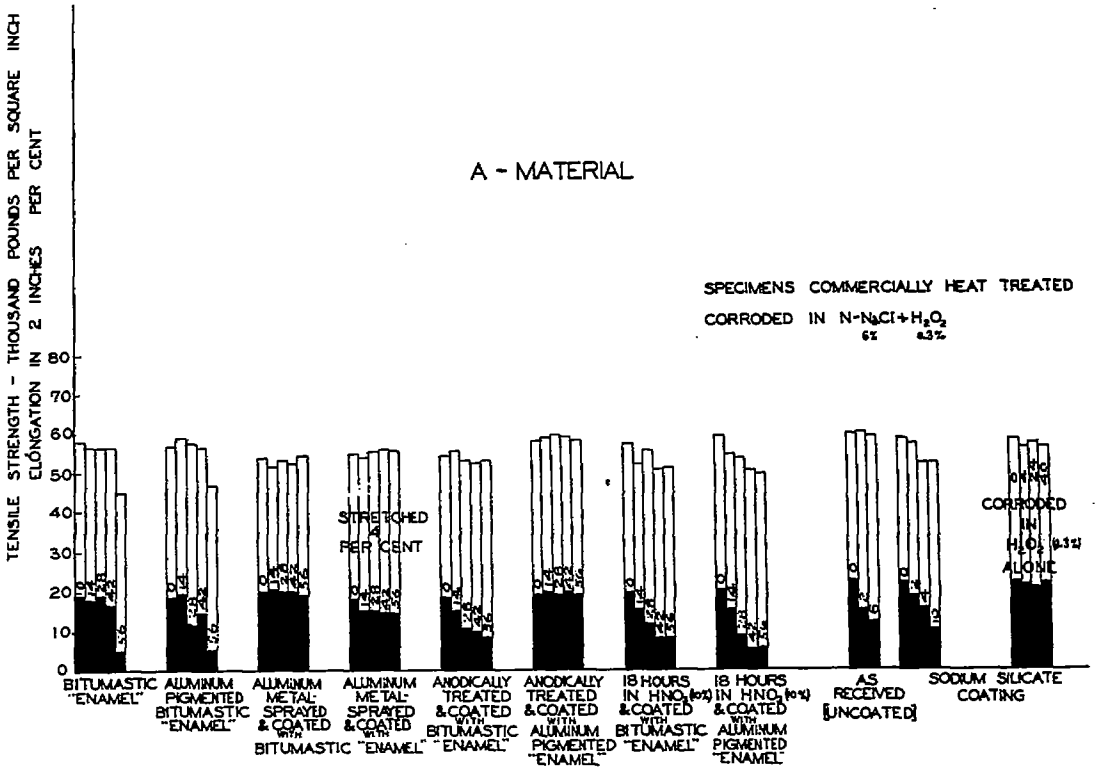

Fig. 3 Protection afforded sheet duralumin by bitumastic coatings and sodium silicate coatings.

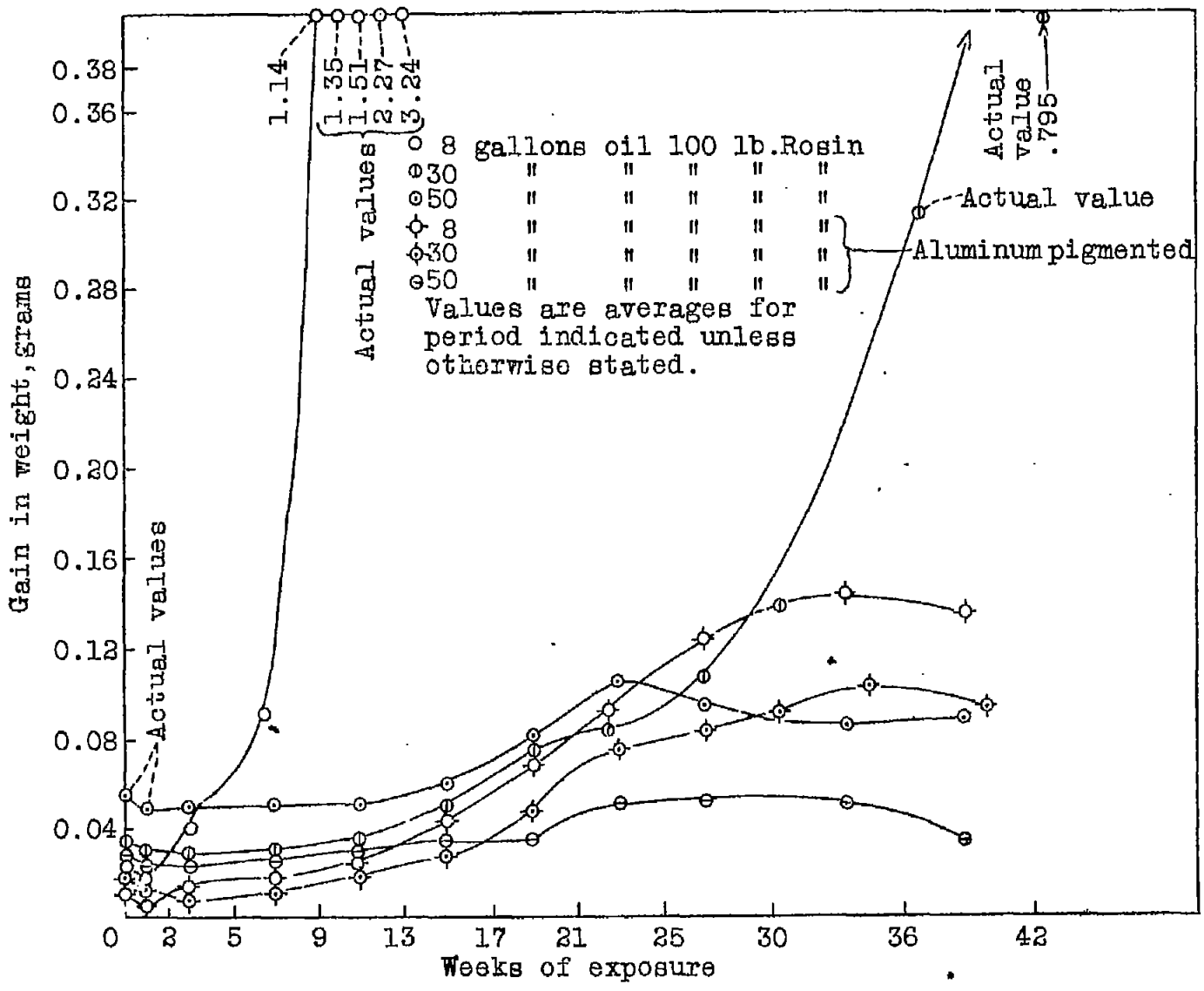

Fig.2 Relative permeability to atmospheric moisture of plain and pigmented varnish coatings. The permeability was determined after each week's exposure, only averages are given above. Note the decided improvement in the "short oil" varnish (8 Gallon) which resulted from the pigment.

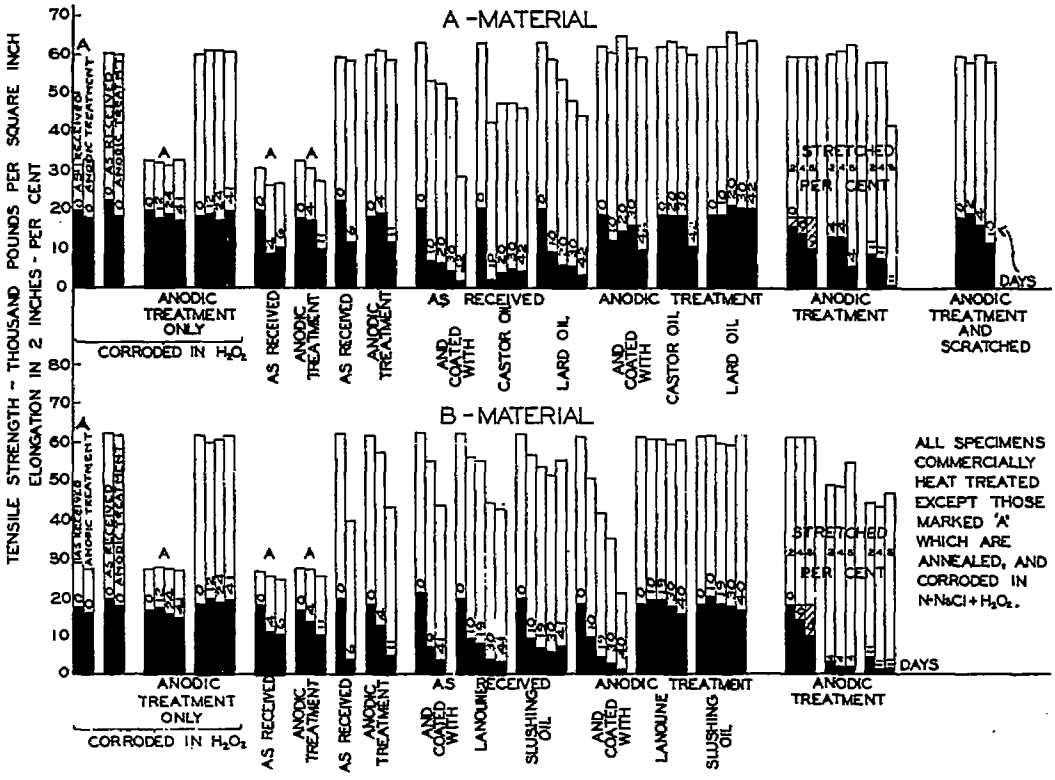

Fig.4 Protection afforded sheet duralumin by oxide coatings produced by anodic oxidation together with various supplementary greasing treatments.

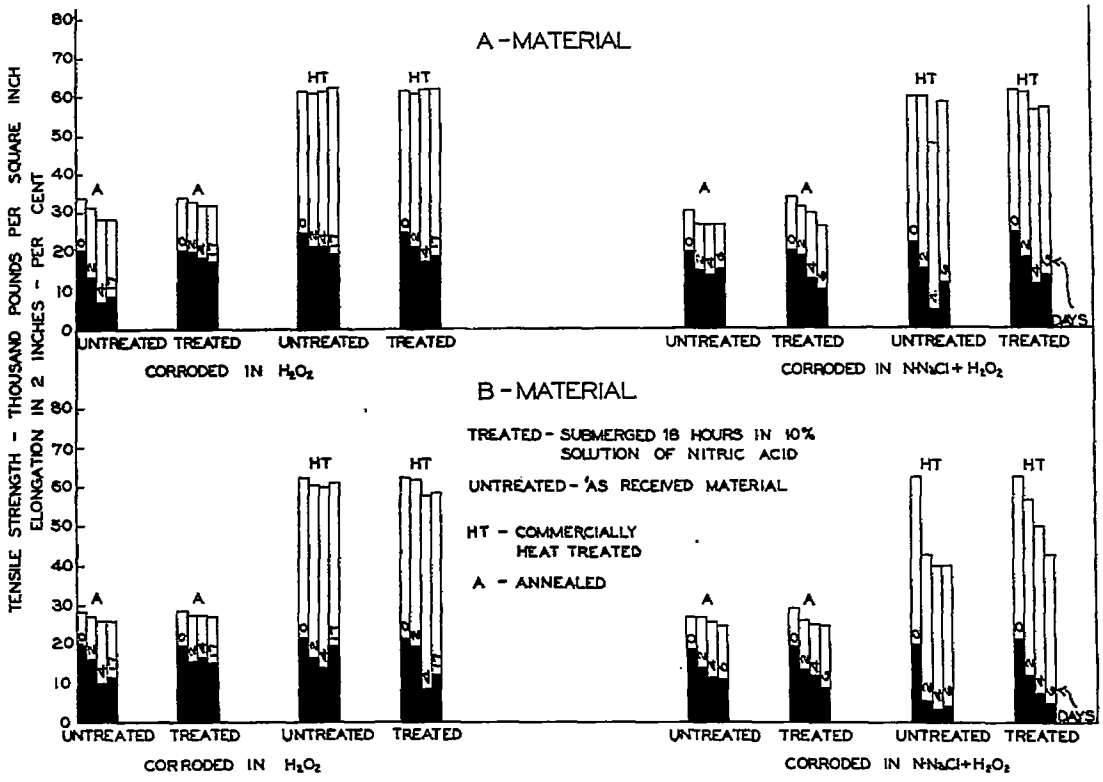

Fig.6 Degree of protection afforded sheet duralumin by oxide coatings produced by dilute nitric acid.

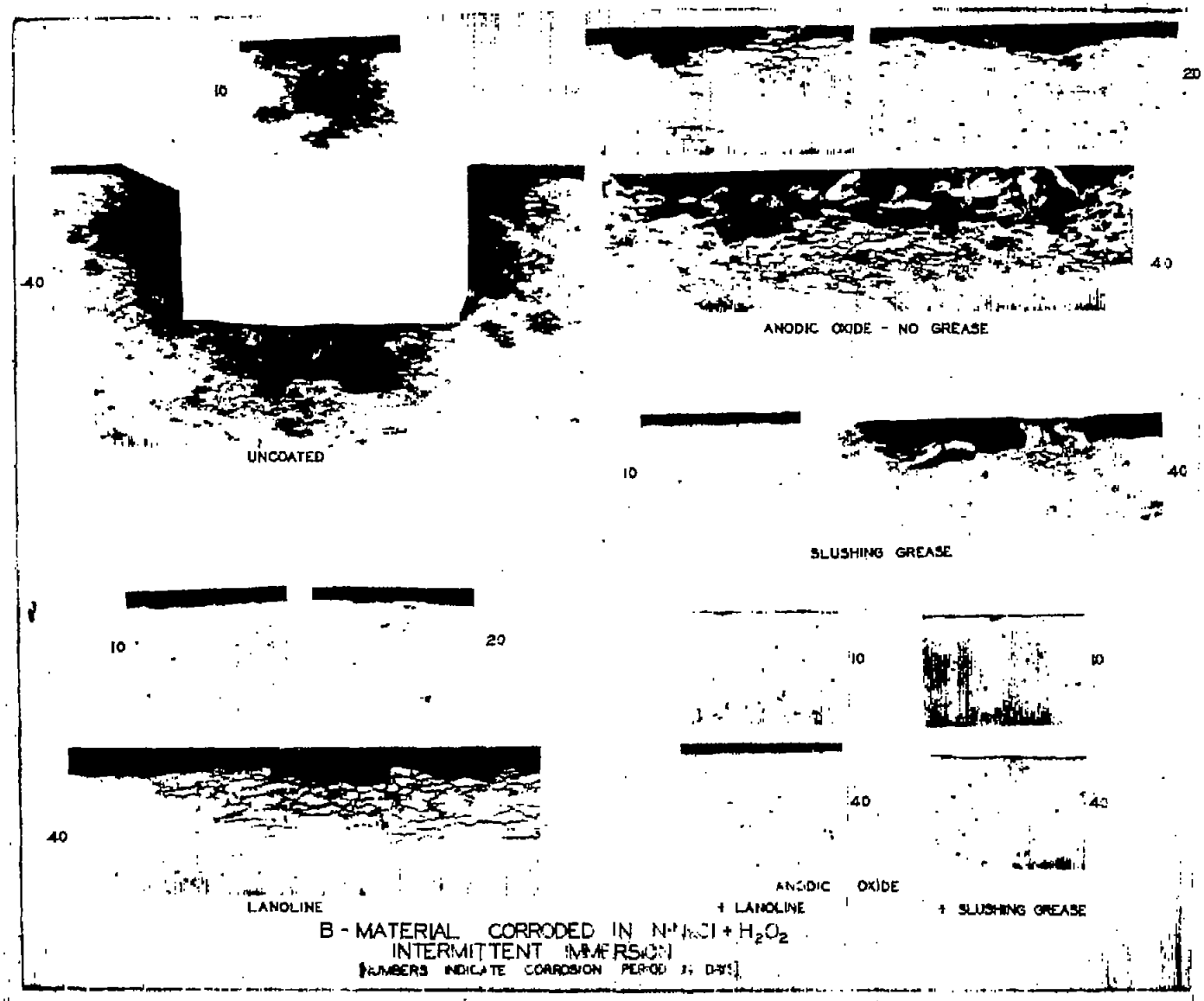

Fig. 5 Micrographs to supplement Figure 4. Original magnification x 250, reduced to x 70 (approx.)

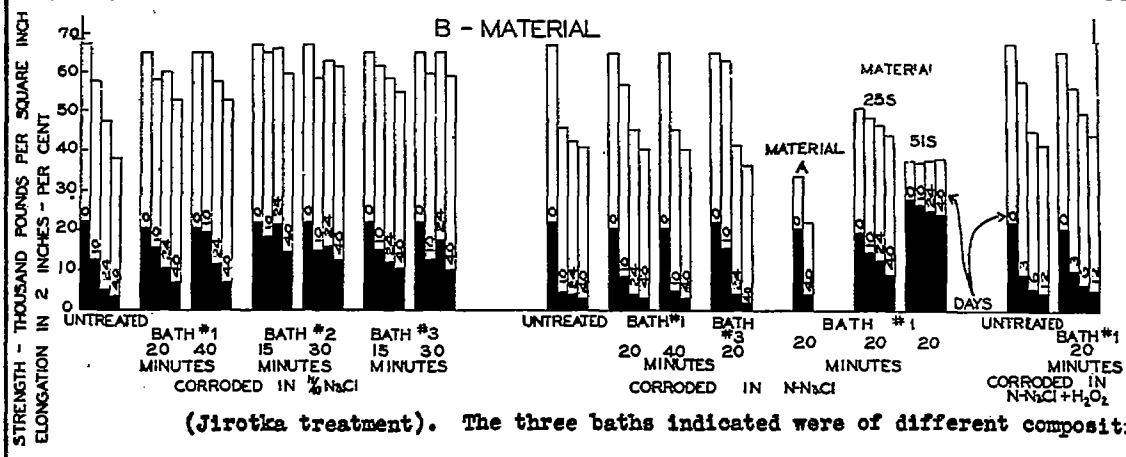

Fig. 7 Degree of protection afforded sheet duralumin by "oxide" coatings produced by immersion in in hot solutions containing chromium salts (Jirotka treatment). The three baths indicated were of different compositions.

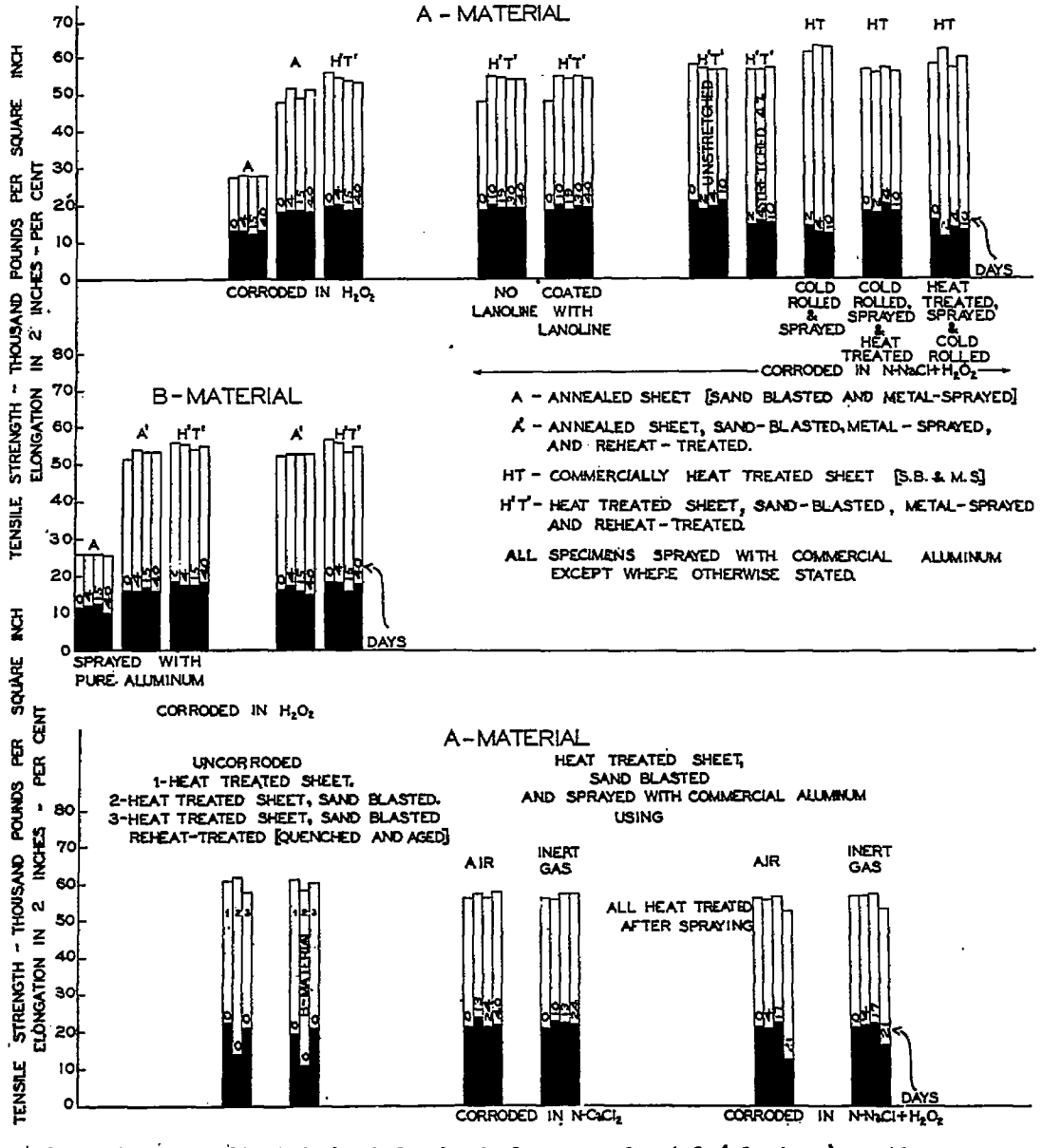

Fig.8 Protection afforded sheet duralumin by sprayed-metal (aluminum) coatings; average weight of coating .0042 oz./ sq.ft.

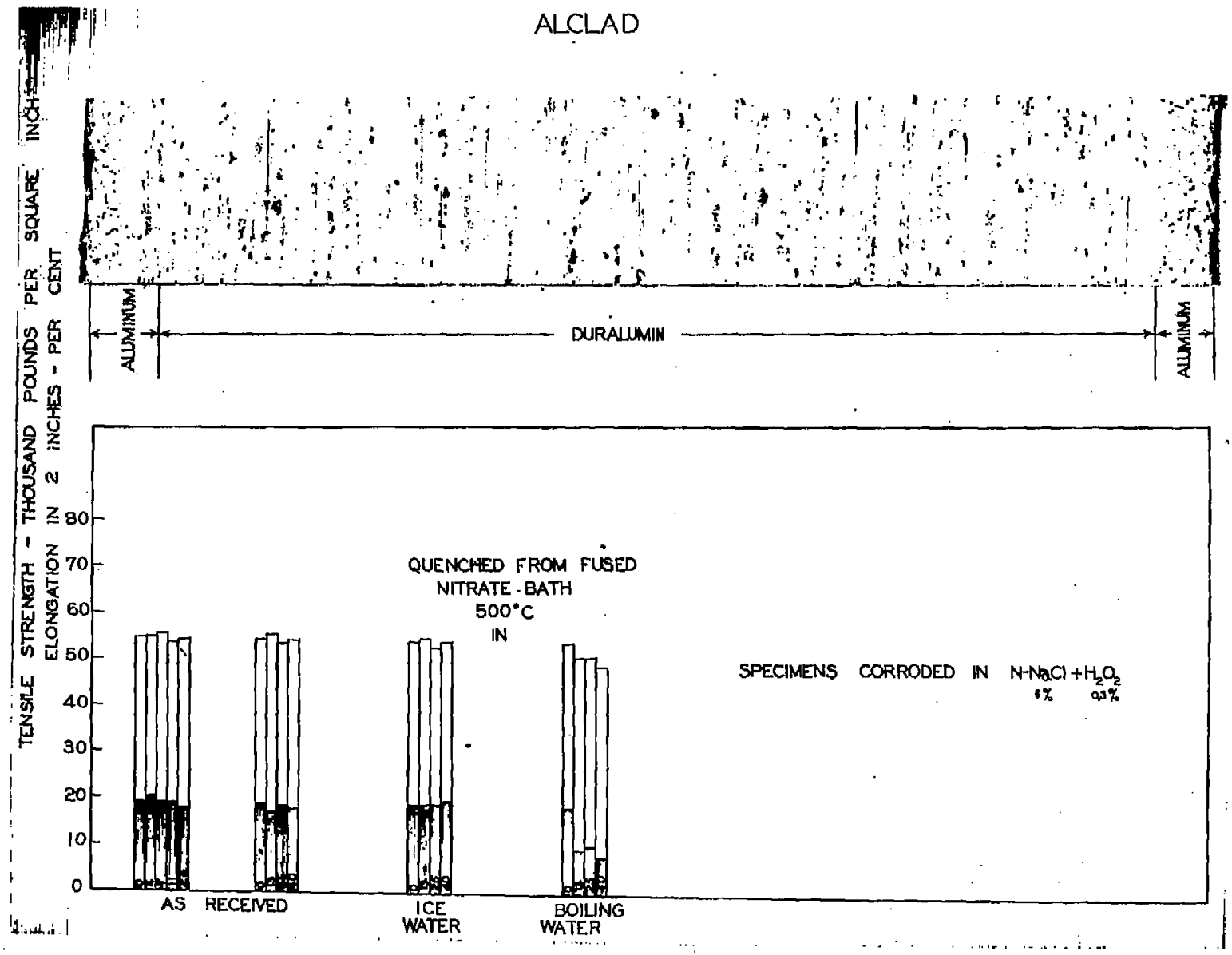

Fig. 9 Structure of "Alclad" sheet and its behavior when corroded.