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The Relation of Water from Humid Atmospheres on the Corrosive Action of Foreign Deposits on Aluminum and its alloys

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NAVAL RESEARCH LABORATORY

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NAVY DEPARTMENT

Report

on

The Relation of Water from Humid Atmospheres on the Corrosive Action of Foreign Deposits on Aluminum and its Alloys.

NAVAL RESEARCH LABORATORY
ANACOSTIA STATION
WASHINGTON, D. C.

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TABLE OF CONTENTS

TABLES

Introduction

(a) Authorization

1. This study was authorized by Project Order No. 42/41.

(b) Statement of Problem

2. In the authorization of this project it was directed that the fundamental aspects of corrosion of aircraft materials be studied with the ultimate view of developing materials with better corrosion resistance and more efficient methods of preventing corrosion. Because of the wide variety of metals and alloys used in aircraft it was immediately evident that initial study must be confined to a few alloys. Aluminium alloys were selected for investigation since they are so widely used and present some of the more serious corrosion problems.

3. First considerations demand a determination of the causes of corrosion and their effects on the metals involved. One of the principle causes is the action of specific chemical compounds or mixtures. Water being present in nearly all corrosion processes, it was deemed advisable to consider its behavior separately from that of the other specific agents affecting the nature of the corrosion processes. The frequent and extensive exposure of naval aircraft during service, storage, and shipment to humid atmospheres and sea water renders this phase of the problem especially important.

(c) Known Facts Bearing on the Problem

4. It is already known that metals and alloys generally corrode more readily in a humid atmosphere than in a dry one and although the importance of this fact has been recognized, very little information on it has been published. Abstracts of most of the publications concerning the action of water on aluminium and the observed relations between relative humidity and corrosion are collected in the appendix.

5. The work of Scala (1), Seligman and Williams (2), Von Ryin (3), Deville (4), Hugounencq (5), and Heyn and Bauer (6), demonstrates conclusively that aluminium is not attacked by pure water even up to white heat temperatures. A slight attack by water when the sample is simultaneously exposed to water and air is indicated in the papers by Scala (1), Mylius and Rose (7), Heyn and Bauer (6), and Bailey (8). Bailey attributed this attack to oxidation of aluminium by oxygen dissolved in the water. When the surface is exposed to water in

impure atmospheres corrosion may be initiated by other substances originating in the atmosphere. Vernon (9) discussed cases where dust caused initial rusting of iron in humid atmospheres. Scala (10) and Hugounencq (5) blamed the corrosion of aluminium, especially commercial grades, on electrochemical action of couples in the metal surface. The apparently inert behavior of aluminium which cannot be due to a low chemical reactivity, was attributed by Ditte (11) to the formation of a film impervious to water on the aluminium surface. From their studies on the behavior of aluminium electrodes, Barnes and Shearer (12) later confirmed the existence of a protective film on aluminium. Blumenthal (13) and Von Ryin (3) reported that if sheet aluminium is amalgamated, it reacts readily with water vapor with or without air to form a hydrated aluminium oxide, hydrogen, and mercury. Such behavior is due either to an electrochemical action caused by aluminium-mercury couples or to the fact that amalgamation continuously renews the fresh aluminium surface. Indications are that the products of the attack by water in the presence of air are a partially hydrated aluminium oxide (10,14), hydrogen (12,13), and in some cases hydrogen peroxide (7).

6. The relation between relative humidity and corrosion has been considered mostly in corrosion studies of iron and steel but these investigations have brought out some facts which have a general application to other metals and alloys. At zero relative humidity metals and alloys do not corrode except in a few instances where an extremely slow reaction is observed. Metallic silver, for example (15), reacts with sulphur to produce silver sulphide. When water vapor is present, the reactivity of a metal is usually much larger and varies in a remarkable manner with the amount of water vapor in the atmosphere. As the humidity is increased, the rate of corrosion in general shows a slight increase until at a certain critical humidity when it rises very rapidly. The numerical value of this critical humidity is characteristic of each metal or alloy but the presence of corrosive substances in the atmosphere or on the metal surface usually lowers this critical value. Copper does not corrode (16) in dry air containing 10% sulphur dioxide but exhibits a slightly decreasing resistance to attack as the relative humidity increases to 63-75% R.H. when the corrosion rate undergoes a tremendous increase. Bengough and Whitby (17) report a similar behavior for magnesium in ordinary air with a critical humidity at about 90% R.H. According to Fleming (18), iron will not corrode in clean air at any humidity below 22°c., and Vernon reported (9) a critical humidity of 65-75% R.H. at room temperature. Vernon (9), Hudson (19), and Patterson and Hebbs (20), showed that rust

spots, dust, or any hygroscopic substance on a metal surface would increase the rate of corrosion.

7. The action of sulphur on silver was shown (15) to proceed with an initial reaction between the silver and sulphur atoms at the points of contact to form a film of silver sulphide followed by a slow diffusion of silver atoms through the silver sulphide to the outer surface where they reacted with more sulphur. The function of and the mechanism by which water takes part in metallic corrosion in humid atmospheres has not received any attention beyond what has already been mentioned in this report.

(d) Theoretical Considerations

8. The role played by water in the corrosion of aluminium and its alloys is through either a direct attack on the metal or its action in promoting attack by corrosive substances. *The first alternative was eliminated by others as discussed in the preceding section. The extent to which water* promotes attack is dependent upon the rate at which it reaches *the surface, the length of time it stays there, and its action while on the surface. The rate at which atmospheric water molecules reach the surface is given by the equation,*

$$M = \text{Mass of water striking unit area per second} = \frac{54}{13}un,$$

where u is the root mean square velocity of the water molecules and n is the number of water molecules per unit volume in the atmosphere above the surface. The factor, n, is a linear function of the absolute humidity or, at constant temperature of the relative humidity. The root mean square velocity, u, is related to the temperature by the relation, $u = \left(\frac{KT}{6}\right)^{1/2}$, where K is Boltzmann's constant and T is the absolute temperature. The rate at which water vapor reaches the surface is, therefore, proportional to the humidity and the square root of the absolute temperature, that is,

$$M = \text{a constant} \times H\,(T)^{1/2},$$

where H is the absolute humidity.

9. On striking the surface a water molecule may instantly rebound back into the air in which case it does not enter into any corrosion process, or it may be adsorbed on the surface of the metal or of a deposit after which it may possibly take part in the corrosion. If it is adsorbed on an insoluble substance, the water forms a film on the surface the completeness

and thickness of which are dependent upon the temperature and the attractive forces existing on the surface. The adsorptive capacity of a given substance will vary on different crystal faces exposed to the atmosphere because of different atomic groupings in these faces. Some of these faces may adsorb water strongly even to the extent of building up multi-molecular layers while others may not adsorb enough water to form a complete mono-molecular layer of adsorbed water. These adsorptive forces are actually weak chemical bonds between the adsorbed water and the solid substance. As in any chemical reaction, in order to form these bonds the water molecules must acquire an energy great enough to activate them. Evaporation of water from the surface requires severance of these bonds and therefore acquisition of energy great enough to do this is necessary. The greater the strength of the bonds the larger will be the energy required to liberate the water molecules. The energy supplied for this is entirely thermal so that the higher the temperature the greater will be the number of molecules escaping from the surface. This can be shown mathematically in terms of the energy involved and the temperature. The rate of adsorption is given by the relation,

$$\frac{dv_a}{dt} = ae^{-E/RT}$$

where v_a = volume adsorbed, t = time, a = constant, e = base of Naperian logarithms, E = activation energy, R = gas constant, and T = absolute temperature. The value of a increases with increasing humidity. In order to evaporate, the adsorbed molecules most acquire an additional amount of energy, Q and the rate of evaporation is given by the expression,

$$\frac{dv_e}{dt} = be^{-(E+Q)/RT}$$

where v_e = volume of water evaporating, b = a constant depending upon the fraction of the surface covered, and the other factors are the same as in the preceding equation. Since the volume of water adsorbed is proportional to the time lag between condensation and evaporation, it is proportional to the ratio of the rates of condensation and evaporation,

$$\text{volume adsorbed} = Ke^{Q/RT}$$

that is, the larger the heat of adsorption Q or the lower the temperature the greater will be the amount of water adsorbed. In general, the heat of adsorption Q is large for hygroscopic substances.

10. If water is adsorbed on the metal surface to an extent great enough to form a layer, this may act as a solvent for materials such as dust particles or other deposits on the surface. If it is adsorbed on the particles deposited on the metal as well as on the metal itself, it forms an interfacial film between the metal surface and the particle. This water film promotes interaction between the solid and the metal by increasing the rate at which ions from the deposit can diffuse to the metal surface or the rate which ions from the metal can diffuse to the surface of the deposited particle where interaction can occur. This promoter action of the film is brought about because the attractive forces causing adsorption of the water vapor also exert an outward pull on the ions which exist in the surface of the particle. Over a period of time these attractive forces sometimes become greater than the inter-atomic forces holding a particular ion in the crystal lattice of the particle and the ion breaks away from the crystal and diffuses through the film to the metal surface where it can react. In the absence of the water film the probability that the same ion would overcome its restraining forces in the crystal lattice and attack the metal is greatly reduced.

11. When the foreign materials deposited on a metal surface are soluble, the same processes are involved but differ only in degree. Water vapor is adsorbed on the surface of the particles but in these instances the intercrystalline forces are very weak as compared with the dissolution forces of the water film. As a result the water film soon becomes a solution containing an appreciable concentration of solute which lowers the vapor pressure of the water in proportion to the concentration and extent of ionization of the dissolved substance. If this vapor pressure becomes lower than that of the water in the atmosphere, more water will condense in the solution surface than will evaporate until the vapor pressures of the solution and atmosphere become equal. Accordingly, the higher the humidity, the greater will be the extent of condensation. With the formation of this solution all intercrystalline restraining forces are removed from the dissolved molecules or ions and rapid attack of the underlying metal takes place.

12. The corrosion can be of two types: first, direct attack on the metal involving interaction of the metal and dissolved substance only, or, second, electrochemical action where the solution acts as an electrolyte and merely carries the current between two areas of the metal having different solution potentials. These solution potentials are determined by the compositon of the metallic constituents in

Data obtained

16. A summary of the observations is given in Tables I and II. Table III gives the solubilities of some of the substances discussed later.

Conclusions and Recommendations

(a) Facts Established

17. Pure water does not affect aluminium appreciably but its presence is necessary in corrosion processes caused by various deposits which may collect on aluminium surfaces. The severity of the attack by a given substance is influenced to a great extent by the relative humidity. The minimum relative humidity at which a metal surface is corroded by deposits of foreign materials is dependent to a great extent upon the specific properties of the substance deposited. At 0% R.H., none of the compounds studied were corrosive; at 30% R.H., only aluminum chloride had any effect; at 100% R.H., lead sulfate, lead monoxide, and lead carbonate were not corrosive.

18. The type of corrosion is more dependent upon the properties of the deposit than on the relative humidity. Of the lead compounds which attack the aluminum, they bring out a direct attack in which aluminium displaces the lead to form metallic lead and an aluminum compound. Aluminum chloride is very hygroscopic and dissolves following which the aluminum is strongly attacked by direct action. Sodium chloride causes an indirect electrochemical corrosion. The products of corrosion by lead salts or during corrosion of 24 ST alloy cause secondary corrosion processes which are chiefly but not entirely electrochemical in nature.

(b) Opinions and Recommendations

19. For all practical purposes it is impossible to keep metal surfaces absolutely clean. However the lower critical corrosion limit of humidity, which will be lowered by deposits on the surface, can be maintained in some instances. The use of drying agents enclosed with materials or parts which can be sealed in packages for shipment or storage, would serve as a means of reducing corrosion caused by humid atmospheres. Also, where corrosion occurs in closed air-spaces due to the accumulation of moisture, the use of highly adsorbent drying agents would be of practical value if they can be placed in accessible positions to allow replacement or rejuvenation. Although the value for the

critical humidity limit below which corrosion occurs has not been determined for these deposits on aluminum and its alloys, this preliminary study indicates that corrosion can probably be prevented in most instances by maintaining a relative humidity below 20% R.H.

Discussion

20. The substances used in these tests represent three types of salts, namely, (a) extremely hygroscopic, (b) moderately soluble, and (c) insoluble. The first type is represented by aluminum chloride, the metallic ion of which is the same as the metal. The second is represented by sodium chloride the positive ion of which is so much more active than aluminum that displacement does not occur. The third is represented by a number of insoluble lead compounds the positive ion of which is less active than aluminum.

21. Sodium chloride deposits on 2S aluminum take up water slowly until they are completely dissolved. Following this, there is a very slow corrosion which consisted of the formation of a very few large pits in the metal surface accompanied by the formation of aluminum hydroxide and hydrogen. The pitting action rather than a general attack over the entire aluminum surface indicates that this corrosion is electrochemical in nature and may be due to a concentration gradient in the solution or to a lack of homogeneity of the metal surface. In such an electrochemical action aluminum hydroxide would be formed on anodic areas and hydrogen on cathodic areas.

22. Aluminum chloride behaves differently in that it is extremely hygroscopic and is dissolved rapidly at 100% R.H. The salt then undergoes a partial hydrolysis with the formation of free hydrochloric acid according to the reaction,

$$AlCl_3 + 3\ H_2O \longrightarrow Al\ (OH)_3 + 3\ HCl$$

The aluminum hydroxide is insoluble and collects as a white gelatinous precipitate but the hydrochloric acid formed attacks aluminum to form more aluminum chloride and hydrogen.

$$6\ HCl + 2\ Al \rightarrow 2\ AlCl_3 + 3\ H_2$$

Hydrogen chloride is volatile so that all of the hydrochloric acid formed does not attack the metal but some escapes into the atmosphere. If such attack occurs in places where air does not circulate freely, this volatilized hydrochloric acid may attack other exposed metal surfaces. The aluminum chloride formed during the action of hydrochloric acid hydrolyzes like the original aluminum chloride forming more aluminum hydroxide and hydrochloric acid. The latter in part attacks the metal and the remainder evaporates. This cycle is repeated over and over until most of the hydrogen chloride has evaporated. The final result is a corrosion process involving a direct chemical attack but being **far** more extensive than can be accounted for by the initial amount of corrosive agent employed. This is attributed to the corrosive action of an intermediate corrosion product, aluminum chloride. The final products are aluminum hydroxide, hydrogen, and hydrogen chloride.

23. The action initiated by lead bromide is a little more complicated. When water is present in the atmosphere, a small amount is adsorbed on the lead bromide and metal surface. Lead bromide is so insoluble that a visible amount of solution is not formed but the thin film of adsorbed water is enough to bring some of the lead bromide into a reactive state. Aluminum, being much more reactive than lead, reduces the latter to the metallic state and forms aluminum bromide which is very similar to aluminum chloride.

$$3\ PbBr_2 + 2\ Al \longrightarrow 2\ AlBr_3 + 3\ Pb.$$

The lead is reduced in situ as a loosely adherent gray mass with a spongy appearance. The mass appeared dry until an appreciable amount of the hygroscopic product, aluminum bromide, was formed. This dissolves in the water adsorbed and hydrolyzes to produce the gelatinous precipitate of aluminum hydroxide and hydrobromic acid. The acid then attacks the aluminum to produce more aluminum bromide and hydrogen.

$$6\ HBr + 2\ Al \longrightarrow 2\ AlBr_3 + 3H_2\ .$$

The newly formed aluminum bromide dissolves, hydrolyzes, and causes still more attack until all of the hydrobromic acid escapes. In addition to this attack, the lead which was set free in the initial reaction causes an electrochemical action by the lead-aluminum couple wherein more aluminum hydroxide is formed at the anodic aluminum surface and hydrogen is liberated at the lead cathode. The electrochemical attack may continue indefinitely although its rate may vary considerably owing to polarization and resistance effects. Other lead halides would behave in a similar manner because of the formation of hygroscopic aluminum halides and subsequent electrochemical action of lead-aluminum couples.

24. The other lead compounds considered in this report, namely, lead sulfate, lead monoxide, and lead carbonate, did not cause any corrosion even at 100% R.H. However, reference to Table III shows that the solubility of each of these compounds is much smaller than that of lead bromide. This lower solubility and probably smaller adsorptive capacity for water would account for the failure of these compounds to react with aluminum.

25. The experimental tests herein reported are of a preliminary nature for the purpose of confirming in a qualitative manner the existence of a critical corrosion limit of humidity, its dependence upon the properties of the corroding deposit, and proposed mechanisms for the corrosion processes insofar as water from humid atmospheres is concerned. Complete analysis of this part of corrosion processes, which has not yet been completed, requires control of temperature, humidity, air-flow over specimens, composition of the air (that is, elimination of components which might possibly complicate the corrosion process), determination of the adsorptive capacities of corroding agents for water vapor at various temperatures and humidities, measurement of corrosion rates to determine the critical humidity limits, and correlation of the last factor with the adsorptive properties of corrosive deposits. The extension of these studies to include all types of surfaces encountered in practice, that is, anodized and unanodized pure aluminum, "commercially pure" aluminum, cast, wrought, and specially prepared aluminum alloys should reveal the specific effects of various metallic constituents and surface treatments and possibly indicate steps toward improvement in corrosion resistance.

Summary

26. It has been shown that pure water has little corrosive action on aluminum, a fact which is attributed to the formation of a protective film on the aluminum surface.

27. It has been shown that in the presence of corrosive deposits, a critical humidity below which corrosion does not occur exists for aluminum as well as for iron, copper, or magnesium and is strongly dependent upon the properties of the deposit.

28. A theory of the mechanism by which water is adsorbed from the atmosphere and participates in corrosion processes has been discussed. A number of preliminary experiments have been carried out to substantiate this theory qualitatively. The actual mechanisms of these corrosion tests are discussed with special consideration of roles played by water, the deposits causing the corrosion, and the corrosion products.

29. An outline of the studies necessary to complete the investigation of this phase of corrosion phenomena has been presented.

Table I

Effect of Relative Humidity on Corrosion by Several Substances

Substance	Surface	Rel. Hum.	Remarks
$AlCl_3$	Alc 24 ST	0 %	no attack whatever.
"	"	30	slight corrosion with the formation of a gray deposit in 5 days.
"	"	100	$AlCl_3$ completely dissolved in 25 hours. Considerable dissolution of metal, especially at air-liquid interface in 5 days.
$PbBr_2$	Alc 24 ST	0	no attack
"	"	30	" "
"	"	100	lead bromide partially reduced to metallic lead: few small pits;
"	24 ST	0	no attack
"	"	30	very slight attack with slight darkening in 14 months
$PbBr_2$	2 S	0	no attack
"	"	30	no attack after 14 months
"	"	100	lead bromide almost completely reduced leaving a spongy, loosely adherent lead deposit. $AlBr_3$ was formed, and, being hygroscopic, dissolved in deliquescent water and then hydrolyzed to gelatinous $Al(OH)_3$
$PbSO_4$	Alc 24 ST	0	no attack
"	"	30	" "
"	"	100	" "
"	24 ST	0	" "
"	"	30	" "
"	"	100	" "
"	2 S	0	" "
"	"	30	" "
"	"	100	" "
PbO	Alc 24 ST	0	no attack
"	"	30	" "
"	24 ST	0	" "
"	"	30	" "
"	"	100	very slight attack causing a darkening of the surface in 14 months
"	2 S	0	no attack
"	"	30	" "
"	"	100	" "
$PbCO_3$	2 S	0	no attack in 14 months
"	"	30	" " " " "
"	"	100	" " " " "
NaCl	2 S	0	" " " " "
"	"	30	" " " " "
"	"	100	bad corrosion with one deep pit 1/4" in diameter; $Al(OH)_3$ formed

Table III

Solubility of deposits

Substance	Temperature	Solubility
$AlCl_3$	15°C.	698.7 gms./liter
NaCl	100	398
$PbBr_2$	0	4.55
$PbBr_2$	100	47.5
$PbSO_4$	0	0.028
$PbSO_4$	40	.056
$PbCO_3$	20	.0011
PbO	22	.013

Appendix

Summary of Publications Bearing on Humidity - Corrosion Relations

1. A. Scala. Atti. accad. Lincei 22,I,43-7.

   Sheet aluminum was formed into a beaker, the inner surface polished, then washed with tap water several times, rinsed with distilled water and finally conductivity water. The aluminum beaker was filled with conductivity water and heated with a free flame for many hours, renewing the water lost by evaporation from time to time. After several hours the aluminum became covered with a yellow film and the water contained colloidal aluminum. More time (3 months±) is required for this change at room temperature or when placed in a dessicator over concentrated KOH solution to eliminate all acids. The yellow film consisted of aluminum hydroxide, aluminum oxide, and traces of iron and silica.

2. R. Seligman and P. Williams. Engineering 133,353(1932)

   Aluminum (99.96% Al) was sealed in a tube with pure water after all gases were exhausted from it. The aluminum was thus exposed to water at 300° C. and 6.7 atmospheres pressure for 217 hours. During this period the aluminum showed no change in appearance or weight.

3. W. Van Ryin. Chem. Weekblad 5,1-5

   Merck's analytical grade aluminum does not react with water at ordinary or boiling temperatures. Pure zinc and magnesium react at all temperatures. Mercury in contact with aluminum causes the liberation of hydrogen from water at all temperatures. This reaction may be electrochemical or may be due to a continuous renewal of an active aluminum surface by amalgamation. Mercury does not accelerate the action with zinc. Nickel, copper, and lead liberate no hydrogen in the presence of mercury.

4. H. St. C. Deville. L'Aluminium. Paris. 1859

   Pure aluminum is not attacked by pure water even up to a white heat.

5. L. Hugounencq. J. Pharm. Chem. (6) 1,537 (1895)

   The fact that pure water does not attack pure aluminum was further verified. Commercial aluminum is attacked because of the electrochemical action of couples in the metal surface.

6. E. Heyn and O. Bauer, Mitt. Materialprufungsamt. 29,2 (1911).

Aluminum is not attacked by distilled water in the absence of air or oxygen or by air alone. The relative rates of hard and soft aluminum sheet attacked by distilled water exposed to air are 45 and 54, respectively.

7. F. Mylius and F. Rose. Zeit. Instr. 13,77 (1893).

When aluminum is immersed in water exposed to air, some hydrogen peroxide is formed.

8. G. H. Bailey. J. Soc. Chem. Ind. 39,121T (1920).

The corrosion of aluminum in water is due to oxidation of the aluminum to alumina at the expense of the oxygen dissolved in the water. The relative rates of reaction at 20° and 70° are 39 and 110, respectively.

9. W. H. J. Vernon. Trans. Electrochem. Soc. 64,35 (1933).

Dust particles deposited on iron samples were shown to be starting points of corrosion. Specimens of sheet iron exposed to a stream of humid air without protection from dust exhibited corrosion developing rapidly in local areas. Samples exposed to the same air but screened from the dust with a muslin cage (with a mesh of one thread per 0.5 mm.) caused a considerable reduction in the corrosion rate. At the same time the slight corrosion that did occur was uniform over the entire surface. A subsequent exposure of the latter samples along with a freshly cleaned specimen caused rapid corrosion of the cleaned specimen but only a very slow attack on the specimen which had been previously exposed behind the screen. This behavior was laid to the formation of an impervious oxide film on the samples behind the dust filter. Investigation of the behavior of iron at various humidities showed that below a certain critical relative humidity (about 65% R.H.) the rate of attack decreases with time whereas the rate is increased many times as the relative humidity rises above 78%. Elimination of rust on the surface brings about a very low rate of attack even at 78% R.H. As the humidity is raised a corroding sample does not exhibit an appreciable increase in the number of rust centers but their individual activity was increased considerably at 65-78% R.H. This increased activity and the influence of dust particles on the rate of corrosion is explained by the hygroscopic nature of foreign materials deposited on the metal surface.

10. A. Scala. Atti. accad. Lincei 22,I,43-7.

Sheet aluminum (99.371% Al, 0.070% Fe, 0.401% Si, 0.039% Na, and traces of Ca), formed into beakers, and strips of polished iron were placed in contact with pure water for some time. After 10 days the beakers alone showed no change but the beakers containing iron showed a black oxide in which iron as well as aluminum was detected. With an iron-aluminum alloy the results were much the same except that the coating was mostly iron.

11. A. Ditte. Ann. Chem. Phys. (3) 43, 11 (1855).

The apparently inert behavior of aluminum was attributed to the formation of a film impervious to water on the aluminum surface.

12. H. T. Barnes and G. W. Shearer. J. Phys. Chem. 12,155,468 (1908).

It was inferred from the behavior of aluminum electrodes that a film is formed over the surface of aluminum exposed to air or to water, and that the reaction in the case of water develops hydrogen peroxide. The development of hydrogen peroxide depends upon the presence of dissolved oxygen in the water.

13. M. Blumenthal. Bull. intern. acad. polon. sci., Classi sci. math. nat. 1938A, 466 (1939).

Amalgamation of sheet aluminum produces a heterogeneous surface which contains active centers at which reaction with water vapor takes place with the formation of $Al_2O_3.nH_2O$, mercury, and hydrogen (in absence of oxygen). The activity depends upon the structure and composition of the solid product formed. When n is less than 3, the reaction becomes partially or totally inhibited. Below 75°C., the velocity of the reaction depends upon the velocity of adsorption of the water vapor; but, above 75°C., products are formed having n less than 3, and adsorption plays only a minor role.

14. E. Kohn-Abrest and J. Carvallo. Compt. rend. 148,410.

Aluminum, when heating in water to 83°C., is oxidized by it, with heat evolution, followed by heat absorption probably during hydration of the oxide first formed. Analysis showed the oxide not to be 100% Al_2O_3.

15. N. F. Mott and R. W. Gurney. "Electronic Processes in Ionic Crystals". Oxford.

A bar of silver was placed in contact with molten sulfur. An immediate formation of a sulfide film took place and, following this, the rate of increase in thickness of the film decreased as it became thicker. This was due to the fact that rate of reaction was dependent upon the rate of diffusion of silver ions from the metal through the silver sulfide film to the silver sulfide - sulfur interface where they react with sulfur.

16. W. H. J. Vernon. Trans. Faraday Soc. 27,264 (1931).

Copper is not attacked at 0% R.H. in an atmosphere containing 10% sulfur dioxide. The rate of corrosion increases slowly with increasing relative humidity up to 63% R.H. Between 63% and 75% the rate increases tremendously.

17. G. D. Bengough and L. Whitby. Chem. Ind. 52,1037 (1933).

Dry air at ordinary temperatures has little or no attack on massive magnesium. The rate of attack slowly increases as the relative humidity rises up to 90% R.H. when a sharp increase occurs. Magnesium hydroxide is first formed but the layer is granular and does not at once form a protective film. No permanent protective film is formed on magnesium during exposure to outdoor atmospheres.

18. W. R. Fleming. J. Ind. Eng. Chem. 4,480 (1912).

Iron will rust in pure water and air if the temperature is above 22°C., and some water remains on the surface for a time. Continual change of the water reduces, if not prevents, corrosion. Friend's results (25) were obtained only below 22°C. The rusting is rapid at 55°C. The extent of rusting is a function of temperature and purity of the iron.

19. J. C. Hudson. Trans. Faraday Soc. 25,205 (1929).

Several metal samples were placed in humid atmospheres and then rapidly cooled below the dew-point. Although conditions were identical, condensation occurred more readily on some surfaces than on others. This was attributed to differences in the hygroscopicity of the corrosion products on the various surfaces. The adsorptive capacity for water of a number of metal corrosion products was determined at 90% R.H. by exposure for 48 hours. The results were as follows:

(a) Corrosion products	Wt. Increase %	Remarks
Cd-Cu	1.7	Dry
Cu	8.0	"
Al	9.2	Caked
Phosphor-bronze	10.6	Slightly moist
80/20 Cu-Ni	40	Caked
70/30 brass	81	Moist and caked
Ni-Ag	92	Wet
Zn	36	"
60/40 brass	55	Moist and caked
70/30 Ni-Cu	32	Wet
Ni	32	"
55/45 Cu-Ni	34	Moist and caked
Cu	11.2	Slightly moist
Al	7.4	" "
60/40 brass	34.	Wet
Ni	38	"
(b) Salts		
$CuSO_4$	0.1	Caked but dry
$CuSO_4$	0.0	" " "
$CdSO_4$	30	Very moist
$CdSO_4$	16	Caked but fairly dry
$Al_2(SO_4)_3$	31	Wet
$Al_2(SO_4)_3$	19	Moist
$NiSO_4$	5.9	Caked but dry
$NiSO_4$	9.0	Caked and slightly moist
$ZnSO_4$	58	About 0.1 cc. solution
$ZnSO_4$	13	About 0.1 cc. solution
$Cr_2(SO_4)_3$	84	About 0.1 cc. solution
$Cr_2(SO_4)_3$	56	About 0.2 cc. solution

(b) <u>Salts</u> (continued)

$FeSO_4$	1.5	Dry
$FeSO_4$	3.2	"
$Fe_2(SO_4)_3$	110	About 0.4 cc. solution
$Fe_2(SO_4)_3$	82	About 0.4 cc. solution

20. W. S. Patterson and L. Hebbs. Trans. Faraday Soc. 27,277 (1931)

The marked effect that rust has in accelerating corrosion can be explained by assuming a gel structure for the iron rust formed. In humid atmospheres of less than 40% relative humidity, water present in the rust is strongly adsorbed by the gel and is held by forces strong enough to prevent the water from causing corrosion. If the humidity is above this critical humidity, the gel fills with water and the forces that hold the water are lessened so far as the adsorption of more water is concerned. Thus, the moisture content increases little above the critical humidity but a much larger amount of water becomes available for further corrosion.

21. C. A. Siebert and H. G. Donnelly. Trans. Am. Soc. Metals 28,372 (1940).

A greater scale loss from low carbon steels during oxidation at 1825 - 2150°F., occurs at high humidities than in dry air. The scale formed at high humidity has a greater ferrous ion content. The authors attributed the greater scale loss to the higher ferrous ion content.

22. T. A. Masterkov. Vertnik Metallprom. 1,83 (1938).

Iron samples already partly covered with rust spots were kept for 30-45 days in air at 75-85% R.H. and 20-24°C. It was found (in contradiction to others) that the effect of moist atmosphere in producing corrosion was independent of rust spots already present.

23. E. I. Duirmont. Soobshckeniya Vsesoyuznogo Inst. Metals 1-2,37 (1931).

Iron samples (0.12%C, 0.44%Mn, 0.02%S, 0.048% P, remainder Fe) were kept in glass vessels filled with water vapor and other gases. The relative humidity was maintained at 96-98% and the temperature at 18-20°C. Gas mixtures used were water-air, water-oxygen, and water-oxygen-carbon dioxide. With these mixtures corrosion became visible in 40,5, and 3/4 hours, respectively. In water-air exposures, the rate of corrosion increases with temperature but the nature of the product changes. At 30-50° this product is yellow, moist, and adheres very poorly to the metal. At 50-80°, a cinnamon-yellow solid layer is formed, while at 80-100°C. the layer is black, compact, and adheres firmly to the metal.

24. E. Cohnstaadt. Ann. der Physik 38,223-38.

By placing sheet aluminum in a vessel, evacuating to a pressure of 0.02 mm. mercury, and measuring the volume of gas coming off the surface subsequently, 0.0003CC. gas per sq. cm. of surface was collected. This gas was mostly water.

25. J. A. N. Friend. Proc. Chem. Soc. 26,179.

It was reported that polished iron or steel samples did not corrode or even tarnish in an atmosphere so humid that water was continually condensing on the surface. (This was investigated further by Fleming (18)).