H. D. Strong V. '03

The Electroplating of Aluminium

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Electro-plating upon Aluminium.

The object of this thesis is to obtain a good firm plate of metal upon aluminium with or without the electric current and incidentally to determine the cause of failures in attempts to plate aluminium in an ordinary electroplating bath. If a sample of aluminium be plated in an ordinary cyanide bath of copper or silver such as is used technically, an even and good looking plate may be obtained but this blisters before a sufficiently heavy plate of metal is obtained. Moreover, if an acid bath is used, say copper sulphate and ammonium sulphate, it is even difficult to cover the aluminium with metal. The literature covering the subject yields a great number of so called successful methods and also several reasons for the failures in attempts to plate aluminium by the electroplating methods in common use for other metals.

The literature yields three different reasons why a good plate cannot be obtained electrolytically. Taucher, a German chemist, states that, when it is attempted to plate aluminium with an electric current, a large amount of hydrogen is given off from the surface of the aluminium. He claims that this prevents the deposition of an even coat. This reason is hardly sufficient however. If it were true more difficulty would be experienced in the electroplating upon other metals as copper, lead, etc. Wm. H. Legate, of Hartford Conn., states in his patent text that, when aluminium is plated in the usual technical plating baths, salts of aluminium form between the surface of the metal and the plate. This ultimately causes the rupture or peeling of the plate. He avoids this difficulty by amalgamating the surface of the aluminium and plating silver upon the amalgam by a somewhat tedious and lengthy procedure. His theory explains why aluminium cannot be plated by ordinary methods and also explains the success of his own method. It is also explained by the following theory which is very plausible and is now generally accepted. The surface of the aluminium is covered by a very thin coating or layer of oxide or hydroxide of aluminium. If in any way this covering is scratched off more oxide or hydroxide, as the case may be, is immediately formed. Thus, when it is attempted to electroplate a metal upon the aluminium, the former is deposited, not upon the metallic aluminium, but upon an oxide covering the metal. That is the deposited metal does not come in contact with the aluminium to form a metallic union and hence peels off. To illustrate this principle a strip of copper or any other metal may be covered with a sheet of paper and the combination electroplated. Metal is deposited upon the paper. It is quite evident that this does not give a permanent plate upon the metal in question. It is a case analogous to the aluminium where the strip of metal plays the part of the aluminium and the sheet of paper that of the oxide supposed to cover the surface of the metal. Aluminium should decompose water. That it does not supports the idea that its surface is covered by an insoluble oxide or hydroxide. Moreover, when dipped into copper sulphate solution copper should precipitate upon the metal. This does not take place. If the surface of the aluminium is scratched under copper sulphate a precipitation of copper is obtained upon the metal. If aluminium is dipped into a copper solution after corrosion in hydrochloric acid copper precipitates upon it. The acid dissolves off the coating more or less perfectly and fresh aluminium is exposed to the copper solution. Lastly, if aluminium be dipped into a copper solution made alkaline with caustic and ammonia a precipitate of copper is obtained. Alumina is soluble in caustic and it is quite probable that this latter dissolves the supposed oxide covering and exposes fresh metal to the copper salt. All the above enumerated facts help to support the oxide theory. In all original experiments made for <u>this</u> thesis the oxide theory was taken into consideration.

In the literature on the subject may be found the details of or comments on a large number of so called successful methods for plating other metals on aluminium. Most of these make use of some chemical or proceedure which will have a reducing, maccerating, or corrosive effect on the surface of the metal. The method of Margot is treated of quite exhastively in the Jahrbuch für Elektrochemie 1896. He scours the aluminium in alkali, washes thoroughly, and dips it into hydrochloric acid (1:10). He removes the metal from the acid, rinses it slightly with water, and dips it into an acidified copper sulphate solution. A deposit of copper is given. The metal is thoroughly washed and put into an electroplating bath. The theory given by Margot is that aluminium chloride is formed on the surface of the metal and that this protects it from oxidation while a copper plate is going on. This method was used in the laboratory. A precipitate of copper was obtained on the surface of the metal but it was spongy and could be rubbed off easily. The method is probably of little value. Several methods are given, using phosphate in the bath. Lanscigne and Le Blanc (Elec. World 32 751 recommend the following;

Silver Bath

20	gms.	Silver Nitrate.
40	"	Sodium Phosphate
40	"	Cyanide of Potassium.
1000	"	Water

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Copper Bath

300 gms.	Copper Cyanide
450 "	Cyanide of Potassium.
450 "	Sodium Phosphate.
5000 "	Water.

This recipe was not tried in the laboratory. It is probable that only fair success could be attained with it. E. Mes took out an American patent in 1900-01 for the use of a mixture of magnesium sulphate and sodium phosphate acidified with sulphuric acid. He dips the metal into this boiling mixture and then plates it in an ordinary plating bath. He gives no explanation as to the action. This method was tried in the laboratory. However only a light plate of copper could be obtained. A heavy coat would not adhere to the aluminum. The details

Copper Bath

300	gms.	Copper Cyanide
450	"	Cyanide of Potassium.
450	"	Sodium Phosphate.
3400	"	Water.

This recipe was not tried in the laboratory. It is probable that only fair success could be attained with it. E. Mies took out an American patent in 1900-01 for the use of a mixture of magnesium sulphate and sodium phosphate acidified with sulphuric acid. He dips the metal into this boiling mixture and then plates it in an ordinary plating bath. He gives no explanation as to the action. This method was tried in the laboratory. However only a light plate of copper could be obtained. A heavy coat would not adhere to the aluminum. The details of the experiments are given farther along in this thesis. There are several methods depending upon amalgamation of the surface of aluminium to obtain an adherent plate. Wm. H. Legate, of Hartford Ct., holds a patent (U.S. Pat. 641,908) for a procedure or succession of baths. This identical procedure is patented in England and Germany under the name of Ryan. It consists of a succession of dipping of the aluminium in hydrochloric acid, water, cyanide of potassium, phosphoric acid, etc. The final step before plating is amalgamation. This method was tried and very fair success was attained. The details of the experiments are given later. Similar to this process is that of F. S. Loeb (U. S. Pat 630,246) By him the aluminium to be plated is dipped into weak hydrofluoric acid, amalgamated, and then the acid treatment repeated. This prepares the metal for the electroplating bath. Loeb claims that the hydrofluoric acid is of value as a corrosive. With experience very good results should be obtained by this method. Amalgamation methods have this objection. If aluminium plated by such is heated the plate rises up in blisters and its tenacity for the metal is lost. An alcoholic solution of cupric chloride has been recommended for an electroplating bath for aluminium. If the oxide theory is allowed the success of this method is doubtful and could not be explained. The properties of an alcoholic solution are not much different from those of an aqueous solution. Weil, Quentaine, and Lefoch took out a patent in England for a method of electroplating aluminium. They have present in the bath a small amount of cane, milk, or malt sugar. The two following baths are patented by them;

Silver Bath		Copper Bath	
Water	5.4 liters	Water	9 liters
Silver Nitrate	68 gms.	Copper Sulphate	158 gms.
Potassium Cyanide	68 gms	Ammonium ·	45 gms.
Ammonium Chloride	90 gms	Milk Sugar	12 gms.
Milk Sugar	3 gms.		

In the laboratory it was attempted to plate with the above copper bath. A very poor result was obtained.

A closely related method is that of Weil and Levy. (English Pat of 1897) They use similar baths but substitute some developer for the sugar, such as pyrocatechin, hydro-quinone, gallic acid, pyrogallate of ammonium, acetic acid, oxalic acid, etc. Before introduction into these baths the aluminium is scoured or cleansed. Very fair success was attained when this method was tried in the laboratory. The details are given later in the thesis. A method which is explained by the oxide theory is that of Betts. This is patented in the United States (675,584), England, and Germany. The essential feature of the process is that aluminium is brought in contact with fused cuprous chloride. The theory of Bett's is that the surface of the aluminium is covered with water free alumina. This is dissolved by the fused salt of the more basic metal copper and the latter is deposited on the freshly exposed surface. Betts has two proceedures. In his first he dips the aluminium to be plated into a fused bath of cuprous chloride. This was done in the laboratory, for this thesis. An imperfect deposit of copper was obtained. It could not be called a plate. Also the metal was badly eaten or corroded by the fused bath. Bett's second proceedure is as follows: A sheet of aluminium is covered with a thin layer of powdered cuprous chloride. The metal is heated on the under side till the chloride on the upper surface fuses. While fused this is stirred or rubbed over the surface of the metal. This method was tried identically as above described. A good plate of copper was obtained. If a thin copper plate is obtained by either method or procedure it may be used as a foundation upon which to build a heavier plate by electric current. Bett's process is open to the following objections: metal plated in fused cuprous chloride is badly corroded by same; the second method is complicated and only applicable to sheet aluminium; the cost of cuprous chloride makes the process an expensive one. The following results were obtained using lead and ferric chlorides in place of the cuprous chloride. A sheet of aluminium was sprinkled with lead chloride and the underside heated till the salt fused. Lead, however, is too easily reduced. When sufficiently high temperature was reached the reaction started and its completion was almost instantaneous. A dense cloud of aluminium chloride was given off and large globules of lead were left on the surface of the aluminium. An even plate was not obtained. Ferric chloride was tried but ~~was~~ not with as good success as with the cuprous chloride, although a deposit of copper was obtained upon the aluminium. As a modification of Bett's method a bath of fused lead chloride was used containing some cuprous chloride dissolved in it. On dipping a piece of aluminium into the above bath a coarse deposit of copper was obtained, similar to that given by a fused bath of cuprous chloride. With the above fused bath it was attempted to get a copper plate by use of a current, using a copper anode. An occasional globule of lead was obtained upon the surface of the aluminium but an even plate of copper, which was desired, was not given. The bath decomposed around the anode giving off gas and a yellowish mass. The latter may have been lead oxide or litharge. There are a number of mechanical methods for getting a metallic plate upon aluminium. The following methods involve an electrolytic principle. Göttig's procedure (Galvan. + Galvan. 123) consists of rubbing the aluminium with a wire brush in presence of a salt solution of the metal to be plated. This latter must not be decomposed by the aluminium. To get a copper plate the scoured aluminium is rubbed with tin powder or foil in presence of a solution of copper sulphate. To get a tin plate a solution of ammonium stannous chloride and a brass brush are used. A galvanic battery is formed between the aluminium, salt solution, and rubbing metal. Several purely mechanical means are claimed to be successful. One method is to rub the heated aluminium with an alloy which has a low fusion point. Another method consists of laying a very thin sheet of copper over a sheet of aluminium. The two are heated and rolled till they are welded together. This method

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is patented. The following methods are recommended. They have not been tried in the laboratory. The cleansed metal is covered with a solution or suspension of sulphide of gold or silver in balsam of sulphur (sulphur in linseed oil). It is then heated in a muffle with the exclusion of air. The heat reaches 800° - 950° Fahrenheit. The following mixtures may be used; turpentine oil, lead borate, and cupric oxide; uranium oxide and gold chloride; uranium oxide and sodium nitrate with sulphur, "dammerharz," and turpentine oil. A solution of collodion with silver nitrate, citric acid, and strontium or calcium chloride will serve the same purpose. Boiling methods use a solution of zinc dust, ferrous chloride, or cupric chloride in caustic soda. The aluminium is immersed in these boiling solutions. A boiling solution of zinc dust in caustic soda was tried in the laboratory. When aluminium was dipped into this solution only a spongy deposit of zinc was obtained. An adherent, smooth plate was not given. Plates obtained by any of these mechanical methods may be covered or increased by electroplating. These methods are, however, too complicated in their manipulation to be used generally for commercial plating.

Up to this point this thesis has been mainly devoted to the theories and methods yielded by the literature devoted to the subject. In the remaining part will be taken up the work done by the author in the laboratory. He tried a number of the so-called successful methods and also a number of original ideas.

Before studying any of the patented processes for the plating of aluminium attempts were made to plate directly in an ordinary bath. Aluminium dipped into a saturated solution of copper sulphate gives no result; i.e. copper does not precipitate. If the metal is scratched with emery cloth before dipping, copper will precipitate in places. After scratch.—

ing the metal with emery it was attempted to electroplate the same but a continuous plate could not be obtained. The following bath was made up according to recipe.

1 Liter water
18 gms. Copper Sulphate
5 gms. Ammonium Sulphate.

This bath gave a very good plate on other metals. It was attempted to electroplate aluminium in this bath after cleansing in caustic; also after pickling in acid, rubbing with emery, or without any previous cleansing. In all cases an imperfect, non adhering, plate of copper was obtained. The bath was used at room temperature, 42 degrees C., and 75 degrees C.

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The only noticeable effect of raising the temperature was to change the color of the copper as it deposited to a yellow or green. A cyanide of copper bath was made up as follows:
(Langbein [Brannt] 264-65]
Copper Sulphate (1)
Sodium Carbonate
Sodium Bisulphate
Sodium Carbonate (2)
Potassium Cyanide
The copper sulphate and soda were dissolved in separate portions of hot water, mixed, and filtered. To the precipitate were added 40 gms. of bisulphate and 45 gms. of soda dissolved in one liter of water. To this was added 45 gms. of cyanide dissolved in one liter of water. A clear solution

was obtained. Other metals were successfully electroplated with this solution. On aluminium, however, a permanent plate could not be obtained. The bath was used hot or cold. Aluminium dissolves slowly in the hot bath. It made little difference with the result whether the aluminium was pickled in acid or cleansed in caustic before plating.

After these preliminary trials the Mies method was taken up. [U. S Pat. 647,858] No theory or details are given in the patent text. The method consists of pickling the aluminium in a boiling mixture of sodium phosphate and magnesium sulphate. The following bath was made up: 100cc saturated acid sodium phosphate (neutral not available), 10 gms. magnesium sulphate, 100cc water, and 30cc sulphuric acid of 1.12 sp. g. This bath was used at the boiling point. The aluminium to be plated was dipped into this boiling bath, into hot water, and then plated in the cyanide of copper bath. Several trials were made leaving the metal in the phosphate 15 sec., 30 secs., and 120 secs. Samples were plated from four to five minutes. They took an even and adherent, though rather soft, plate. One sample was left in the copper bath 20 minutes so that it might take on a heavy coat of metal. The plate rose up in blisters and peeled off in thin sheets. The experiments tend to show that only very thin plates

can be obtained by this method.

The next method to be taken up was that of W. H. Legate of Hartford, Conn. U. S. Pat. 641,709. Legate's process consists of corroding the metal in hydrochloric acid, phosphoric acid, and then amalgamation. The details and his theory (See early part of thesis) are stated clearly in the patent text. For amalgamation the following bath was made up according to Legate's formula;

Mercuric Chloride 14.5 gms.
Ammonium Chloride 3 gms.

After a few preliminary trials of the above amalgamating baths, solutions were made and used in the order given by Legate in his patent text.

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Solutions used.

Striker I

Water	540cc
Silver Chloride	2.2 gms.
Potassium Cyanide	194 gms.
Ammonia	16 gms.

Striker II

Water	540cc
Silver Chloride	2.7 gms.
Potassium Cyanide	194 gms.

Striker III

Ammonia	64 gms
Copper Carbonate	69 gms.
Zinc Carbonate	3.6 gms.
Potassium Cyanide	64 gms.
Water	540cc.

To follow these striking solutions a silver cyanide bath was made up according to Langbein.
99 gms. of silver nitrate were dissolved in 1.18 liters of water. The silver was precipitated with moderately strong potassium cyanide and separated from the solution by filtering This

precipitate was dissolved in a solution of 99 gms. of cyanide in 1.18 liters of water. Also 50 degree Baumé, and 1.15 sp. g solutions of phosphoric acid and potassium cyanide respectively were made up. These solutions were used to carry out Legote's method in detail as follows; (1) dip into 1.12 hydrochloric acid, (2) boiling water, (3) 1.15 cyanide, (4) boiling water, (5) 50 degree Baumé phosphoric acid, (6) boiling water, (7) cyanide, (8) amalgamating bath, (9) boiling alkali, (10) boiling water. After this treatment the aluminium to be plated was dipped in succession into the three striking solutions and thence into the plating bath of silver cyanide. The current in the striking baths should be stronger than in the regular plating bath. The metal was left in the silver strikers till a noticeable amount of silver had been deposited and in the copper striker till the silver deposited had been covered by copper. It was left in the main plating bath about thirty minutes. Heavy plates of silver were obtained by this process which adhered firmly to the aluminium and did not rub through when polished with a a cloth wheel. A satisfactory copper plate could not be obtained using this system of solutions and strikers. Modifications of this procedure were tried with a view to determining its essential parts. For one sample the hydrochloric acid treatment was left out, for a second the phosphoric acid, for a third the cyanide, amalgamation etc. The results show that the hydrochloric acid may be left out; that either hydrochloric or phosphoric acids are necessary; that amalgamation is essential; that the process works best when used intact. Without doubt, however, a similar succession of baths could be devised which would work successfully and not come under the control of the patent. The principal objection to Legate's method, in the investigator's opinion, is that the plate obtained by him in the laboratory was very hard and diffiault to finish up or burnish. Several samples plated by this method

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were finished up by an expert hand at the finishing of silver. Previous to finishing a few of the samples were plated with nickel and then silver by a techinical plater after having previously received a fairly heavy coat of silver by Legate's method here at the Institute. In all cases the samples took a high polish. In a few cases there was a tendency to blister on the part of the plate and in nearly all the metal was more or less pitted or corroded which was probably due to excessive use of acid. The surface of the metal in most cases was striated but this was caused by over buffing or polishing previous to plating.

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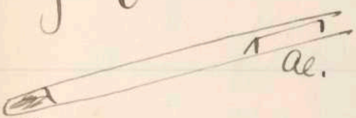
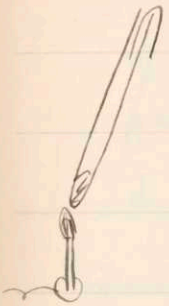
The patented method of Betts suggested the use of a volatile or gaseous metallic chlorides. The first chloride tried was ferric chloride. A combustion tube was arranged in a combustion furnace containing ferric chloride and aluminium



The lamps were first lighted under the metal and then under the ferric chloride. The idea was to have the tube at all points above the boiling point of ferric chloride and hence have the hot metal exposed to gaseous ferric chloride. This experiment was not successful. Theoretically it should work. It is worthy of a careful trial with differently designed apparatus. In this instance the fused ferric



chloride at the end of the tube sputtered so violently that the metal at the other end was sprayed with liquid chloride and hence the results could not be relied upon. A similar experiment was performed as follows. An ignition tube containing ferric chloride was held in a vertical position. The tube was about a foot long. Over the end was hung a piece of aluminium. The tube was heated till gaseous ferric chloride was given off. After this treatment the metal was dipped into copper sulphate solution. In places a deposit of copper was obtained which could not be rubbed off by energetic rubbing with a towel. This indicates that iron was deposited, in places, upon the aluminium. Chloride of antimony, iodide of antimony, and bromide of arsenic were used. A porcelain crucible was filled with antimony iodide and heated by a Bunsen burner.

Over the top of the crucible a piece of sheet aluminium was held with a pair of pincers. A Bunsen flame was played over the surface of the metal. Dense fumes of antimony iodide played against the hot under surface of the aluminium. The metal was blackened in places but there was little if any evidence of a deposit of antimony. A sample treated as above was electroplated with copper but the plate obtained was not permanent. Arsenic chloride was used in place of the iodide. There was no evidence given of a deposit of metallic antimony during the experiment. This was repeated using arsenic tri bromide. No sure indications that arsenic had been deposited were given. The piece treated with arsenic was put into a copper electro bath. Little copper was deposited but this small amount resisted energetic rubbing with a cloth.

The following scheme was tried. Stibine was evolved from a jet with burning hydrogen. A piece of aluminium was held in this jet. A copious deposit of antimony was obtained which rubbed off easily with a piece of cloth.

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If the aluminium was first heated and while hot was held in the flame from the jet a more permanent deposit of antimony was obtained. This did not take an adhesive coat of copper.

Several fused baths were tried. It was attempted to get a flux that would dissolve alumina and also copper oxide potassium bi-sulphate was tried. First a piece of aluminium was dipped into fused potassium bi sulphate containing copper carbonate dissolved in it. No copper whatsoever was deposited on the aluminium. Next a current was used with a piece of copper for an anode and one of aluminium for a cathode.

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There was no precipitation of copper. Probably the bath was too acid. It was attempted to neutralize the acidity by adding more copper carbonate. This was not successful. A bath was made by fusing together the theoretically necessary weights of potassium bisulphate and caustic soda to give the following reaction;

$KHSO_4 + NaOH = KNaSO_4 + H_2O$

Copper carbonate was dissolved in the above fused bath. When a piece of aluminium was dipped into this bath an uneven deposit of copper was given. For some unexplainable reason, however, this bath ceased to work. Once only a very good deposit of copper was obtained in places by removing a piece of aluminium from a fused sulphate ($KHSO_4$)

bath and dipping into water containing, dissolved, potassium bi sulphate and copper sulphate. This was tried again repeatedly with no result. A fused bath of borax containing copper carbonate was used. On dipping a piece of aluminium into this a deposit of copper was obtained but not a smooth one. The metal was more or less corroded. Fused borax is too reactive for technical use. Fused potassium nitrate was tried. This had little apparent action on the aluminium when dipped into the same. Moreover it would not dissolve copper oxide and hence could not be used to deposit copper.

As another modification or rather suggestion from Bett's process and others, fused cuprous sulphide was used. This latter is made by heating in an ignition tube a mixture of copper turning and sulphur. This was powdered and sprinkled over the surface of the aluminium and the latter heated on the under surface till the cuprous sulphide fused. This fused sulphide was rubbed over the surface of the metal. No apparent precipitate of copper was given. This was repeated, with no better result, mixing the cuprous sulphide with potassium sulphide. Again a mixture of the above was fused in a crucible and a piece of aluminium dipped into the fused bath. It required the blast lamp to get a bath fused to sufficient thinness. This raised the temperature too high and the aluminium melted in the crucible. This method gave no promise of success.

It was attempted to plate aluminium in a solution of cuprous chloride in pyridine. The metal was dipped into the solution and the surface scratched with a knife while in the liquid. Copper deposited on the scratches but was easily rubbed off. A piece of copper was put in as an anode and the current turned on. A spongy deposit of copper was given. The idea of this experiment was to make use of a solution or solvent which was free from oxygen and hence would not have any tendency to oxidize the surface of the aluminium.

The following method patented in England was tried. The patent is taken out by Weil and Levy (English Pat. of 1897 No. 22961) for a bath composed as follows: $CuCl_2$, NH_4Cl, KCN, and gallic acid, pyrocatechin, oxalic acid, acetic acid, or other reducing agent. The following bath was made up according to recipe:

540 cc	H_2O
13.5 gms.	$CuCl_2$
16.2 "	NH_4Cl
14.9 "	KCN
1.44 "	Gallic Acid

After corrosion in boiling $MgSO_4 + Na_2HPO_4$ acidified with H_2SO_4, the sample was plated in the above bath. A very good plate of copper was obtained which finished well and gave no indications of blistering. This copper plate, in a few instances, was covered with silver. The silver plate polished up very well except for numerous pin head pits in the surface of the plate. The bath, however, could not be used more than five to eight hours. After this time it seemed to loose its efficiency, for all samples plated in a bath, which had aged as above described, blistered when a reasonable thickness of plate had been obtained.

The following modification of the above was used. A bath was made up of 332 cc H_2O, 8 gms $CuCl_2$, 10 gms. NH_4Cl, 5 gms. Tartaric Acid. It was attempted to plate a sample of aluminium in this bath after first cleansing in a boiling bath of $MgSO_4 + Na_2HPO_4$. Copper was precipitated on the metal, but in a spongy state and could be readily rubbed off.

Another modification tried was the following bath; 540 cc H_2O, 13.5 gms. $CuCl_2$, 16.2 gms. NH_4Cl, 14.9 gms KCN, and 10cc of 40% formaldehyde solution. A sample was dipped into boiling $MgSO_4 + Na_2HPO_4$ and then plated in the above bath. A fairly satisfactory plate was obtained which was free from blisters. Like the previous bath this one deteriorated on standing. A bath was made up like the one containing gallic acid except that the latter was replaced by caustic soda, the idea being that the caustic would dissolve the oxide or hydrate coating of the aluminium. However it is the opinion of the investigator that caustic, besides cleansing the surface of aluminum, leaves a deposit of hydrate on the metal. Its color is darkened by dipping into caustic, indicating a deposit on the surface. A piece of aluminium was plated in the above copper bath, having first been corroded in boiling magnesium sulphate and sodium phosphate. A heavy coat of copper was obtained which was permanent except for a few small blisters around the edges. This bath was tried at 90° approximately. At this temperature the caustic attacked the aluminium vigorously. This bath was not permanent. That is after standing a short time, say three hours, no plate, with any permanancy at all could be obtained.

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A Weil and Levy bath ($CuCl_2$, NH_4Cl, gallic acid) which had deteriorated by aging was revived, so to speak, by adding more gallic acid. A sample of aluminium was corroded and plated in this bath. Little blisters formed in the plate. Gallic acid was added to a common copper cyanide bath and a sample of aluminium plated in the same. A blistered plate was obtained. An ordinary copper cyanide bath was used at or near its boiling point. A blistered plate was obtained. At this temperature the weakly alkaline bath acts on the metal giving off a gas. A bath was made up of 5 gms $CuCl$, 5 gms NH_4Cl, 200cc H_2O, 5 cc HCl (1.16). In this solution a precipitate of copper could be obtained upon the surface of the aluminium with or without the current. It was spongy, however, and could be easily rubbed off. In summing up the results of the above experiments the investigator would say that there is some virtue in the Weil and Levy bath, which consists of $CuCl_2$, NH_4Cl, KCN, and a small amount of gallic acid. or other reducing agent; that the above bath works to the best advantage when freshly prepared and loses its utility on ageing; that the reducing agent in the bath is necessary; that caustic in the place of the reducing agent is of little value; that the plate obtained by the above bath was, almost without exception, pitted with

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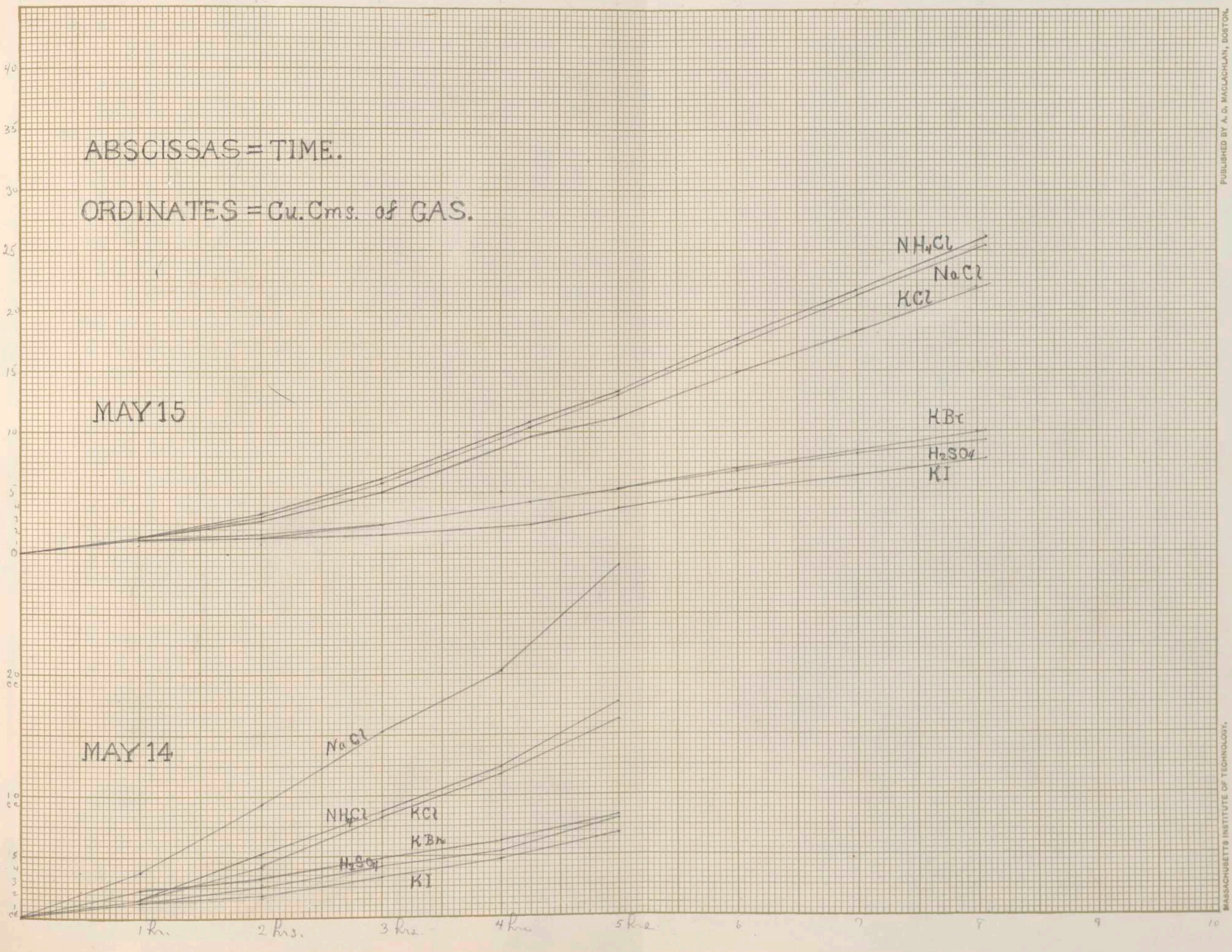
pin hole perforations; that the above bath shows promise of success when manipulated by an experienced plater; that owing to its lack of permanency the bath might not be feasible for technical work; also that a chloride bath of copper cannot be successfully used.

In conclusion it may be said that of the patents and methods recommended in the literature and which were tried in the Laboratory, only two gave any promise of success. These two are the patented methods of Legate and Weil and Levy. The former is objectionable, being complicated and since it involves amalgamation the plate cannot be heated. The objection to the Weil and Levy bath is its non permanency; that is the bath loses its permanency in a short time.


ABSCISSAS = TIME.
ORDINATES = Cu. Cms. of GAS.
MAY 15
NH_4Cl
NaCl
KCl
KBr
H_2SO_4
KI
MAY 14
NaCl
NH_4Cl
KCl
KBr
H_2SO_4
KI
40
35
30
25
20
15
10
5
4
3
2
1
0
20 cc
10 cc
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4
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1 hr.
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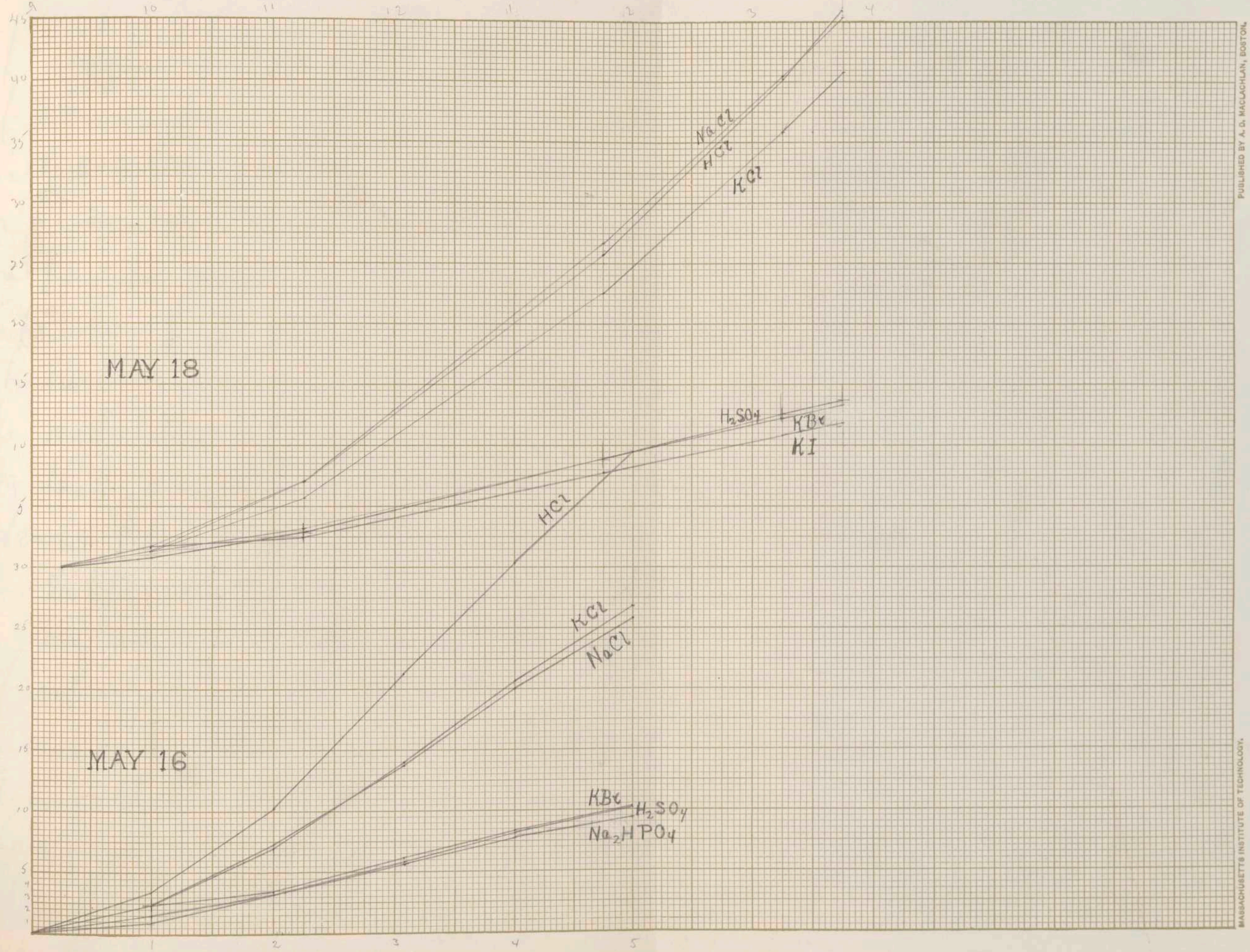
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3
2
1
MAY 18
NaCl
HCl
KCl
H_2SO_4
KBr
KI
HCl
KCl
NaCl
MAY 16
KBr
H_2SO_4
Na_2HPO_4
1
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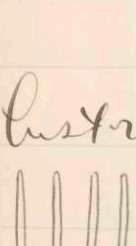
In connection with this thesis a brief study was made of the action of certain salts upon the surface of aluminium. The metal is covered with a coating or membrane of oxide or hydrate. The negative ion of sulphuric acid is only partially capable of penetrating this membrane. That is its entrance or contact with the metallic aluminium is hindered by this membrane of oxide. Hence aluminium dissolves slowly in sulphuric acid. If certain salts are added to the acid the speed of solution of the aluminium is increased. Chlorides are capable of doing this. If the membrane theory is correct it is quite probable that the oxide coating is easily penetrated by the chlorine ion of the salt added. This ion is accompanied by a hydrogen ion. An aluminium ion leaves the metal to join the chlorine and the hydrogen ion is liberated as gas. The aluminium chloride or aluminium and chlorine ions may withdraw through the membrane and more hydrogen and chlorine ions enter. Related work has been performed by Taylor (Philosophical Magazine, March 1903) and Kahlenberg (American Chemical Society Journal 1903)

An experiment was tried to illustrate this principle, As shown in the



sketch a series of endiometer tubes were filled with 1:1 H_2SO_4. Into each were put equal lengths of aluminium wire. The ends were closed by capillaries and the endiometers inverted. Onto all but one respectively were put amounts of different salts which corresponded

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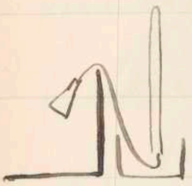
to their equivalent weights. The hydrogen given off collected at the top and readings of the volume of gas were taken from time to time. In this way the rates of solution or the effect of the different salts upon the solubility of aluminium could be determined. After making a large number of runs of about twenty four hours each it was shown that chlorides of sodium, potassium, ammonium, and magnesium increase the solubility of the aluminium about equally. Potassium bromide increased it some. Nitrates decreased its solubility greatly. Probably this was not a decrease in solubility but less hydrogen was evolved since it was used up in reducing the nitrate. Several contradictory results were obtained. This concentration of acid was the weakest which would give off, in reasonable time, a measurable amount of gas. There were other local causes which seemed to effect the solubility of the aluminium. The following apparatus was designed and used.



A series of 30 c.c. Ehrlenmeyer flasks were immersed in a water thermostat kept approximately at 65°. These flasks were each connected by delivery tubes to eudiometer tubes. These flasks were filled with sulphuric acid (50 c.c. in 1000), a corresponding amount of salt added to each, and equal lengths of wire put in. The amount of salt added in each case was one cubic centimeter of normal salt solution. Four runs were made with this apparatus. Results were obtained

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which checked closely. Plots are shown. The abscissas represent the times at which readings were taken and ordinates the volume of hydrogen evolved. As shown by the plots, chlorides increase, equally or nearly so, the solubility of the metal. For the run of May 14 two pieces of wire were used. The discordance of the sodium chloride is due to the fact that three pieces instead of two of the same length of wire were used. If its values are divided by two thirds they check with the other two chlorides. On the other three runs three pieces of wire, of same length as in that of May 14, were used. The hydrochloric of May 16, and 18 do not check. If either are to be relied

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upon that of May 18 is the most reliable. After these experiments similar ones were made upon the solubility of magnesium wire in water, it being too soluble in acid to us the latter. The same apparatus was used. By these experiments it was found that magnesium was only very slightly soluble in water alone. That is only an extremely small amount of gas was given off. Potassium iodide and bromide increased the solubility only slightly and equally. Chlorides increased the solubility greatly but not equally and were erratic. That is tubes containing ammonium chloride and hydrochloric acid ran far ahead of those containing potassium chloride and sodium.

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chloride and moreover did not check well in duplicate experiments. The runs with magnesium wire were made to find out if there was any analogy between the actions of the two metals. It may be said that they acted quite similarly with the salts used. It would be interesting to make a similar study of other metals such as zinc, iron, etc.