

Hitherto electro-deposition has been resorted to mainly for decorative purposes; that is on an article made of a common metal or alloy to deposit one with a greater surface brilliance. But the process can now be applied not only for such ornamental work, but to overcome some of the many difficulties that confront marine engineers.

That one metal could be coated on to another by dipping in suitable solutions was known to the ancients, and the Greek historian Zosimus in the 5th century described how swords and shields were so coated with copper. The same effect was described as the actual transmutation of metals by Paracelsus in the 16th century. Probably the first commercial instance of one metal being used to coat another was in 1742 when Thomas Bolsover by welding silver on to a copper foundation established the now extinct industry of Sheffield plate manufacture. The process was entirely mechanical and consisted of welding and rolling thin silver sheets to a thicker copper one. Various articles such as trays, teapots, candlesticks etc. were made from the sheets so treated, and had therefore all the appearance of silver although the bulk of the metal was copper. The industry attained considerable importance until the advent of electro-plating. As this does the same thing in a much better and cheaper way the manufacture of Sheffield plate is no longer practised.

Before going into the principles of electro-deposition it may be as well to take a rapid survey of its history. The first attempt at electrolysis or analysis of a liquid by an electric current was probably by Dieman and Paets or by Van Trootswyk who in 1789 at Haarlem decomposed water by electricity. A little later Ritter precipitated silver by the same means. This was in the early days of electrical development and when only frictional machines giving a very high voltage and a very small current were available, and these, as we now know, are not the conditions generally necessary for electrolytic work.

In 1800 Volta's pile was introduced and as this gave a very large current with a low voltage the way was opened for further development in electrolytic work. The most important was the brilliant electro-chemical discoveries of Davy who by decomposing the oxides of the alkalis and alkaline earths proved that these were not elementary substances as had hitherto been thought, but the oxides of the metals Lithium, Sodium,

Potassium, etc., which metals he for the first time separated from their compounds. In 1801 Wollaston deposited Copper on silver and in 1803 Cruickshank deposited several metals from their solutions. Wollaston obtained his deposit by inserting the silver in contact with a more oxidizable metal in a solution of copper, thus making a small battery of the solution itself. Cruickshank had constructed a battery of considerable size for his experiments. In 1805 Brugnatelli deposited gold on to silver medals. The researches of Oerstad and Arago, the construction by Faraday in 1831 of the first magneto-electric machine, the invention by Pixii in 1832 of the prototype of the modern dynamo and the introduction of Daniell's battery, besides giving fresh sources of electrical energy, widened the interest in electrical work. In 1836 De la Rue noticed that the copper which deposited on the cells of a Daniell's battery exactly reproduced every line or mark on the surface on which it is deposited but he failed to appreciate the possibilities of this discovery. Three years later three men—Jacobi in St. Petersburg, Spencer and Jordan in England, independently and almost simultaneously described the process of electro-typing. In 1836 Elkington obtained a patent for gilding copper and brass objects, and in 1838 one for zinc plating by a method similar to Wollaston's. Spencer in describing his electro-typing process also stated that non-conducting substances, such as wood and Plaster of Paris, could be made conductive and covered electrolytically if they were first covered with a film of bronze powder ; and in 1840 Murray discovered that moulds of non-conducting material could be made conductive by brushing them with plumbago, so that metallic moulds were no longer essential. The first print from an electrotype block is believed to have appeared in the *London Journal*.

In 1840 Wright after experimenting with many solutions discovered the use of the cyanide bath for the production of good deposits of gold and silver. No good results had before this been obtained in depositing these metals, because the few salts that are soluble gave very poor deposits, for as Gold and Silver are electro-negative to most ordinary metals they are easily thrown out of solution by the other metals. As we shall see later good deposits are seldom obtainable by this "simple immersion" method. Solutions of the double Cyanides of Potassium and Gold or Silver however permit

of good electrolytic deposits. This solution was patented by Messrs. Elkington, and from this time onward the industry of silver plating became firmly established and completely superseded Sheffield plate.

But though the development of Dynamo-electric machinery and other branches of Electricity has advanced by leaps and bounds but very little further progress has been made in electro-plating. Indeed it can be safely said that the industry is practically limited to the electro-deposition of Gold, Silver and Nickel. Copper is deposited on to iron before nickel plating and brass is also deposited, but most of the attempts to deposit metals on to iron or steel have not been very successful. Before going into the reasons for this, it will be as well to consider briefly the principles that govern electrolytic action.

Many theories had from time to time been advanced to account for the phenomena of electrolysis, but interesting though it might be to trace the developments through the theories of Davy, Berzelius, Faraday, Grotthus, Clausius, etc., it is beyond the scope of this paper. The laws stated by Faraday are still found to be true, namely: (1) The quantity of an element set free or deposited by an electrical current is proportional to the strength of the current and the time. (2) The amount of an element set free or deposited is proportional to its chemical equivalent. These two laws may be combined in one as—The same quantity of electricity (in coulombs or ampere hours) passing through an electrolyte sets free deposits, or transfers to other combinations, always the same number of valencies.

The theory now generally accepted, and known as the Dissociation Theory or the Theory of Ions was first enunciated by Arrhenius in 1887, following up valuable work done by Van 't Hoff. This theory was foreshadowed by Faraday and the terms used in explaining it, such as ion, kation, anion, etc., were due to him. Briefly this theory states that all electrolytes (according as they are good or bad conductors) are more or less dissociated or broken up in solution into ions carrying positive or negative charges of electricity in proportion to their valency. These ions are in a state of continual motion migrating to every part of the solution and the electric current simply acts as a directing force causing the ions to migrate in a definite course to each electrode and

there to deposit their electric charges, after which they appear as the usual chemical elements or groups, and may be set free as such, or undergo further chemical decomposition with the electrode or solution. The latest theories deal with the extension of the Dissociation theory, owing to the conception of the materialistic nature of electricity.

As we have to deal with metals or metallic salts in solution, we will take the case of a metal and a metal salt in solution and consider the modern theory as applied to these conditions. It is advisable to do this, because it concerns not only the electro-deposition of metals, but also the electrolytic corrosion of metals and alloys.

It is well known that all metals and alloys if immersed in water—pure or containing matter in solution—or dilute acids, will tend to pass into solution. If this tendency exists, and that it does, can be proved, it must be due to some force or pressure. This is known as the solution pressure of the metal, and for each metal it is a constant depending on temperature for each particular solvent. It is analogous with the vapour pressure of a liquid. Water for instance at all temperatures tends to evaporate, and the higher the temperature the greater the tendency to do so. For any one temperature the vapour pressure is a constant and can be measured. Vapour pressure, then, expresses the tendency of a liquid to pass into the vapour form and solution pressure expresses the corresponding tendency of a solid, when immersed in a solvent, to pass into solution and is also a constant depending on definite changes of condition such as temperature. Now if a metal or salt of a metal going into solution is to form an electrolyte—and all metals do—it must, according to the theory of Dissociation, break up into ions. These ions will carry large charges of static electricity, and will distribute themselves uniformly all through the solution. Not only the substance going into solution—the solute, but the solvent also may be thus ionized. Here it may be remarked that the ideas concerning alkalis and acids can be easily understood from this theory. If the substance going into solution results in the formation of OH or hydroxyl ions, these will give the alkaline reaction. If H or hydrogen ions are formed the reaction will be acid. The solution will be neutral if hydrogen and hydroxyl ions are present in equal quantities. Alkalinity is not a property “per se,” of the alkali metals, Lithium, Sodium, Potassium,

etc., but depends on the fact that these metals decompose water with the resultant formation of hydroxyl ions.

It is known, then, that metals and their salts due to their solution pressure, tend to go into solution either in water or some other solvent. If there is no force acting against this it is evident that it would only be a question of time for all the metal of whatever amount to go into solution. But we know that some force must be acting against it because if the amount of the solvent is limited, the metal or salt will dissolve to a certain extent, and then dissolve no more. The force that thus acts against solution pressure is a property of the solvent, or more strictly of the ions in solution, and is called Osmotic pressure. We have compared solution pressure with the vapour pressure of a liquid and we know that if a liquid is placed in contact with air in a closed vessel, evaporation will go on due to vapour pressure until the air becomes saturated, and then evaporation will cease. The vapour passing into the air increases the pressure on the surface of the liquid, and at the point where this pressure balances the vapour pressure evaporation will cease. Marine engineers are of course familiar with all that has to be done with these two pressures in the raising of steam. But the pressures they are used to are those that can be shown directly by means of pressure gauges and they may find it difficult to conceive of these analogous internal pressures. But Osmotic pressure is analogous to a gas pressure such as steam pressure as solution pressure is to vapour pressure. It is sometimes of considerable magnitude, for the Osmotic pressure of a half-saturated solution of Ammonia has been calculated to be equal at 32°F. to 671 atmospheres. That vessels containing such solutions are able to withstand it, is due to the fact that a greater pressure, known as surface tension, acts on the surface and at right angles to it and is directed inwards. Some conception of Osmotic pressure can be obtained by considering a simple piece of apparatus. In (Fig. 1) A is a pot of porous material such as unglazed china and is filled with a Copper Sulphate solution and then immersed in a vessel B containing Potassium Ferrocyanide. The Copper Sulphate will start to work into the pores of the pot from the inside, and the Potassium Ferrocyanide will do the same from the outside. About the centre, as indicated by the dotted line, they will meet, resulting in the formation of a thin membrane of Copper Ferrocyanide.

The remaining Copper Sulphate and Potassium Ferrocyanide is washed away leaving the membrane. This has the peculiar

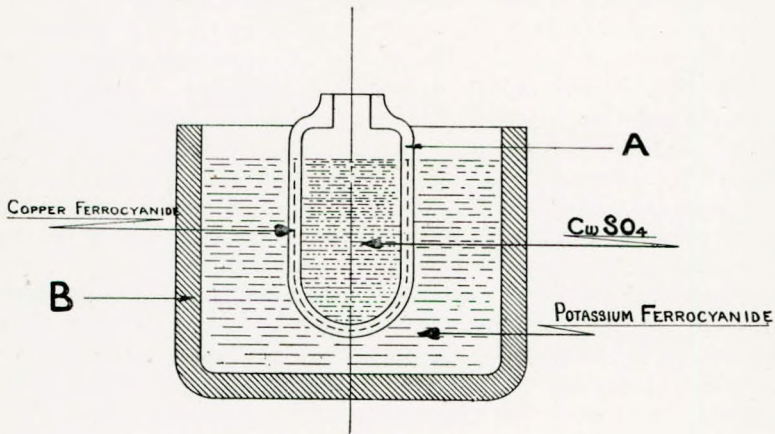


FIG. 1.

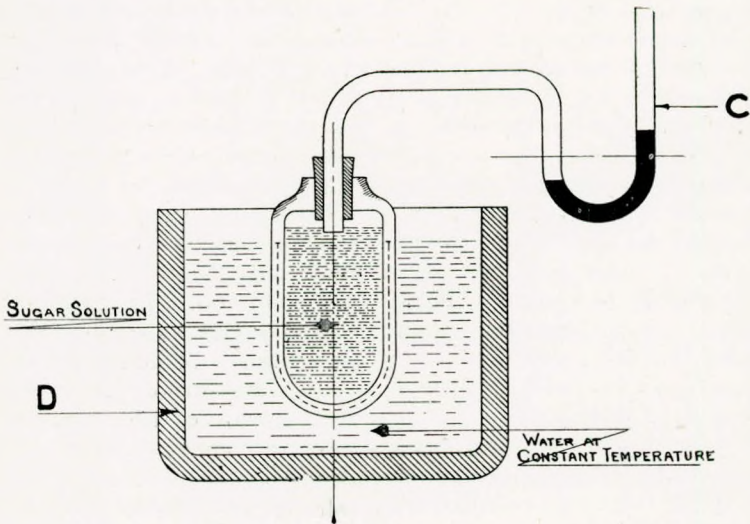


FIG. 2.

property of allowing water to pass through but not matter in solution. Such semipermeable membranes are found in plant and animal life and are of great importance in organic func-

tions. To the top of the porous pot is attached a glass tube connected to a manometer (Fig. 2). The porous pot is filled with a solution of sugar, and while this solution is in contact with the atmosphere there is no evidence of Osmotic pressure. This is because surface tension and atmospheric pressure are balancing both Osmotic and Vapour pressure. If now the glass tube is connected to the manometer C containing mercury and the porous pot immersed in a vessel D containing water at constant temperature, we shall have an indication of Osmotic pressure. Inside the porous pot we have a solution of sugar, and if there is any sugar undissolved it will tend, due to its solution pressure, to go into solution and acting against this will be the Osmotic pressure of the sugar already in solution. We will suppose that in this case there is no undissolved sugar so that the only force we have to consider is Osmotic pressure. If this could act like gaseous pressure it would show itself by expanding in the tube leading to the manometer, depressing the mercury. It does this, but in an indirect way. It will tend to still further dilute the solution and as the sugar cannot pass through the semipermeable membrane, water will be drawn from the outside vessel till the Osmotic pressure is balanced by the head of the mercury as shown by the difference of its height in the two arms of the tube. It is not possible to do this experiment here, because the action is slow and it may be two or three days before the mercury reaches its final level. A conception of Osmotic pressure may be obtained in an even simpler way. In Fig. 3 is shown a plain glass tube, closed at one end and open at the other. In this tube we will suppose that there is a piston with a perfect fit, yet frictionless and also made of some material having semipermeable qualities. On the underside of this piston we will suppose the tube to contain a solution and on the upper side pure water. Now if the pressure of the water column is greater than the Osmotic pressure of the solution, the piston will sink, and the solution will become more concentrated. If, however, the pressure of the water column is less than the Osmotic pressure of the solution, the piston will rise, and the solution, taking up more water, will become more dilute. In both cases the piston will move till it comes to such a position that Osmotic pressure is just balanced by the column of water.

It has been proved by Van 't Hoff, that the Osmotic pressure

is proportional to the quantity of substance or number of molecules in unit volume. A law of gases well known to Marine Engineers is that of Boyle or Marriotte, which states that the pressure of a gas at constant temperature is inversely proportional to the volume occupied. This then is also a law for Osmotic pressure. Van 't Hoff further established that the law of Charles or Gay-Lussac for any single gas at all temperatures or  $PV = CT$ , is also true for the Osmotic pressure of solutions. Another law of gases, of more importance to the chemist than to the engineer, is that of Avogadro, which states that "equal volumes of gases under the same conditions of temperature and pressure, contain the same number of molecules." Van 't Hoff proved that this also applies to solutions, and stated the following general principle:—"The same number of gaseous or of dissolved molecules are contained in a given volume of any gas or of any solution respectively, when at the same temperature, the gaseous pressure and the osmotic pressure have the same value." Stated as an equation:—

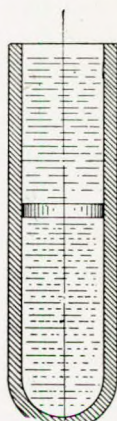


FIG. 3.

	$P.V. = n.R.T.$
where	$P.$ = Pressure
	$V.$ = Volume
	$n.$ = number of mols. (molecular weight expressed in grammes)
	$R.$ = a constant
	$T.$ = absolute temperatures.

$P.V.$

$T.$  has a constant value for one molecule of a perfect gas. This value  $R.$  is called the gas constant.

These theories were not accepted without considerable opposition. For instance it was found that nearly all acids, bases and salts, which are soluble in water, have a greater Osmotic pressure than that calculated from their molecular weights. But the same difficulty had presented itself in the case of the molecular theory of gases. For instance gases such as Nitrogen peroxide and Phosphorous pentachloride show a greater pressure than that calculated by Avogadro's law. This can only be explained by assuming that there are a greater number of molecules present than would be if the



gases remained in a normal condition, that is the gases must have a certain number of their molecules dissociated or broken down. The same assumption is applied to solutions, and that it is justified and true is borne out by many experiments and can be supported by thermodynamic reasoning. It was objected to by many scientists because they could not see how a compound of great strength such as Potassium chloride held together by great chemical affinity, should so easily break up and dissociate merely by going into solution, nor could they understand why, if potassium was thus free, it did not decompose the water as it normally would do. They further argued that it was against the law of the Conservation of Energy, that a substance such as potassium chloride, which combines with great energy, should separate spontaneously on going into solution. Before the theory could be accepted these apparent contradictions had to be removed. This was done by Arrhenius. He proved that there were two kinds of dissolved molecules, one active and a conductor of electricity, and another inactive and a non-conductor of electricity. The active molecules are those that are dissociated, the inactive ones are not. Hence it follows that only those substances in solution conduct the electric current, which are to some extent dissociated, and that the greater the degree of dissociation the more readily does the substance conduct the current, or to put it briefly, it is only the dissociated molecules that conduct electricity.

Chemically pure water does not conduct electricity, and chemically pure hydrogen chloride does not conduct either. A solution of hydrogen chloride in water, however, is an excellent conductor, but a solution of hydrogen chloride in chloroform does not conduct. This is because it is only when in solution in water that hydrogen chloride is dissociated or ionized and therefore made a conductor. That this is so, is supported by the fact that the Osmotic pressure of the chloroform solution of hydrogen chloride is found to be that calculated by taking the molecules as normal undissociated ones, whereas the Osmotic pressure of the water solution is greater and can only be explained by taking the molecules as dissociated. That a substance such as potassium chloride can dissociate without any show of energy is explained by the charges of electricity that each ion carries. Chemical energy has simply been changed to electrical energy. Metallic

and hydrogen ions carry positive charges and are called "kations"; hydroxyl ions and halogens and acid radicals carry negative charges and are called "anions." When simply dissociated in solution these ions, both kations and anions, behave like the molecules of a gas; that is, they are in a state of continual migration among the molecules of the solvent to every part of it.

If plates or electrodes, connected to some external source of electricity, be now inserted, in the solution, the migrations of the ions will assume an orderly feature. The kations, carrying their positive charges, will move in the direction of the current to the kathode or positive electrode, and giving up their charges will return to their ordinary molecular condition. The anions, carrying their negative charges, will move to the anode or negative electrode, and will also give up their charges of negative electricity and return to their normal molecular condition. Kations are generally expressed by their chemical symbols with one or more dots according to their valency, and hence number of charges. Anions are expressed in the same way by their chemical symbols and one or more dashes.

If we suppose ordinary salt or sodium chloride ( $\text{NaCl}$ ) to be placed in pure water, we know that, due to its solution pressure, it will go into solution, and will for the most part dissociate or break up into ions. The metal ion will carry a positive charge and will be expressed as  $\text{Na}\cdot$  (one dot, since sodium is monovalent). The chlorine as a halogen will carry a negative charge and will be expressed as  $\text{Cl}'$  (one dash, as chlorine is also monovalent). This dissolving will continue until the solution is, what we term, saturated, but as we now know that a pressure—Osmotic pressure—is opposing the solution, we can say that dissolving stops when solution pressure is balanced by Osmotic pressure. As the ions  $\text{Na}\cdot$  (positive) and  $\text{Cl}'$  (negative) are equal, the solution will remain electrically neutral. (Some whole and undissociated molecules will also have passed into solution.)

If, instead of a salt, we take the case of a metal such as zinc, immersed in a solution of one of its salts, we know that this will also tend to go into solution due to its solution pressure, and that this will be resisted by the Osmotic pressure of the solution. But as the zinc in going into solution will only send out positively charged zinc ions  $\text{Zn}\cdot\cdot$  (two dots, since zinc is divalent), the solution will tend to become positively charged.

The zinc, since it is giving off positively charged ions, will itself become negatively charged. A difference of electrostatic potential will therefore exist between the electrode and the solution, and this will hold the kations in solution in the neighbourhood of the electrode. This electrostatic tension will assist Osmotic pressure in overcoming solution pressure, and consequently as soon as a few zinc ions have gone into solution, solution pressure will be balanced by Osmotic pressure + electrostatic tension, and no further dissolving of the zinc will take place. This difference of potential between the metal and the solution is known as the "electrode potential" of the metal. It gives rise to an electrical double layer, consisting of negative charges on the electrode and positively charged ions in the solution held by attraction in the immediate vicinity of the electrode. The electrode potential is different for different metals and has been measured for a large number of metals in normal solutions of their salts.

Now if zinc is placed in a solution of a copper salt, it will, as before, go into solution giving off positively charged ions,  $Zn^{+}$ . But the solution already contains ions of copper. As copper has a lower solution pressure than zinc, the copper ions will easily give up their positive charges to the zinc electrode, and will separate out as metallic copper. The zinc electrode being thus prevented from becoming negatively charged, no electrical double layer will be formed, so the zinc will continue to go into solution till all the copper has been precipitated. Then the formation of the double layer will take place and the zinc will cease to dissolve.

We see, then, that zinc placed in a solution of its own salt goes only very slightly into solution, due to the formation of an electrical double layer, but that in a solution of a salt of a metal having a lower solution pressure than itself the formation of the double layer is prevented and the zinc continues to go into solution. Obviously, then, if by any other means we neutralize the negative charge of the zinc electrode, the formation of the electrical double layer will be prevented and zinc will go into solution in a solution of its own salt. The connection of the zinc to an external source of electricity will do this, for we have already seen that the passage of a current of electricity alters the behaviour of the ions, inasmuch as their migrations are now confined to an orderly procession of the kations carrying their positive charges to the kathode

and the anions carrying their negative charges to the anode. To balance this, then, the anode must be connected to the positive pole of the external source of the current, and the kathode to the negative pole. To simplify matters, we will suppose that both anode and kathode are of zinc, so that we do not have two metals with different solution pressures to consider. Arriving at the kathode and giving up its positive charge, the zinc kation will resume its normal molecular condition as metallic zinc firmly attached to the kathode. If the zinc salt is sulphate of zinc,  $\text{Zn SO}_4$ , the anion or negative ion will be the radical, sulphion  $(\text{SO}_4)''$ . This, on giving up its negative charge to the anode, will assume its molecular condition. But  $\text{SO}_4$  does not separately exist, so it will combine with the zinc going into solution from the anode to again form sulphate of zinc  $\text{Zn SO}_4$ . This will dissociate or ionize, leaving the sulphion again with two negative charges and the zinc with two positive charges, and so the cycle will continue, or rather would continue if there were no other factors to consider. There are, however, other factors, and one that is of considerable importance is the migration velocity of the ions. Obviously if the kations move to the kathode at the same rate that the anions move to the anode, the condition of the electrolyte will remain constant. But this is not always the case, and in the present instance the anion  $(\text{SO}_4)''$  will travel faster than the kation  $\text{Zn}^{++}$ . This will mean that there will be an increase of the concentration of the solution round the anode and a decrease round the kathode, although the total quantity of  $\text{Zn SO}_4$  in the solution remains constant. The changes of concentration can be shown diagrammatically as in Fig. 4. The anions  $(\text{SO}_4)''$  are represented

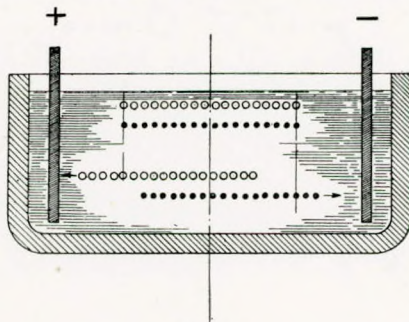
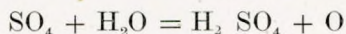


FIG. 4.



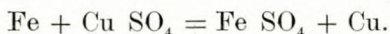
If, therefore, the supply of dissolved zinc falls off, it will happen that the discharged  $\text{SO}_4$  ion, being unable to find a zinc atom to combine with, will break down as shown into  $\text{SO}_3$ , liberating an atom of oxygen. This atom may escape to the surface, but it is more likely that it will in the presence of water, combine with the zinc anode to form zinc hydroxide  $\text{Zn}(\text{OH})_2$ . This compound is insoluble in water, so that if it once forms on the surface of the anode, it will still further prevent it dissolving. The trouble therefore becomes cumulative.

We have seen that it is only the dissociated ions that conduct electricity, and it is found that metallic salts do not dissociate to the same extent that acids do, and are not, therefore, such good conductors as acid solutions. Acid, therefore, added to the solution will considerably increase its conductivity. Let us suppose we add a little of an acid, such as sulphuric acid,  $\text{H}_2\text{SO}_4$ , to the zinc sulphate solution. This will ionize as  $2\text{H}^+$  and  $(\text{SO}_4)^{--}$ . The sulphion  $(\text{SO}_4)^{--}$  will behave as it did with zinc sulphate. The two  $\text{H}^+$  ions will travel to the kathode, and on giving up their positive charges will resume their normal condition as free hydrogen. These will attach themselves as gas bubbles to the kathode and prevent the deposition of zinc. If instead of sulphate of zinc we were dealing with sulphate of copper, the hydrogen would turn out the copper which would be deposited in its stead, leaving the hydrogen to combine with the  $\text{SO}_4$  radical to re-form sulphuric acid. But it will not do this with zinc sulphate; so although the addition of sulphuric acid is an advantage with a sulphate of copper solution, it is worse than useless with a sulphate of zinc solution. Even if sulphuric acid is not added to the solution, it is very likely to be formed there if the anodes are not dissolving at the required rate. The excess of  $\text{SO}_4$  ions liberated at the anode may not all break down to  $\text{SO}_3$ ; they may combine with the water to form sulphuric acid thus:—

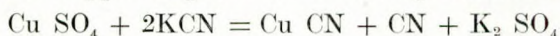


In either case oxygen is liberated at the anode, with the probable resultant formation of the insoluble zinc hydroxide. The two chief troubles with the electro-deposition of zinc, therefore, are the depositing of hydrogen on the kathode and the formation of zinc hydrate at the anode. If the kathode is of iron—and in practice it would be, since iron is the metal we usually require coated with zinc—further trouble would

result from the presence of free acid. If the surface of the iron were perfectly flat, the distribution of the current would be equal all over it, so that its potential relative to the solution would be equal for all parts of its surface, and an even deposit of zinc would be formed. But in a very large class of iron goods this condition will not prevail and there will be projections and recesses. Naturally the projections will receive most of the deposit, and the recesses little or none. A rise in the voltage between the anode and kathode might force the current into these recesses, if it were not for the fact that with ordinary aqueous solutions a rise in voltage would only result in decomposing the water into its constituent gases, hydrogen and oxygen. The recesses in iron goods, then, not only do not receive a proper deposit, but are liable to be corroded by the free acid in the solution. With an acid copper solution iron would be further affected, since it displaces copper from its salt thus :—

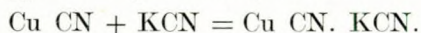


That is, copper would be deposited without the aid of an electric current. Since, however, the deposit is on to a surface that has been corroded, this simple immersion deposit is not of any use. There are many difficulties, therefore, to be overcome in the deposition of zinc, and in depositing any metal on to iron and steel, and many attempts have been made to overcome them. We have stated that the deposition of silver was made possible by Elkington's patent of the cyanide solution, and the principle of this solution has been applied for depositing copper and zinc on to iron. If potassium cyanide is added to copper sulphate the following reaction occurs :—



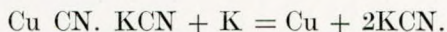
(Copper sulphate) + (Potassium cyanide) = (Copper cyanide)  
+ (Cyanogen) + (Potassium sulphate).  
(Cyanogen is a deadly poisonous gas.)

The copper cyanide is dissolved in more potassium cyanide, resulting in the formation of a soluble substance—the double cyanide of copper and potassium, thus :—

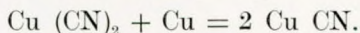


When in solution this ionizes as  $\text{K}^+$ , the kation, and  $\text{Cu}(\text{CN})_2^-$ , the anion. The metal copper, therefore, is carried to the anode with the complex  $\text{Cu}(\text{CN})_2$  group and the metal potassium

is carried to the kathode. The deposition of copper is due to a secondary reaction with the undissociated double cyanide thus :—



At the anode the following reaction takes place with the copper going into solution :—



This Cu CN is the single cyanide and is insoluble until converted into the double cyanide by the potassium cyanide set free at the kathode. The solution, therefore, must be considerably agitated and a slight excess of KCN kept in the solution to dissolve the single copper cyanide. For depositing copper on to small articles of iron, zinc, lead, pewter and Britannia metal, this solution is considerably used, and a similar solution of zinc is also sometimes used for coating iron with zinc. But it requires too much attention and is too expensive to be carried out on any considerable scale. Then as the solution contains a deadly poison, it is quite unsuited for dealing with iron goods on a large commercial scale.

Attempts have been made to deposit zinc from a zinc sulphate solution by using insoluble anodes of lead and neutralizing the acidity of the solution, and at the same time regenerating it by pumping it through filter beds of zinc dust. Zinc dust is a by-product of zinc distillation, and contains both zinc and zinc oxide. It is cheap, but being a by-product, its constituents cannot be guaranteed, and the percentage of zinc may vary from 5 to 80 per cent. It is therefore extremely difficult to arrange that the solution will be so regenerated that no free acid is ever in contact with the iron kathodes. It has the further disadvantage that on the surface of the lead anode peroxide of lead is formed, and this sets up a considerable back E.M.F. so that a high voltage is required to overcome it.

A new solution, the invention of two Italian electro-chemists, Messrs. Marino, father and son, and with which the present author is connected, overcomes practically all the difficulties of depositing metals and alloys on to iron and steel in a very simple way. The solution is prepared by dissolving equal parts (about 5 per cent. of total solution) of sodium boroglyceride and sodium borobenzoate in water, and adding



the required salt or salts of the metal or alloy. Sodium biborate or borax is familiar to engineers, for it is extensively used in welding, brazing, etc., because of its property of dissolving metallic oxides. It has, however, not hitherto been applied to do this in electro-plating solutions, because it unfortunately also has the property of being decomposed by metallic salts. Prepared according to Messrs. Marino's method with glycerin and benzoic acid, it is not affected by the metal salts, and retains all its power of dissolving metallic oxides. If iron has to be coated with any metal such as zinc, tin, lead, copper or alloys, this solution not only does not attack the iron, but if there is a film of oxide formed after the iron has been cleaned, the solution will remove this, so that the deposit is on to a clean metallic surface, and perfect adhesion obtained. The glycerin, besides preventing the borax being decomposed, has several valuable properties of its own. It mixes thoroughly with water in all proportions, and 100 parts of glycerin will dissolve 50 parts of borax. It prevents the formation of metal hydrates, and thus keeps the anodes in a soluble condition; it is not decomposed by an electric current of the voltage usually used in electro-plating, so that a deposit can be forced into recesses and hollows without the risk of decomposing the electrolyte; and it further gives metallic deposits that are reguline, ductile and adherent. It is evident, therefore, that this solution overcomes all the difficulties of depositing metals, particularly on to iron and steel, in a very simple and inexpensive way.

Besides the solution, the mechanical details of electro-plating have also been open to considerable improvement. For ordinary silver-plated ware, the original methods of suspending the articles by wires from the kathode rod, is still the one usually practised. But for dealing with iron articles that have to be coated with zinc, copper, brass, nickel, etc., this method is too slow and cumbersome, and various mechanical devices have been introduced to save the loss of time and money in wiring up articles. Fig. 5\* shows a very efficient revolving apparatus, introduced by Messrs. Canning & Co. for plating cycle rims. Figs. 6\* and 7\* show two designs of plating barrels by the same firm to deal with small articles, and Fig. 8 shows an American machine which claims to electro-plate, wash and dry small articles automatically. Revolving plating barrels have the advantage also, that articles are

\* These illustrations are not reproduced in this number.

polished by rolling over each other at the time they are being electro-plated. But, in the present author's opinion, both these barrels have the defect that a perforated barrel, made of some non-conducting material, is between the anode and the work or kathode. This means that the process of deposition is slow and a considerable amount of power is lost in getting the current through all the obstructions.

Figs. 9 and 10 show the construction of a plating apparatus designed by the author for zinc plating, and Figs. 11 and 12 show the general arrangements of these barrels for cleaning, plating, washing and drying. Fig. 9 shows the simplest form of the apparatus. It consists of a tee iron ring about 5 ft. in diameter, on which is formed the two cone-shaped wooden portions. One end of the wooden staves butts into the angles of the tee iron, and the other end butts into angles in a spider frame carried on the central shaft. One of these spider castings butts against a collar on the shaft and the other is set up by a nut on the shaft which thus forces the whole structure firmly together. The flange of the tee iron extends about  $\frac{1}{2}$  in. beyond the wood into the interior of the barrel, and forms the kathode connection, a brush pressing against it conveying the current from the work inside. The anodes are hung inside on the shaft which forms the conductor carrying current to the anodes. As the barrel revolves the work is carried partially round till gravity brings it back; the cone-shaped sides ensure that the articles do not merely slide back but are turned over each other, so that fresh surfaces are continually being exposed.

Fig. 10 is a modification of the first design; a parallel part between two tee iron rings allowing more work, such as bolts, etc., to be put in the barrel. In this design also the shaft is made a fixture, and the barrel allowed to rotate on it. This is to allow the anodes to be fixed in their proper positions and to permit of a non-conducting hood being fixed over them, so that, if by any chance, some of the work is carried round too far, it will not fall across the anode and cause a short circuit. Barrels made on this principle allow the current to be carried to the anode and back from the kathode with the least possible loss, since its path is as short and direct as it can be, and there is no obstruction between the anode and the work. Arranged as shown in Figs. 11 and 12, work can be handled with the minimum of labour and trouble. Starting

CALVANISING APPARATUS

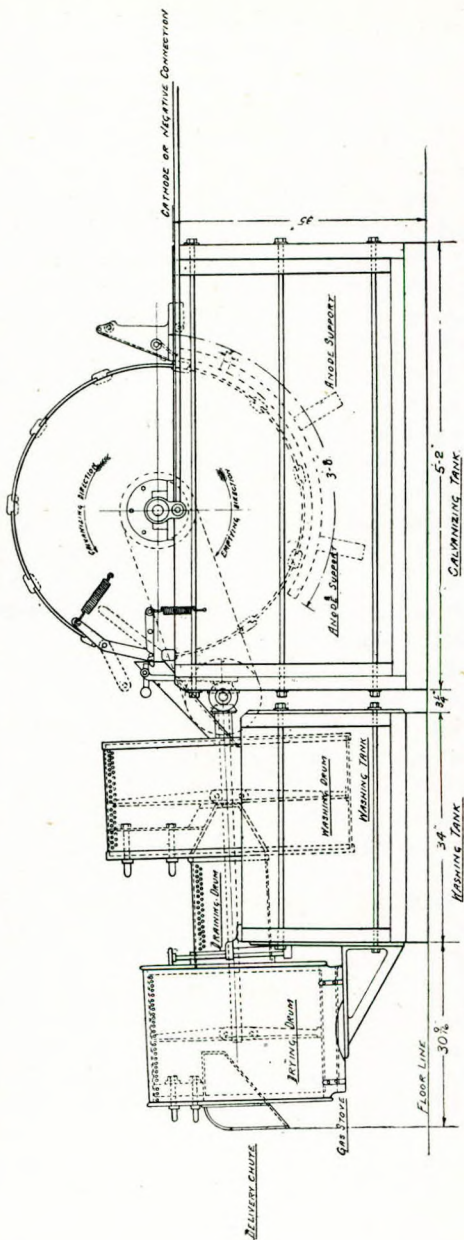
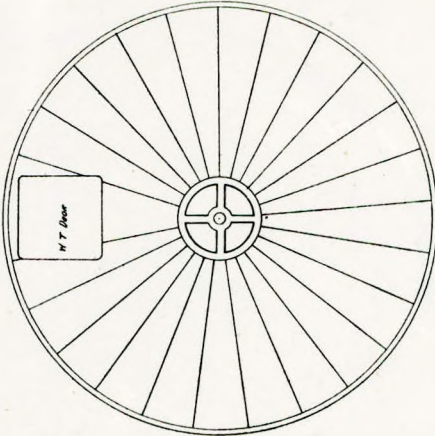


FIG. 8.



CALVANISING DRUM

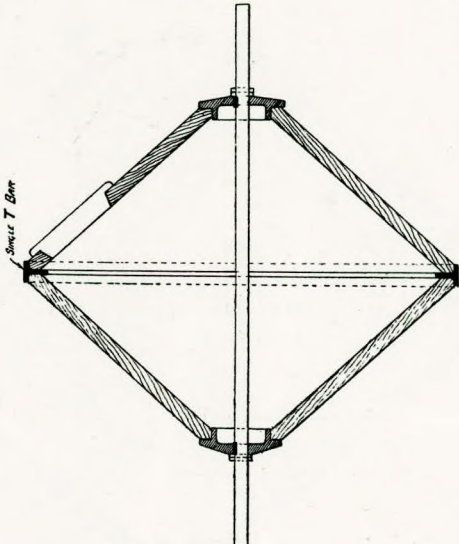


FIG. 9.

CONSTRUCTIONAL PLAN OF RUMBLER 5' DIA

SCALE 3" = 1 FOOT

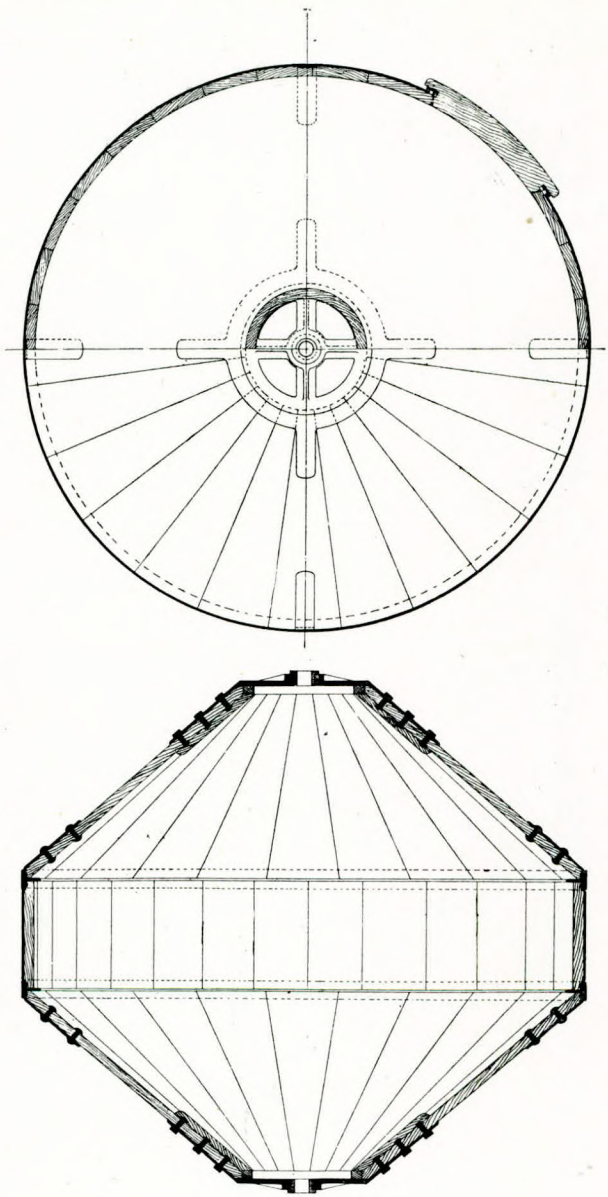


FIG. 10.

from the top platform it is put into the top barrel for cleaning. This may be done electrolytically, in a potash solution, with sand, etc., or in whatever way the class of goods require. When the cleaning is completed, the door of the barrel is opened and the work and solution allowed to slide out on to an inclined shoot. Part of this shoot is arranged to turn up and act as a stop, keeping the work on the perforated part of the shoot till all the solution drains off into the tank below. From this tank the solution is pumped up to a storage tank above, passing first through a filter which removes all scale, dirt, etc. From the storage tank the cleaning solution is led back to the top of the barrel, ready to be let in when a fresh supply of work is put in. When the work already cleaned is sufficiently drained, the hinged stop is turned down and the work allowed to slide over it to a second similar stop. In this position the work is under jets of water which thoroughly wash away all dirt and traces of the cleaning solution to the tank below. After this is finished, the second stop is turned down to guide the work into the next barrel, which is the plating barrel. When this has received the work, the door is closed and the barrel started rotating till sufficient deposit is obtained. The door is then opened and the work allowed to slide out and drain as before, then to slide down into a tank of hot water. From this an inclined elevator lifts it out, and draining it, discharges it on to a conveyor which carries it over jets of hot air. This ensures the work being thoroughly washed and quickly dried, for this is necessary if the deposit is to retain its good colour. The solution from the plating barrel is also pumped to a storage tank above and filtered. The complete arrangement enables a large variety of iron and steel goods to be easily and satisfactorily handled. The solutions being constantly filtered are always in an efficient condition. This filtering is very necessary with revolving plating barrels because pieces of metal, scale, etc., are liable to be rubbed off even after passing through the cleaning barrel. The samples of chain shown have been zinc covered in a barrel similar to those described, and the bright polished appearance is due to the polishing action of the barrel, for nothing has been done to them outside the barrel.

It is obvious that all classes of goods cannot be handled in these revolving barrels, for there is a limit to the size and weight that can be safely dealt with in them. For work that

is too heavy or too big for the barrel method, the author has designed another arrangement. This consists of vats or baths, 30 to 40 feet long, for cleaning and for plating. The baths are provided with endless chain conveyor gear which carry the work along the kathode connection between rows of anodes. The work as it moves along is made to rotate by a toothed wheel running in a rack. This rack is staggered first on one side and then on the other of the toothed wheel, so that the work rotates first in one direction and then in the other. This ensures that every part of the work will receive a proper coating. The work travels through the bath at such a rate that when it has travelled from one end to the other it has received a proper coating. This method thus ensures that all articles will receive the same amount of deposit if sent through at the same rate. The first two anodes are supplied by a separate dynamo at a higher voltage than that supplied to the rest of the anodes. The kathode or negative pole is common to both. This is to force the deposit into all recesses and hollows, and once this has been done by a slightly higher voltage, it will be maintained by the normal voltage.

The question that will be of most interest to engineers, in any system of metal depositing, will be that of cost. It is rather difficult to state this exactly, because the amount of metal deposited will depend on the area covered and the thickness of the deposit, and area does not always bear any special relation to weight in the usual class of iron or steel goods that would require coating with another metal. But for a guide we will take the case of sheet iron coated with zinc. one ampere hour deposits 1.2119 grammes of zinc. This is the theoretical amount and would hardly be reached in practice, but in the Marino solution, since there is no loss in decomposing the electrolyte, 1.2 grammes can be obtained. We will suppose, however, that only 1 gramme is deposited per amp. hr. and that we have to cover an area of 100 sq. ft. An ample coating for this would be 50 ozs. of zinc = 1417 grammes.

This would require, therefore, 1417 amp. hrs. The voltage necessary would be 2 volts. The units would be

$$\frac{1417 \times 2}{1000} = 2.834 \text{ units.}$$

Taking the generator and transmission, etc., efficiency at

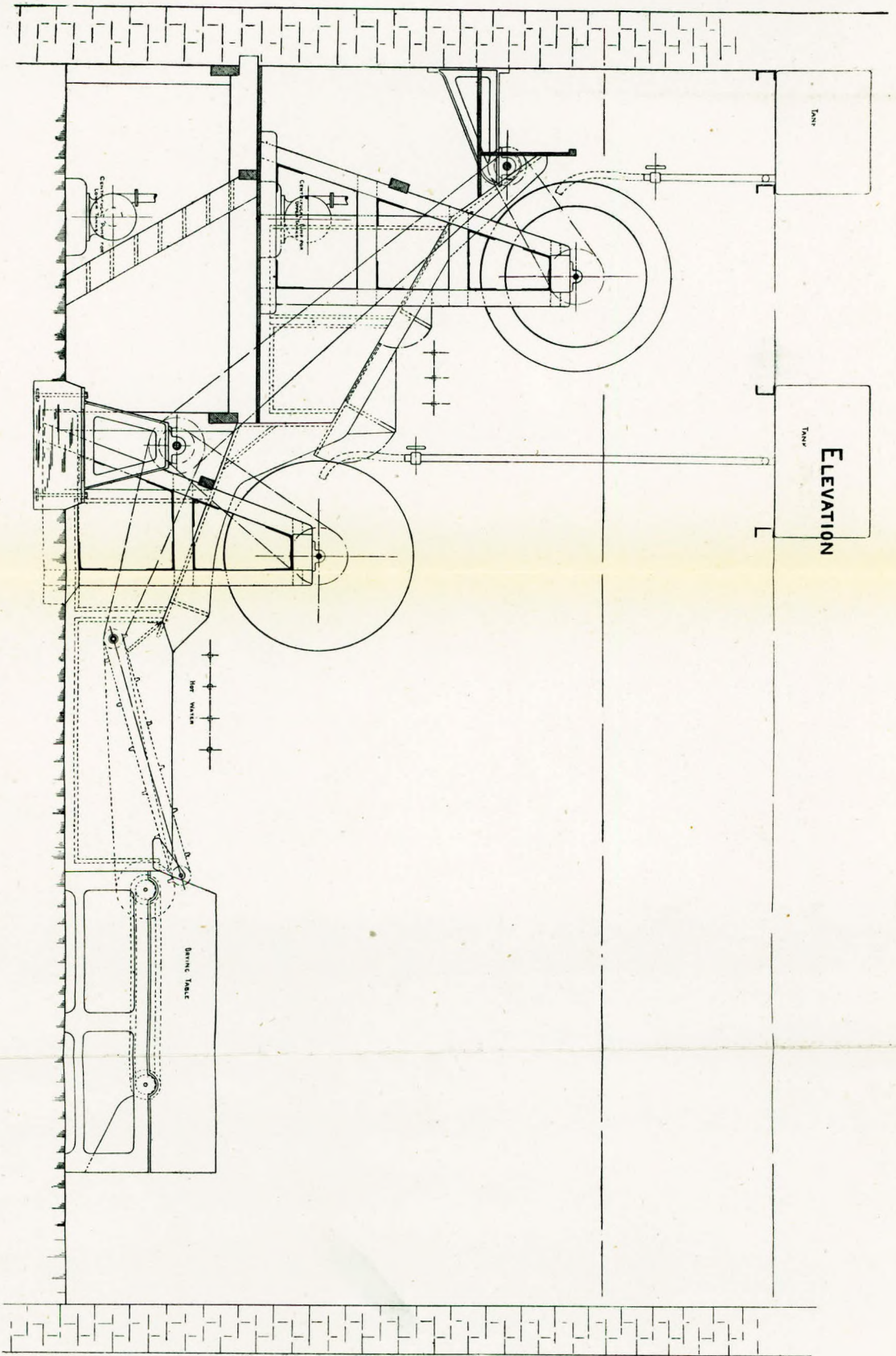


FIG. 11.





only 50 per cent., the supply units would be 5·668. Taking current at 1*d.* per unit the cost would be 5·668 pence.

Cost of Zinc, 50 ozs. at £30 a ton = 10·044 pence.

The shoots would require cleaning, and this would be very satisfactorily done by our electrolytic method. For this an area of 100 sq. ft. would require 400 amps. at 6 volts for 10 minutes

$$= \frac{400 \times 6 \times 10}{1000 \times 60} = \cdot 4 \text{ units.}$$

Again, taking 50 per cent. as the efficiency of the generator, transmission, etc., the supply units would be ·8, and at 1*d.* per unit would cost 8 pence.

Cost of zinc	=	10·044 pence
Current for depositing	=	5·668
„ for cleaning	=	·8
		16·512

With plates  $\frac{1}{16}$  in. thick a surface of 100 sq. ft. (taking both sides) would weigh about 126 lbs. Take it as 1 cwt., and plates  $\frac{1}{8}$  in. thick 2 cwts. etc. The cost of zinc coating sheet iron  $\frac{1}{16}$  in. thick would therefore be  $1/4\frac{1}{2}$  per cwt. of iron, sheet iron  $\frac{1}{8}$  in. thick  $7\frac{1}{4}d.$  per cwt.,  $\frac{1}{4}$  in. thick  $3\frac{3}{8}d.$  etc.

This is a very generous estimation because 1 ampere hour would deposit more than 1 gramme, the generator and transmission efficiency would be more than 50 per cent.; current would be generated, and in most industrial centres bought, for less than a penny per unit, 100 sq. ft. of the various thicknesses would weigh more than the 1, 2, 3, etc. cwts. taken, and lastly a coating of 50 ozs. per 100 sq. ft. is more than is necessary. Wire and sheet iron coated by the hot system and wiped would not have anything like this coating. By the electrolytic method of course any required thickness can be put on.

The figures given, of course, only include the cost of zinc and current for cleaning and depositing. To this would have to be added labour, establishment and capital charges, etc. For work that can be handled in the revolving barrels the labour charges would be small, and the cost of power for driving the barrels should not exceed a penny per cwt.

There can be no doubt, therefore, that the electro-galvanizing system is very much cheaper than the hot system. This is

not surprising, when we consider the sources of loss that are inherent to the old process, such as the loss due to burning the zinc, the loss for radiation, the loss from volatilization, and the difficulty of preventing lumps and ridges solidifying before the excess of zinc can be drained off. A most important advantage of the electro system is the fact, that, unlike the hot process, it has no detrimental effect on the material treated, so that steel springs can be coated without affecting their temper, and there is no loss of strength in steel chains, angle irons, girders, etc. Then as will be seen from the samples of bolts and nuts, the threads can be completely covered and still be usable.

Electro deposition by the Marino system is of course not limited to depositing zinc, copper, tin, lead, aluminium, brass and other alloys can also be deposited with equal facility.

Before leaving the subject of zinc coating, the writer would like to make some remarks concerning the tests to which zinc-coated iron is subjected, particularly by the Admiralty, Post Office and other Government departments. The tests consist of dipping the zinc-coated iron into a solution of Copper Sulphate for 1 minute, and then washing it in water. This is repeated four or more times, at the end of which, to pass the test, there must be no trace of copper deposited on to the iron. Now this is a test simply for the amount of zinc, and in the present writer's opinion this is not the important point. He is aware that zinc is electro-positive to iron, that is, it has a higher solution pressure, and that this is usually put forward to account for the fact that a zinc coating protects iron. But a little consideration will prove that this view is quite wrong. Every engineer knows that if iron is exposed to certain damp conditions it will corrode very rapidly, and that the iron will disappear in great flakes of rust. He also knows that if iron coated with zinc is exposed to the same conditions, there will be no sign of corrosion, at least not for a considerable time. But as zinc is electro-positive to iron it should, according to theory, disappear quicker than the unprotected iron did. Why then does it not do so? The reason is very simple. We have already seen that one of the troubles of zinc depositing was the formation of an insoluble zinc hydroxide on the zinc anode, and it is evident that this same hydroxide will be formed in a moist atmosphere. It is the presence of this insoluble hydroxide that gives zinc its value as a protective

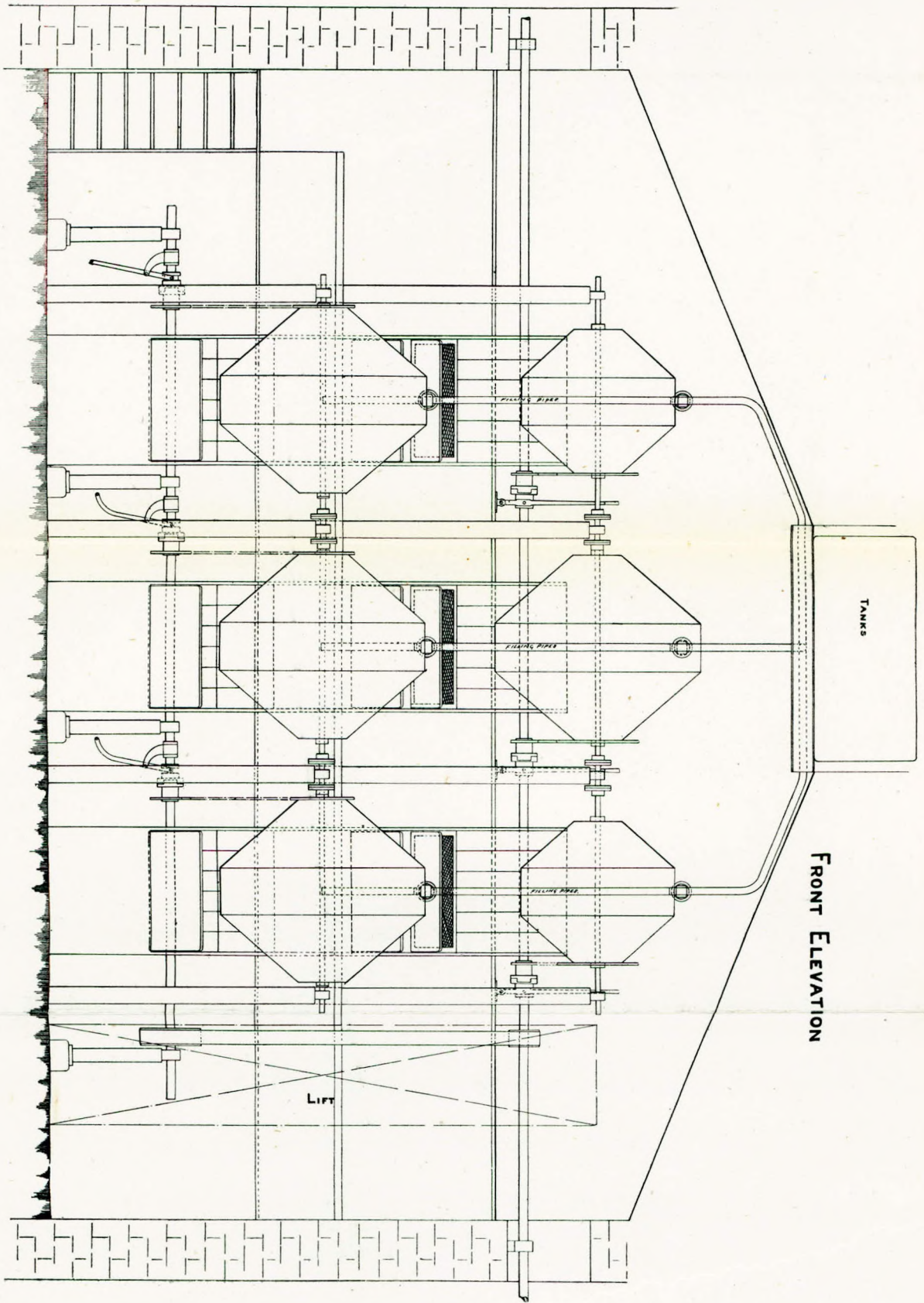


FIG. 12.



coating, and not the fact that it is electro-positive to iron. When exposed iron corrodes, the oxides even if insoluble are spongy and allow further oxidising to continue, so that unlike zinc hydroxide they afford no protection. Various writers have stated that even if a zinc coating becomes chipped and exposes the iron in places it will still prevent it corroding. But any engineer who is observant knows that if only the slightest surface of iron is exposed it will notify the fact by a spot of red rust.

If the hydroxide of zinc is the protective coating, the amount of the zinc is not of great importance so long as it completely covers the iron and is adherent, reguline and ductile. In any case the Sulphate of Copper test seems rather absurd, for the simple reason that zinc-coated iron will never be exposed to its action under the usual conditions of its use. What it probably will be exposed to is an atmosphere containing moisture,  $\text{CO}_2$  and  $\text{SO}_2$ . A sensible and legitimate test therefore would be to subject the zinc-coated article to an atmosphere containing these to an exaggerated degree, for instance, from 10 to 15 per cent. of  $\text{CO}_2$  and  $\text{SO}_2$ . As the atmosphere probably never contains more than .03 per cent. of  $\text{CO}_2$  and .3 per cent. of  $\text{SO}_2$ , an exposure of a few days to such an artificial atmosphere combined with moisture and variations of temperature would give some genuine results. As it is the Government departments specify that zinc-coated goods must pass the Sulphate of Copper test, and some goods such as the threads of bolts must be wiped to leave the threads clear and certainly cannot then pass the test genuinely. They do pass it, for there are tricks in most trades, but it is neither the zinc nor the zinc hydroxide that gets it through.

Besides the solution for dealing with plating on to iron, Messrs. Marino have also discovered solutions for many other purposes, such as depositing metals on to aluminium, depositing alloys of silver and nickel silver and cadmium, silver and tin, etc., depositing metals on to wood, etc., and on to china and glass ware. The deposition of alloys of silver which has not hitherto been possible, such as nickel and silver, is of interest to shipowners, as they are large users of plated ware. The alloy of nickel and silver besides, of course, being much cheaper, has all the appearance of silver combined with the hard wearing and non-tarnishable qualities of nickel. This paper is already probably beyond its limits, so there is no space left to

go into details of the various other processes. As, however, there are several samples here of silver and copper plated china and glass ware, the process of doing this may be briefly explained. The only acid that has any effect on china or glass is Hydrofluoric Acid H. Fl. and the chief use of this acid is for etching glass. Mr. Marino, therefore, dissolves a metal in Hydrofluoric Acid, usually by first reducing the metal salt to a carbonate, and applies this solution to the surface of china or glass required to be metallized. The solution then will begin to attack the china or glass carrying the metal in solution with it. By applying another metal with a higher solution pressure than the one in solution, either in the form of a powder or as a revolving brush, it will replace the first metal from its solution. The precipitated metal will therefore be firmly embedded in the pores of the china or glass and forms a foundation on which any other metal may be electrolytically deposited in the usual way.

