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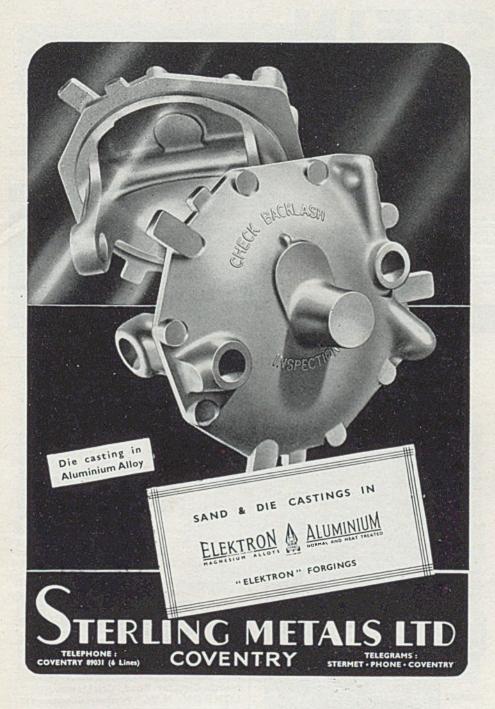
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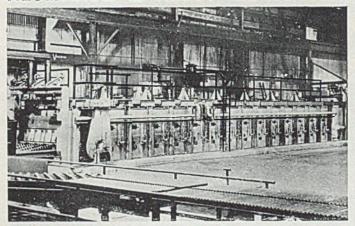
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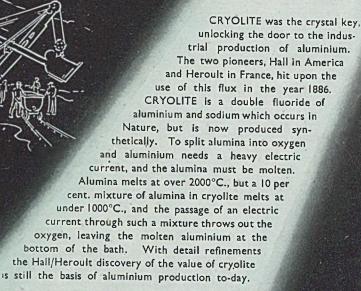
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#### EDITORIAL OPINION

#### Don't Shoot! Call The Doctor!

NLY with the greatest reticence do we add our voice to that growing volume of opinion which says "Well, thank goodness the war is nearly over." We certainly believe this statement to be true, but, at the same time, feel a little anxiety over our readiness to meet the situation which will arise when peace breaks out.

For a long time now the world has been divided into two camps—post-war planners, on the one side, and those who say "Let's wait until the show is over," on the other; it must be admitted that, lately, frequent desertions have occurred from the latter group.

The more cautious of those who realized early the need for initiating schemes of post-war reconstruction were, from the beginning, only too ready to admit that the final shaping of any plans would depend upon the result of innumerable political, economic, social and other factors which would emerge when hostilities ceased. Others, less restrained, were deceived by a mirage and saw the Golden Age already looming on the horizon. Even now, at this stage, it is still too early to make hard and fast decisions. Only one essential can be postulated. Plans for the post-war period there must be, and they must exist in a presentable, workable form within the space of the next 12 months.

It is inevitable that many of the schemes about which we have heard so much will prove impracticable, but it is vital that all internecine quarrels be eliminated: times are too critical to mock the unsuccessful enthusiast with a cry "Physician heal thyself"; rather the doctor must be called in, schemes recast, plans readjusted and purged to meet conditions as they will be, and not as it was hoped they might have been.

The difficulties which face us all are alarming in their number and immensity. Argument, friendly or acrimonious, is waged over details, and the onlooker may be tempted all too readily to draw false conclusions from the picture as he sees it presented in the popular Press, or hears it stated from the public platform. We might cite, as an example, the somewhat undignified bickering which has broken out over world monetary plans for the New Age. Partisans have arranged

themselves round this or that centre of dissent, and quite a false appearance of incoherence has been created. Once again we hear whispered the possible outbreak of a "war of the metals." (The title of an alarming report presented by "Fortune" in 1939.)

Raw-material competition we must expect, for only by this means can real progress be assured; but we believe that this will be friendly competition based on the respective merits of the materials concerned, and not the sinister political gambling which certain nervous subjects have been led to fear. For, in the long run, the ultimate destiny of all the new materials—metals and non-metals—which have come into current use to a greater or lesser extent during the past 25 years will be this: the bag will be shaken down and the contents sieved and sorted, the final position being such that each will stand complementary to the other. Such has been the course of evolution from the Stone Age upwards. If the Eskimo still uses bone needles for sewing his skins, it is only because, in the Arctic, the "little shop round the corner" is a long way off and may not sell steel ones, anyway.

The force of this elementary argument seems to have escaped many, some of whom would have us believe that the years to come will see the dawn of an "All-Plastic" Age; others, well meaning but equally misguided, talk in terms of an "All-Aluminium" Age. Whilst from the viewpoint of purely personal interest the consummation of this latter dream would be desirable, we know that it cannot be so.

Each group of interests will, quite rightly, strive to push to the forefront its own particular creation, and, by publicity of all types, make certain that the vast consumer field is fully appreciative of its merits; but balance is required and past experience teaches us that to some projects we must regretfully say "no," even though, in so doing, we lose the opportunity of selling a few more thousand tons of light metal or a few more square miles of polyvinyl-chloride sheet.

Perhaps, because of this, it is vital, in the formulation of our own particular post-war plans, that we are fully aware from the beginning of our precise stand. This can be achieved only by taking full advantage of every possible opportunity for corporate and individual research. Positive data we know we must have to meet the flood of inquiries which will come in; negative data, even if we do not broadcast it, should be filed to prevent others making mistakes which we ourselves must not commit again.

Aluminium and magnesium have won their places in the engineering world not solely on account of sales talk, but, fundamentally, because they have fulfilled physical needs. Light-metal forgings and castings, rivals though they may have appeared in the past, have each attained their own level in response to definite mechanical and economic demands.

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# Chemical Protection of MAGNESIUM ALLOYS

Summary, with Commentary, of Some Recent Patents Embodying Comprehensive Detail Regarding Fundamental Theory of Chromate Processes and Their Commercial Application

F the numerous chemical methods developed for the protection of magnesium and its alloys, those using chromate solutions have proved outstandingly successful. A range of such treatments exists, varying with respect to solution composition and time and temperature of treatment. They are employed for giving protection to wrought alloys in the form of sheet, rod, etc., as well as to castings during storage, during fabrication processes and for protection under service conditions. In addition they are used as preparatory treatments prior to painting or enamelling. All these processes need careful control in operation in order that the best results may be obtained. Such control is applied by periodic analysis of solutions, by pH measurements and by stipulating the amount of work that can be treated before fresh additions become necessary. However, the function of each bath ingredient specified, and variation in effectiveness with the use of a solution over a period of time are not always fully appreciated.

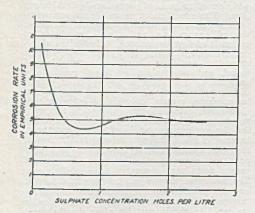


Fig. 1.—Curve showing relationship between sulphate content of treatment bath and the corrosion rate of treated alloy.

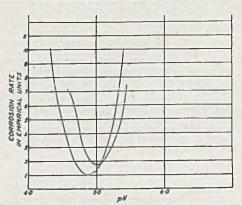


Fig. 2.—Curve showing relationship between pH of bath and corrosion rate of treated alloy.

The Magnesium Metal Corpn., Ltd., has recently completed British patents 558983 (1944), and 559071 (1944), which are, in effect, treatises on the subject of chromate protection, giving much detail on the influence of the chromate itself, metallic salt and other additions, pH control and the influence of the factors of time and temperature.

B.P. 558883 relates to the surface treatment of magnesium-base alloys, especially those referred to in D.T.D. specifications, but also others outside this range. The functions of the treatment are, first, to give protection to the metal during transit and storage, whether in the form of castings, sheet, extrusions, or forgings; secondly, to serve as a base for paint, etc., giving superior adhesion and enhanced protective powers to the applied film

protective powers to the applied film.

The use of dichromates and of chromates to inhibit the corrosion of magnesium has long been known. The protection afforded is due to the formation of a protective film by reaction on the surface of the metal. Simple dichromate solutions do not have much practical value because rate and extent of film formation are severely limited. Consequently, a number of processes have been devised (many of them patented), whereby the film can be built up and given the necessary qualities to yield the protective powers desired.

A treatment that combines all the desired attributes would embrace the following:-

(a) Minimum dimensional change should occur so that articles machined to close tolerances can be treated without harm.

(b) Raw materials employed must be inexpensive and, due precautions being taken, relatively harmless to operators. Rate of consumption must be reasonably low, and bath stability should be high.

(c) Time of treatment must be as short as possible, for example, preferably not more than a few minutes.

(d) Treatment should, ideally, be capable of operation at ordinary shop temperature.

(e) The process must be easy to operate mechanically and the solutions must be stable and readily maintained.

The present patent claims to differ from all that have hitherto appeared, in so far as it closely fulfils this schedule. It surveys, furthermore, existing patents that cover one or more of these points. Thus: B.P. 287450 describes the use of an acid, such as nitric acid, added to the solution with the object of increasing rate of film formation. This patent states that hydrochloric or sulphuric acids must not be used, whereas the present patent finds sulphuric acid to be eminently suitable. The objection found with the nitric-acid type of solution is that it is operated at high acidity, which makes it unpleasant in use and causes marked dimen-

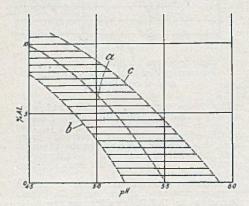


Fig. 3.—Curves showing relationship between aluminium content of alloys treated and pH (optimum, minimum and maximum) of chromate solution for satisfactory treatment.

sional loss in the work. Again, due to the extent of reaction, the solution rapidly becomes exhausted.

These objections are overcome by **B.P.** 305197 which omits the acid addition, but requires the solution to be used boiling; this is a disadvantage, not offset by any decrease in treatment time, which, in actual fact, is stated to be one hour or longer.

B.P. 331853 used a heated solution at 95-100 degrees C., the solution being neutral or acid, and containing an alkali metal dichromate together with an aluminium salt or compound such as potash alum; the function of this aluminium salt is not specified. The process requires long treatment time (1-10 hours) and it entails careful attention, to ensure that losses by evaporation are made up.

B.P. 353415 uses an aqueous solution containing a chromate or dichromate which may be of an alkali metal, of an alkaline earth metal or

of ammonia or of one of the substituted derivatives of ammonia which are stable in hot aqueous chromate or dichromate solutions. The solution also contains salts of one or more of such metals or bases without the use of compounds of magnesium or of aluminium or of salts of the heavy metals. Again, the function of the salts is not stated. Sodium sulphate is given as an example. Disadvantages to this process are as follow:— The specification calls for pH value to be maintained between 3 and 5, hence frequent small additions of acid are required; in the range of pH 5 to 7, where these additions are unnecessary, the solution is less effective. Again, it is a hot solution requiring lengthy treatment time. In the present specification, short treatment time, and ease of operation in the most effective pH range are secured. For this purpose a sulphate chosen from the group comprising those of which the cation remains stable at the concentrations and pH ranges employed is added. The quoting of a minimum concentration, and a critical choice of the remaining constituents comprising the dichromate, a buffer acid and a salt mixture to control the pH in the effective range, are also features of the present patent.

B.P. 450589 uses a cold solution of dichromate

B.P. 450589 uses a cold solution of dichromate and magnesium sulphate. An objection to it is that the work must be racked out of electrical contact with the suspension and a long treatment time of one to two hours is necessary.

B.P. 506836 describes a dichromate solution containing chromic sulphate and is preferably used at boiling point. The present patentees state that such solutions are unsuitable as hydrogen ion concentration changes rapidly and

that they tend to sludge.

B.P. 510353 covers a process with or without the application of electric current, using a cold aqueous solution containing chromic-acid ions and ions of one or more activating salts. Constituents are chosen and proportions arranged so that with additions of acid or alkali the pH range required for producing the desired film in the cold is achieved in a maximum of two hours. The solution is such that its pH value is not changed by more than two by the addition of 12 gms. of potassium hydroxide per litre. The specification reveals that activating salts are used to provide a buffering effect over the pH range 3-5 and that the choice of cation is of first importance. Aluminium alums or aluminium salts are preferred, whereas chromium and iron alums are unsuitable and nickel and magnesium sulphates particularly unsuitable. The anion of the activator salts is of less importance and it is stated that it may be sulphate, nitrate, chloride or other salt of aluminium, although the chloride is not very satisfactory. In contrast with this, the anion for the present patent is of first importance, because it has a different role to fulfil. Again, the same patent claims the use of potassium or other permanganate, whereas the present patent finds permanganates to be deleterious. The treatment time is half an hour in the cold, but the solution cannot be heated to shorten this period, otherwise the speed of reaction is too rapid to obtain coatings of good adherence. Contrasted with this, the present patent can yield satisfactory coatings in less than 10 minutes in the cold.

B.P. 482689 and 510487 describe treatment of magnesium alloys by immersion in a heated solution of alkali dichromate and chromium sulphate sulphate, or nickelammonium sulphate, plus an acidifying agent which may be acetic acid or ammonium acetate. The first of these specifications states that, at 35-50 degrees C. three-quarters of an hour's immersion is necessary, whereas at 90-100 degrees C. five minutes is required. At the same time the bath is less stable at the higher temperatures. A further objection to the process is the use of heavy metal salts, as there is always a tendency to produce in the coating heavy metal deposits which may give rise to corrosion. In contrast with this, the present patent gives good commercial protection in a short time at room temperature, even in one to three minutes in certain circumstances. Again, when higher temperatures are required for speeding-up the process, as, for instance, to fit in with other operations, the bath is still stable. Heavy metal salts are definitely avoided because they either form heavy metal deposits in the coating, or precipitated or colloidal matter with spontaneous change in pH. Double decomposition between the bath constituents may also occur.

The object of the present patent is to provide an improved process for the protection of magnesium-base alloys using the dichromate method, incorporating short time treatment at room temperature, avoidance of strongly acid baths and the use of economic, stable solutions. To this end, particular ingredients and concentrations are employed which constitute an essential and new combination with respect to the following factors:-Dichromate concentration, sulphate concentration, hydrogen ion concentration and the use of a buffer agent, the cations of all salts being chosen to meet particular requirements as follow:--1.--Within the specified pH range, cations shall be stable in aqueous solutions and not undergo changes of their own account. 2.—The cations shall be stable in the presence of dichromate ions. 3.— The cations shall not react with other constituents in such a manner as to prevent the attainment or maintenance of the sulphate and dichromate ion concentrations specified. 4 .-The cations shall not react with magnesium, or form other metal deposits on the surface of the magnesium.

The essential requirements of the claim are:-(a) Dichromate ion concentrations not less than 0.05 molar and preferably between 0.2 and 0.5 molar. This region is the optimum when the other factors are also at their optima. venient sources of dichromate ions to ensure that the cation simultaneously introduced shall satisfy all the foregoing requirements, are the dichromates of hydrogen, lithium, sodium, magnesium, potassium or ammonium. may be used singly or in combination. Sulphate ions in concentration in less than 0.2 molar and preferably between 0.6 and 1.0 molar. The most convenient sources of sulphate ion are the sulphates of hydrogen, lithium, sodium, magnesium, potassium or ammonium, singly or in combination. Sulphates of aluminium, nickel, chromium and the alums of nickel, ammonium, sulphate are not suitable. When a piece of magnesium is immersed in a dichromate solution the magnesium reacts with the

dichromate and the reaction products form a film on the surface which inhibits further attack, but is too thin to be of practical value when the solution is withdrawn. The film is highly porous and film formation would proceed further if magnesium cations could diffuse outwards through the pores. They can only do this if the corresponding anions can diffuse into the pores to permit further dissolution of magnesium and continued film formation by reaction with the dichromate. For satisfactory film formation it appears that there must be a balance between inward diffusion of anions and the rate at which the protective reaction products can be formed. The rate of diffusion of anions into the pores depends on their size and charge and sulphate ones are claimed to be the only suitable ones in this respect. Chloride ions are too small, diffuse too quickly and cause pitting. The same is true to a lesser extent of

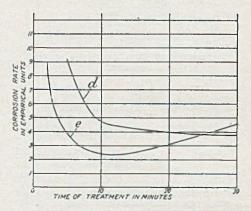


Fig. 4.—Curves showing relationship between duration of treatment and subsequent corrosion rate of the treated alloy.

bromide ions, and, whilst iodide ions might be satisfactory, they are unsuitable because they are oxidized by the dichromate. Nitrate ions are about the same size as sulphate ions, but have only a single charge. Nitrate ions would be oxidized. All other ions are too large or form insoluble reaction products with magnesium which clog the pores and stop further film formation. Not only is sulphate essential, but its concentration is important. Fig. 1 graphically shows the relationship between sulphate concentration in moles per litre and corrosion rate in empirical units employing uniform treatment times. There is an optimum concentration of 0.26 to 1.0 molar. There is little loss in protection with higher concentrations, but below this region concentration is critical and protection rapidly falls so that less than 0.2 molar is of no practical value. (c) Ammonium ions improve the protective value of the film for any given time of treatment. The concentration is sufficient if the ammonium salt be used for one of the other ingredients (a) or (b). (d) The rate of film formation increases with increase in acidity of the solu-

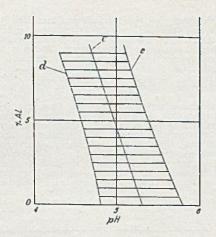


Fig. 5.—Curves showing optimum, minimum and maximum pH values of bath for magnesium-base alloys of varying aluminium content.

tion. At the same time the weight of metal dissolved from the work piece increases and, therefore, dimensional tolerances limit the per-missible increase in acidity. The protective value is also affected if acidity falls outside certain limiting ranges for each type of solution. The effect of pH variation upon protection for two particular alloys using solutions covered by this invention is shown in Fig. 2. There are marked indications of an optimum pH value for each alloy. Generally speaking, the optimum depends upon the aluminium content of the alloy as shown in Fig. 3, which gives the relation between hydrogen ion concentration and percentage of aluminium in alloys treated with certain solutions of this invention. The degree of protection falls off rapidly on either side of the optimum values for each alloy, but all values fall within the extreme pH range of 4-6. The pH values quoted were determined by the glass electrode method; other methods of pH measurement may be used, but allowance must be made for variations from the glass electrode values. (e) Buffer agents. The maintenance of pH value at the optimum, or within the permissible range for a given alloy, is complicated by the fact that the pH rises as magnesium dissolves during treatment. controlled additions of acid are necessary, but can be greatly reduced by incorporating in the solution a weak acid and one of its salts capable of buffering the solution within the desired pH range. Acetic acid is the best and cheapest organic acid for the buffer mixture, together with its sodium or ammonium salt. Any of the other bases listed before under (b) may be used for this salt. Again, other weak acids of suitable dissociation constant and salts of them if of sufficient solubility may be used in place of, or in addition to, the acetic acid and acetate. The buffer acid must not form an insoluble salt with magnesium and must not be oxidized by the dichromate ingredients. The following somewhat diverse group of acids, it is claimed, is capable of meeting these requirements:—

Propionic.	Malonic.
Butyric.	Succinic.
Valeric.	Glutaric.
Pimelic,	Adipic.
Phthalic	

The bath capacity is roughly proportional to the concentration of the weak acid and its salt. Periodic major changes to pH can be secured by additions of the major acid or alkali, namely, sulphuric, chromic or nitric acids, ammonia, caustic soda or other alkali from the above list. The acids and their salts preferred for cold solutions are single or mixed acids and single or mixed salts of those acids of the acid group just mentioned, the cations of the salt being those of lithium, sodium, magnesium, potassium or ammonium. For hot solutions the single or mixed acids and salts are chosen so that the buffer agent is sufficiently soluble at the operating temperature, and the following list is given of suitable ones, the salts being of the same basis as before:—

Oenanthic.	Suberic.
Malonic.	Pimelic.
Succinic.	Benzoic.
Glutaric.	Phthalic.
Adinic.	

When it is desired to secure maximum possible protection, sulphate ion concentration should not exceed the optimum region indicated before under (b) and in such cases the major pH adjustment should be made using the chromic or nitric acid additions. All salts employed for introducing the dichromate and sulphate anions, the salt of the buffer acid and the base for pH adjustment must be chosen so that their cations meet the following requirements:—

1.—Within the pH range 4-6 they shall remain in stable solution in the presence of dichromate ions, sulphate ions and the buffer acid. Cations which do not satisfy this require-

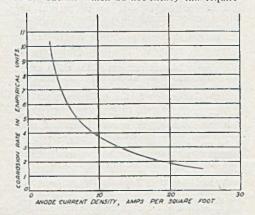


Fig. 6.—Curve showing relationship between anode current density in electro-chromate treatment, and subsequent corrosion rate of the treated alloy.

ment cause loss of dichromate, the formation of precipitated or colloidal matter or change in pH with time. This renders the process impossible or difficult in operation. To test the suitability of any given type of cation, a sulphate or dichromate containing this type is used in compounding the solution; such solution must be easily filterable through a filter paper without any appreciable residue and on standing must not show a change in pH.

2.—When magnesium-alloy work is treated, the cations shall remain in the solution and shall not form metallic or undesirable deposits on the surface of the work which would reduce the protective value of the film. This can be determined by a simple corrosion test noted

below.

The cations of hydrogen, lithium, etc., already mentioned, satisfy the requirement and are eminently suitable for the solutions covered by the patent. Examples of other cations which satisfy the requirements are tetra methyl ammonium ions, tetra-ethyl-ammonium ions and n methyl-pyridinium ions.

Treatment time to obtain best results for any particular alloy depends upon the composition of that alloy. Generally speaking, time of treatment must be increased as the aluminium content of the alloy increases. In some cases there is an optimum region for the time of treatment as shown by the shape of curve e. in Fig. 4. This curve applies to an alloy of the following composition:—

ie ionowing con	DOSE	HUII."				
				Pe	r cent.	
Aluminium					7.5	
Zinc					0.4	
Manganese					0.2	
Curve d applie	s to	an :	alloy		ining:—	
Aluminium						
CO.		113				
Manganese				1	0.2	
The maximum	curv	ature	on	curve	d corr	e

sponds to approximately nine minutes. curve e the maximum is approximately seven minutes. It is noted, however, that with the alloy d an increase time of treatment up to 30 minutes is not detrimental, whereas with curve e an increased time, other things being equal, reduces the degree of protection, i.e., it increases the corrosion rate in respect of the effect obtained by treatment at a lower time corresponding to the knee of the curve.

In general, the optimum value for any of the variables can be determined by accelerated corrosion tests representative of the particular service conditions to which the article is going to be subjected. Salt-water immersion or spray is commonly recognized as simulating marine-atmospheric exposure, and it is on this basis that the data given in the patent specifications have been based. Variations in the ionic concentrations do not cause sudden changes in the effectiveness of the solution, and it is possible, therefore, to select working limits having regard to the degree of protection required. Drag-out losses are always minimized by using the lower concentrations in any range and by allowing a few seconds draining time after treatment before removing the work from above the vat. Dichromate concentration tends to fall with use, and additions must be controlled by analysis. Sulphate concentrations may rise if this acid

is used in preference to chromate or nitric for major adjustment of pH value.

An advantage arising from the fact that good protection is obtained by a short period treatment in the cold is that the treatment may be applied as a simple swabbing process when it is necessary to finish parts that are already assembled.

Cut edges of sheet, welds, repairs and even maintenance are given as examples in this respect. On the other hand, if the same solutions be heated, the time of treatment may be further reduced and in some applications this

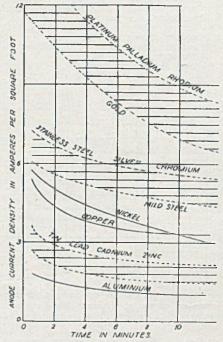


Fig. 7.—Current-time curves for various cathode materials.

than offset the disadvantages тоге involved by the heating. The solutions are stable on heating with the possible precaution to avoid evaporation loss or volatile acid, such as acctic, in which case this acid can be substi-tuted in part, or solely, by one of the less volatile acids already stated to be suitable for

In all cases pre-cleaning is desirable. Solvent degreasing is advocated and this can be fol-lowed, if necessary, by one of the standard methods for cleaning magnesium, except that sand and shot blasting or the use of hydro-fluoric acid dips should be avoided, because they reduce the protective value of the treatment. A quick pickle in cold dilute acid such as nitric or sulphuric or a mixture of the two is satisfactory, except, again, if dimensional loss has to be minimized, then either chromic acid or alkaline cleaner can be used. It is recommended, in the latter case, that the treatment time should be extended. Another treatment is anodic polishing in accordance with British Patent Nos. 550175 and 550176. Specific

examples are then given as follow:—
For magnesium alloys substantially free from aluminium and containing up to 2.5 per cent. manganese. For example, D.T.D. 118, 140A and 142, three minutes' immersion at room temperature in the following solution gives a high degree of protection:-

Ammonium, sodium or potassium dichromate, singly OI mixed

50-100 parts by wt.

Ammonium sulphate (or, if desired, the equivalent amount of sodium sulphate if the ammonium salt is used for one of the other constituents) . .

80-120

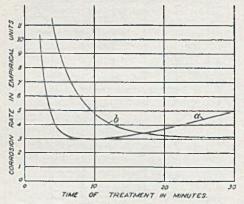


Fig. 8.—Curves showing relationship between duration of electro-chromate treatment and subsequent corrosion rate of the treated alloy.

Acetic acid 10 parts by wt. Hydrated sodium acetate (or the equivalent amount of ammonium acetate. particularly if the ammonium salt be not used for the other constituents) ... 25 Water to make up to 1000

With this solution the pH value must be adjusted; for example, with ammonia to 5.2-5.9, preferably 5.5. The resultant film examined after washing is greenish or gold brown, thoroughly adherent, protective in itself and providing an excellent basis for paint coating. Good protection is also given by this solution with the treatment time reduced to one minute or, alternatively, with the three-minute time and concentrations reduced by as much as 50 per cent.

For alloys containing aluminium, for example, D.T.D. 59A, 88B, 136A, 120A, 281, 285, 289, 325, 348 and 350, a high degree of

protection is obtained from this solution with an immersion time of eight to 12 minutes, but with the pH value adjusted in accordance with Fig. 3 to suit the aluminium content. In this figure the curve a represents the pH values for maximum protection and the curves b and c give the working range for good protection. For example, for an alloy containing aluminium 6.0 per cent., zinc 1.0 per cent. and manganese 0.2 per cent., the pH range should be 4.8-5.3 and preferably 5.0-5.1. For an alloy containing aluminium 7.5 per cent., zinc 0.4 per cent. and manganese 0.2 per cent., the pH range should be adjusted to 4.6-5.2 and preferably 4.8-4.9. The resultant film is an adherent black protective film, also providing an excellent basis for paint. Here, again, for a good degree of protection the treatment time may be reduced by five to eight minutes or the concentrations down to 50 per cent. with the eight to 12-minute time.

The recommended range of ingredients is as

follows:

Dichromate (Cr2O1) over 0.05 molar (up

to saturation point).

Sulphate (SO4) over 0.2 molar. (In cases where the dichromate concentration is increased, the sulphate concentration should preferably follow suit up to saturation point.)

Buffer mixture, e.g., acetic acid and sodium acetate, total acetate concentration as acetic acid plus sodium acetate together,

over o.1 molar CH,COO-

When other weak acids and their salts are used as buffer mixtures, these concentrations must be altered having regard to the equivalent weight of the acid relative to that of acetic acid.

pH 4-6 depending on alloy composition

and time of treatment.

Time of treatment: This depends on the composition of the alloy, the solution composition and its pH, and varies between 0.5-30 minutes.

Where the degree of protection is that corresponding to temporary protection of parts during fabrication, storage or transit, the follow-

ing formulations are suggested:-

Dichromate (Cr.O.) over o.1 molar (up

to saturation point).

Sulphate (SO4) over 0.3 molar. (In cases where the dichromate concentration is increased, the sulphate concentration should preferably follow suit up to saturation point.)

Buffer mixture, e.g., acetic acid and sodium acetate, total acetate concentration as acetic acid plus sodium acetate together,

over o.r molar CH<sub>3</sub>COO—, When other weak acids and their salts are used as buffer mixtures, these concentrations must be altered having regard to the equivalent weight of the acid relative to that of acetic acid.

pH 4-6 depending on alloy composition

and time of treatment.

Time of treatment varies between 0.5 and 30 minutes as in the previous example.

For parts requiring a good average degree of protection, the formulations recommended are:-Dichromate (Cr2O1) o.1 to o.6 molar.

Sulphate (SO,) 0.4 to 2.0 molar.

Buffer mixture, e.g., acetic acid and sodium acetate, total acetate concentration as acetic acid plus sodium acetate together, from 0.2 molar CH<sub>3</sub>COO—to 1.0 molar CH.COO—.

When other weak acids and their salts are used as buffer mixtures, these concentrations must be altered having regard to the equivalent weight of the acid relative to that of acetic acid.

pH 4-6 depending on the alloy composition and time of treatment.

Time of treatment varies between 0.5 and 30 minutes.

Optimum composition for protective values

of the highest order is given by:—
Dichromate (Cr<sub>2</sub>O<sub>7</sub>) 0.2 to 0.5 molar.
Sulphate (SO<sub>4</sub>) 0.6 to 1 molar.

Buffer mixture, e.g., acetic acid and sodium acetate, total acetate concentration as acetic acid plus sodium acetate together, 0.2 to 1.0 molar CH<sub>3</sub>COO—. When other weak acids and their salts are used as buffer mixtures, these concentrations must be altered having regard to the equivalent weight of the acid relative to that of acetic acid.

Ammonium ions (NH<sub>1</sub>), 0.4 to 3 molar. pH 4.6-5.9 depending on the alloy composition and time of treatment.

Time of treatment: 1-30 minutes depending

on the alloy composition.

Major pH adjustments in this case should preferably be made by nitric, not sulphuric, acid, to maintain the sulphate ion concentration at the optimum.

An earlier type of solution which may be employed, which is not now considered as good as the solutions given in the previous paragraphs, comprise:—

Sodium dichromate	Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> .2H <sub>2</sub> O	By weight 100 parts
Ammonium dichromate	(NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	100 parts
Ammonium sulphate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	100 parts
Sodium acetate	CH <sub>3</sub> ,COO N <sub>a</sub> ,3H <sub>2</sub> O	50 parts
Acetic acid	СН3.СООН	20 parts
Water to	_	1,000 parts

This solution is used at room temperature and under such conditions forms a protective coating on magnesium and magnesium base alloy surfaces in a time not exceeding ro minutes. For example, on a magnesium-base alloy conforming to D.T.D. Specification 118, a protective coating is formed in from one to two minutes. The composition may need to be adjusted slightly to suit particular alloy compositions. As the solution is not strongly acid, no special care need be taken with regard to containers and manipulation.

The effect of increased temperature may be profited by to shorten treatment time. A magnesium alloy containing 7.5 per cent. Al, o.4 per cent. Zn and o.2 per cent. Mn is given a cleaning pre-treatment as described and treated for 10 minutes in the optimum solution (containing adipic acid and sodium adipate and of

pH 4.85 (measured in the cold by glass electrode) heated to 60-80 degrees C. After washing, the specimen is found to be coated with a black adherent film. When tested by a saline test in known manner, the protective value of this film is found to be of the order of twice that obtained by treatment at room temperature under the optimum conditions; instead of taking the benefit of the heat by increased protection for the same time of treatment, it may be taken by similar protection for a shorter time of treatment.

British Patent 559071 (1943) relates to the electrolytic protective surface treatment of magnesium-base alloys. It refers to B.P. 558983 and states that the same degree of protection can be obtained with reduced time by subjecting the work to an electrolytic treatment in solutions containing the same constituents as those stated for the chemical treatment, but at a slightly different concentration range of sulphate.

Alternatively, a higher degree of protection is claimed by applying the electrolytic treatment for the same treatment time. The patent points out that several electrolytic treatments have been proposed, but none of them satisfy all the Thus, essentials previously set out. Thus, B.P. 498626 describes an anodic treatment for magnesium and its alloys. This consists in making the work the anode in the solution containing one or more oxidizing agents or ions from the water soluble compounds of the group consisting of chromates, dichromates, oxalic acid, acetic acid, nitrates, permanganates and chlorides in the presence of one or more water soluble salts having an ion of the group consisting of sulphates, fluorides, phosphates, borates and molybdates, the pH of the solution being maintained on the acid side. The pH of the solution is preferably between 2 and 5, temperature from 20-80 degrees C, and current from 1-100 amps./sq. ft. Treatment time depends upon the strength of the solution, the current density and the thickness of film required. example, is given 45-60 mins. at 5-10 amps./sq. ft. at 50 degrees C.

The discovery upon which the patent is based is stated to be the presence of oxidizing ions in the solution that will enter the film formed on the magnesium. There appears to be some doubt here concerning the ability of some of the compounds mentioned to behave as oxidizing agents. The present patent claims the essential combination to be dichromate plus sulphate plus acetic acid or some other buffering agent.

B.P. 510353 covers treatment with, or without, the aid of electric current in cold water solution of chromic acid ions and ions on one or more activator salts. The solution has a hydrogen ion concentration curve which remains for a considerable variation of added acid or alkali, this pH range being that required for producing a protective adherent film in the cold for a period not exceeding 2 hrs. The pH value is such that it does not change by more than 2 by the addition of 12 grams of potassium hydroxide per litre of solution. The activator salt is intended to provide buffering effect from pH 3-5 and the choice of cation is stated to be of primary importance. Aluminium alums or other aluminium salts are preferred, but chromium and iron alums are unsuitable and nickel and magnesium sulphates are even more

unsuitable. It is to be noted that magnesium sulphate is a suitable addition for a different

purpose in the present patent.

Again, in B.P. 510353 the anion of the activator salt is stated to be of secondary importance and it may be sulphate, nitrate, chloride or other salt of aluminium, but the chloride is said to be not very satisfactory. The anion in the present patent is of greatest importance. Potassium or other permanganate is claimed, but for the present patent is deleterious,

B.P. 515648 covers immersion of the work in an electrolyte, in which is also immersed a metal more electropositive than magnesium and which remains substantially unattacked by the electrolyte and connecting this metal with the workpiece by means of a conductor out of contact with the electrolyte. Preferably the electrolyte is a solution of alkali-metal chromate or dichromate containing 5-12 per cent. and preferably 10 per cent. of chromate or dichromate and 0.05 per cent.-0.5 per cent. of alkali metal and 0.05 per cent.-0.5 per cent. Of alkan metan bisulphate when dichromate is the base and 5-15 per cent. of this addition when chromate is the base; pH is adjusted to 3.8-3.9 for the dichromate solutions and 4.5-6.0 for the chromate solutions. No buffer agent is mentioned.

The present patent, B.P. 559071, resembles B.P. 558983, except for the electrolytic feature and sulphate-ion concentration. The range covered for this item is not less than 0.5 molar and preferably between 1.0 and 1.5 molar. The optimum pH value for particular aluminium contents is shown in Fig. 5. Fig. 6 shows the relationship between anode current density and corrosion rate. Fig. 7 shows the effect of time of treatment with reference to anode current density with respect to a number of metals. Fig. 8 gives the relationship of time of treatment against the rate of corrosion from the aspect of illustrating optimum conditions.

The magnesium-alloy workpiece is immersed in the solution and made the anode. The cathode consists of a metal from the hydrogen side of magnesium in the "standard electrode

potential series."

The degree of protection has been found to depend on the magnitude of the current passing from anode to cathode as indicated in Fig. 6. This curve shows that when the current is increased beyond that corresponding to the knee of the curve, there is not much improvement in protection. In general, this corresponds to about 10-20 amps./sq. ft. of work surface. With higher current densities there is a danger of films becoming powdery instead of adherent. The higher current densities have to be obtained with external current, but the lower ones are produced by merely connecting the work to the cathode. With increased anode current density there is a tendency for dichromate to be reduced at the cathode and the reduction compounds to form a sludge. resulting loss of dichromate causes a drop in current efficiency. This tendency depends on the material used for the cathode and it becomes less in the order aluminium, lead, nickel, chromium, iron, stainless steel, silver, gold, palladium, platinum and rhodium. Cathodes of stainless steel, silver or chromium are preferred, or, better still, gold, palladium, platinum or rhodium. They can be used in the form of

a thin electro-deposited coating on cheaper base

The tank itself can be used as cathode, but with irregular-shaped work, shaped cathodes ensure greater uniformity of the protective film. The nature of the connector between anode and cathode is important. With the preferred materials named, the connector should be nickel or copper, or, preferably, tin, lead, cadmium, zinc, aluminium or magnesium and the connector need not be insulated from the solution. The time of treatment to secure the best results is determined by the cathode surface and by the composition of the magnesium alloy. In general, it must be increased with increasing aluminium content.

In some cases there is an optimum region as shown by curve a in Fig. 8. This curve applies to an alloy containing 7.5 per cent. aluminium, 0.4 per cent. zinc and 0.2 per cent. manganese. Curve b applies to an alloy containing 6 per cent, aluminium, 1 per cent. zinc and 0.2 per cent, manganese. Both were electrolytically treated, using a stainless steel cathode and current density of 5-8 amps./sq. ft. The maximum curvature in curve a corresponds to about 6 mins. and in b 11 mins. In the case of b increase up to 30 mins, is not detrimental, but prolonged treatment causes loss of adhesion.

Cleaning pre-treatments for the electrolytic processes are as mentioned with the chemical

immersion process.

Specific examples of the treatments may be cited as follow:- The solution in which the protective treatment is applied consists of-

Ammonium, sodium or dichropotassium singly mate. mixed 50-100 parts by wt. sulphate, Ammonium or if desired the equivalent amount of the other sulphates mentioned above .. 15-50 Acetic acid IO Hydrated sodium acetate (or the equivaamount lent ammonium acetate) 25 Water to make up to 1000

For a magnesium-base alloy workpiece of composition according to D.T.D. 118, 140A or 142, a higher degree of protection is secured by immersing the workpiece in the above solution of pH adjusted to between 4.8 and 5.8, but preferably 5.3. Also immersed in the solution, but not touching the workpiece, is a cathode plate composed of stainless steel or mild steel or of copper, nickel or mild steel sheet plated with a thin deposit of chromium or rhodium. The workpiece and cathode are connected to a supply of current in such manner that, in terms of the convention previously mentioned, the current flows from the cathode to the workpiece. The supporting clamp for the workpiece is adapted as the electrical connectors, and that part of it in contact with the solution should be of mild steel, zinc, tin or cadmium, coated mild steel or copper, but preferably aluminium base alloy. The portion outside the solution may be of the same material or any other usual electrical conductor material. Depending on the

contour of the workpiece one or more flat or shaped cathodes are used and suitably spaced so that the current can be adjusted to be reasonably uniform between 10 and 20 amps./sq. ft. of anode surface. After treatment in this manner for 3-5 mins, the workpiece is taken out, washed, dried, and found to be coated with an adherent greenish brown to black protective film which will also serve as an excellent basis for the usual type of paint adapted for this

In cases where a good but not such a high degree of protection is sufficient, the treatment time may be reduced to 1-3 mins. Alternatively, the above concentration may be reduced by as much as 50 per cent, and the treatment time

kept at 3-5 mins.

If any sludge be formed, which is least likely to happen with a precious metal-coated cathode, and tends to adhere to the cathode surface, it can easily be removed by light swabbing. the contour of the workpiece permits the cathode to be placed sufficiently close to give the same current density, which is assisted by heating the solution, an equal or suitable degree of protection is secured without the external source of current merely by connecting the

workpiece directly to the cathode.

For a workpiece of composition according to Specifications D.T.D. 59A, 88B, 136A and 120A, a high degree of protection is secured in identical manner except that the treatment time is increased to 5-10 mins, and the pH of the solution adjusted to suit the aluminium content of the alloy as indicated in Fig. 1. In this figure the central curve c represents the pH values for maximum protection. A tolerance is provided at each side of this curve as shown by the curves d and e. The shaded area between the curves d and e gives the workand o.2 per cent. Mn, the pH range should be 4.5 to 5.3, but preferably 4.9. For an alloy containing 7.5 per cent. Al, o.4 per cent. Zn, and o.7 per cent. Al, o.4 per cent. Zn, and o.5 to 5.3, but preferably 4.9. For an alloy containing 7.5 per cent. Al, o.4 per cent. Zn, and 0.2 per cent. Mn, the pH should be adjusted to between 4.4 and 5.2, but preferably to 4.8. After treatment the workpiece is washed and dried and found to be coated with an adherent black protective film which also provides an excellent basis for the usual type of paint coatings adapted for the purpose.

In cases where a good but not such a high degree of protection is sufficient, the treatment time may be reduced to 3-5 mins. Alternatively, the above concentrations may be reduced by as much as 50 per cent, and the treatment time

kept at 5-10 mins.

In all cases the same solution may be repeatedly used, occasional major adjustments in pH to maintain the desired values being made by additions of sulphuric acid until the sulphate concentration reaches 200 parts by weight, when nitric acid should be used instead.

A further recommended range of ingredients

comprises:--

Dichromate (Cr2O,) over 0.05 molar (up to saturation point).

Sulphate (SO<sub>4</sub>) over 0.05 molar.

Buffer mixture, e.g., acetic acid and sodium acetate, total acetate concentration as acetic acid plus sodium acetate together, over o.1 molar CH,COO-.

When other weak acids and their salts are used as buffer mixtures, these concentrations must be altered having regard to the equivalent weight of the acid relative to that of acetic acid.

pH 4-6 depending on alloy composition

and time of treatment.

Time of treatment: This depends on the composition of the alloy, the solution composition and its pH and varies between 0.5 and 30 mins.

Where the degree of protection required is that corresponding to temporary protection of parts during fabrication, storage or transit, the formulation suggested is:

Dichromate (Cr.O.) over o.1 molar (up

to saturation point).

Sulphate (SO,) 0.05-2 molar. (Note: For cases where the dichromate is above about 0.3 molar, the sulphate concentration should be correspondingly increased.)

Buffer mixture, e.g., acetic acid and sodium acetate, total acetate concentration as acetic plus sodium acetate together, over

o.1 molar CH, COO-

When other weak acids and their salts are used as buffer mixtures, these concentrations must be altered having regard to the equivalent weight of the acid relative to that of acetic acid.

pH 4-6 depending on alloy composition and

time of treatment.

Time of treatment as in previous example, namely, 0.5 to 30 mins.

Optimum composition for protective value of the highest order is:-

Dichromate (Cr.O,) 0.2-0.5 molar.

Sulphate (SO4) 0.1-1.5 molar. (Note: For cases where the dichromate is above about 0.3 molar, the sulphate concentration should

be correspondingly increased.)

Buffer mixture, e.g., acetic acid and sodium acetate, total acetate concentration as acetic acid plus sodium acetate together, 0.2 to 1.0 molar. When other weak acids and their salts are used as buffer mixtures. these concentrations must be altered having regard to the equivalent weight of the acid relative to that of acetic acid, pH 4.6-5.9 depending on the alloy composition and time of treatment.

Time of treatment 1-30 mins, depending on the alloy composition.

An earlier type of solution which may be employed, but which is not now considered as good as solutions given in the previous example, comprises the following ingredients:-

This solution is used electrolytically at room temperature and, under such conditions, forms a protective coating on magnesium and magnesium-base alloy surfaces in a time not exceeding 10 mins. For example, on D.T.D. 118, a protective coating is formed in from one to two minutes. The composition may need to be adjusted slightly to suit particular alloy compositions. As the solution is not strongly acid, no special care need be taken with regard to containers and manipulation.

General Considerations

By working substantially cold, no special skill in manipulation is required to avoid undue loss of ammonia by evaporation with consequent change of pH. High concentration of ammonium ions appears to be desirable, and apparently anions other than sulphate do not yield the desired results.

In connection with the buffering of the solution, it appears that the buffer capacity (or resistance of the solution to change of pH) is roughly proportional to the concentration of the weak acid and the salt.

The new treatment provides an excellent basis for the usual type of paint coating applied to magnesium alloys. Adhesion of the paint film and corrosion resistance in the painted state are good.

Electrolytic treatments do not necessarily give the same degree of protection with all alloys. For instance, whereas the electrolytic treatment causes marked improvement in the case of magnesium-base alloys containing aluminium, the improvement in the case of magnesium-base alloys containing manganese additions only is but slight. These effects are illustrated by the following table based on a process in which acid-cleaned specimens were connected externally with a stainless steel electrode immersed in the bath, and after treatment compared by standard 3 per cent. NaC1 solution immersion test with specimens similarly treated but without the stainless steel. The following corrosion test results are the average of three specimens in each case:-

stable on standing. Containing vessels may be of steel or stoneware or any type of vessel suitable for any other chromate solutions. The solution has a long life, and can be replenished, when the pH becomes too high, by the addition of chromic or sulphuric acid.

The abstracts presented here indicate the intensity and thoroughness of work done towards perfecting commercially practicable treatments for the corrosion protection of magnesium and magnesium-base alloys. The free availability of these metals in the post-war period and, in fact, the probability of there being an excess, renders the research by no means premature. It portends the establishment of commercial treatments, using solutions prepared from simple chemicals, controlled within optimum limits by routine but simple chemical tests and maintained by straightforward additions of chemicals at regular intervals. The position should develop in a manner similar to that established for iron and steel using phosphate-base solutions, in which field parkerizing, bonderizing, granodizing, etc., have become universally established processes, foolproof in operation and control, and certain in effectiveness.

A secondary issue arising from what might be termed this "codification" process in regard to chromate treatments, is the beneficial effect it is likely to exert on paint-research programmes covering the ultra-light alloys. The problems here are similar to, but somewhat more intense than, those besetting the paint technologist when he comes to deal with aluminium-base alloys. Granted that, in both cases, schedules have been worked out which have proved satisfactory for the stringent demands of the aircraft industry, yet, here, the scope is limited largely within the boundaries of pure "protection." Moreover in actual practice, paint treatment of magnesium alloys for aircraft purposes is mainly in the hands of specialists. If, as we hope, the

Alloying additions	Treatment	Time o treatment	Corrosion test time	Equivalent weight loss
8% Al, 0.3 Mn 0.3 Zn to D.T.D. 59A	Ordinary Electrolytic	5 mins. 5 mins.	17 hours 17 hours	0.43 0.14
1.8% Mn to D.T.D. 118	Ordinary Ordinary Electrolytic Electrolytic	2 mins. 5 mins. 2 mins. 5 mins.	2 days 2 days 2 days 2 days 2 days	0.067 0.075 0.053 0.066

During the electrolytic treatments the current density dropped from 19 mA/cm² just after immersion to 13 mA/cm² at the end of the treatment. On the aluminium-containing alloys the dimensional change after five minutes' electrolytic treatment was about 0.0002-0.0003 in. From these figures it follows that the improvement in resistance in the case of the aluminium-containing alloys by using the electrolytic treatment is three times that obtained by the non-electrolytic treatment.

These and other tests on pure magnesium and alloys to D.T.D. 118 and 59A show that the dimensional change caused by the application of treatment is too small to measure with an ordinary (thousandths) micrometer. This is extremely useful because machining tolerances do not have to be altered. The solution is

ultra-light alloys do achieve in the civilian field that success for which their qualities most assuredly fit them, then a call will be made for surface treatment techniques capable of being carried out by non-specialists even though these may be highly skilled workmen.

may be highly skilled workmen.

If it be borne in mind that, even at the present time, problems on the surface preparation of aluminium for painting have by no means been finally solved despite the known value of anodic treatment and the degree of perfection already attained in the technique, the contribution made by this clearing up of the "chromate position" for magnesium may be assessed at its true value.

Finally, the possibility is not to be ruled out that the post-war period may see the development of radically different methods.



ALUMINIUM ALLOYS FARNHAM ROAD . SLOUGH .

HIDUMINIUM APPLICATIONS

BUCKS.

HIGH DUTY ALLOYS LTD. . REYNOLDS TUBE CF LTD. - REYNOLDS ROLLING MILLS LTD.

# HUMPHREYS & GLASGOW LTD.

Installations for the Production

Carburetted Water Gas Blue Water Gas

Producer Gas

Special Gas for Synthetic Processes

Hydrogen

Ancillary Plant

for

Waste Heat Steam Production; Gas Cooling & Cleaning; Fuel Handling & Charging; Ash & Dust Disposal; etc.

London Address: Humglas House, Carlisle Place, London, S.W.1



Temporary Address:
Winkfield Manor,
Ascot . Berks.
Phone: Winkfield Row 2107

Established 1892

## NEWS—General, Technical and Commercial

#### Aluminium-alloy Hopper Cars

THE Missouri Pacific Lines recently placed an order with the American Car and Foundry Co. for 25 aluminium-alloy hopper cars -the first lot to be purchased by any railroad

for regular revenue service.

The cars, designed by Car and Foundry in co-operation with the engineering staffs of the Missouri Pacific and the Aluminum Co. of America, are to be constructed at the South St. Louis plant of the railroad equipment builder.

L. W. Baldwin, chief executive officer of the Missouri Pacific Lines, said the cars were especially adapted to the transportation of sulphur and coal. An order was subsequently issued in Federal Court here, authorizing the purchase, subject to the approval of the War

Production Board.

The order brings a step nearer to reality the widely heralded use of lightweight metals in post-war railroad freight transportation. Because aluminium is lighter than steel, it was pointed out that the new cars will carry a load of 761 tons without imposing any more weight on the axle and without requiring any more locomotive effort than an all-steel car carrying a load of only 70 tons.

#### Aluminium Finishes are Important

THE March issue of "News-Letter" (Alcoa, U.S.A.) contains an interesting illustrated page on the many surface finishes that may be applied to aluminium-alloy articles.

It stresses the importance of the subject, for, it is stated, metals are being increasingly sold on surface appearance: designers, manufac-turers and merchants have become surface conscious. Finishes give the metal the longest possible life, as added protection is conferred, and they may give new characteristics, such as the high light reflectivity used in the field of illumination. Intensive research work continues.

#### Alcoa Imagineering Again

THE Aluminum Co. of America is continuing its suggestive imagineering notebook in a "News-Letter" series called "The Aluminum Shape of Things to Come." Two pages of the Notebook have appeared in the issues for February and March dealing with aluminium in transport and in the home respectively.

The first page quotes the opinion of a prophesying American scientist that things that move will be made of aluminium and magnesium, things that stay put of iron and steel. In 1939, 29 per cent. of American aluminium went into land, air or water transportation equipment. Although drastic modifications in car design are not expected immediately after the war, ultimately the lighter weight car will come with its greater efficiency and

economy. To the normal uses of aluminium in automobile construction will be added rear axle housings, wheels, front axles, among other running gear parts, it is suggested. The advantages of aluminium in truck bodies and coach construction are already appreciated.

In the home, aluminium ware is already too well known to be stressed, but Alcoa predict new attractive finishes for domestic utensils. In decoration, aluminium strip may be used to relieve the harsh lines of door or panelled wall, or as detail on wooden tables and chairs. Aluminium mesh, either singly or in combina-tion with textiles, will find use as curtain material. Aluminium chairs and tables, popular before the war in offices, hotels and trains, will find ready acceptance in the home. In the illustration it is interesting to see that American designers have broken away from the preconceived notion that metal furniture must of necessity be tubular.

#### Aluminium in Ecclesiastical Architecture

NDER the title "Aluminum Goes to Church," Alcoa's "News-Letter" for March recalls the fact that the dome and parts of the roof of St. Joachin's Church in Rome were covered with 14-gauge commercially pure sheet as long ago as 1897.

Illustrations are given of American examples of aluminium applications in church architecture and fittings, including a church spire at the German Evangelical Protestant Church, Pittsburgh, consisting of aluminium castings hung on a steel framework, and part of the high altar structure at the Cathedral of the Immaculate Conception, St. Cloud, Minnesota, where, incidentally, the pulpit is constructed of aluminium and bronze.

#### Light-metal Scrap in U.S.A.

THE Non-ferrous Scrap Dealers' Report No. 16 of the Mineral Industry Surveys of the United States Department of the Interior (Bureau of Mines), released on June 22, 1944, indicates that, in U.S.A., "stocks of aluminium reached a new all-time high at the close of April with 31,543 tons, compared with 29,973 tons (revised) at the end of the previous month.

"It appears that there need be no great concern over the mounting inventory of aluminium scrap other than wrecked aircraft reported by scrap-metal dealers, for a study of dealer transactions in other types of scrap, such as copper and brass with which dealers are more familiar, indicates that working stocks should be anywhere from one-third to one-half again as large as monthly shipments to consumers.

"Leaving out wrecked aircraft, which is a separate problem, dealers' shipments of other types of aluminium scrap in April, 1944, totalled 14,143 tons, and closing stocks of scrap, excluding aircraft, totalled 26,156 tons.

#### Humour in Advertising

As a result of correspondence and an Acditorial comment on the place of pure art and humour in advertising, which appeared in "Light Metals" for August, further letters have now reached us; these are reproduced in extenso. Only in one instance is humorous publicity denounced as quite out of place in technical periodicals, but, in all cases, caution is advised as to when and where it be employed. Quite correctly, correspondents draw attention to the need, at all times, for a factual basis for technical advertising, whether or not non-informative matter—humour or purely decorative art—be grafted on to this foundation.

#### Aspects of Publicity

"This matter of technical advertising is one on which I feel I have special claims to speak, for I have had opportunity to view it from an

unusually wide range of aspects.

"I was educated and have worked as a metallurgist and engineer; I have been advertising manager to a famous engineering company, and sales promotion manager to the largest producer of steel and allied products in the British Empire. Until very recently I have edited the export engineering supplement of a well-known journal, and for the past 10 years I have been a partner in an advertising consultancy which specializes in and handles nothing but technical advertising. Out of this experience I have formulated very definite ideas on 'the right kind' of advertising.

"In normal circumstances (i.e., before the war) the art of general advertising of 'consumer' commodities is to work through the emotions—display, pride, envy, greed or sex. This stimulation may be exquisitely disguised or crudely apparent, but the basis of appeal is

emotional.

"A motorcar or a radio set is a product of engineering skill of a high order, but it is not (in general) bought by technically minded persons, and so is not advertised as a technical

product.

"A man will buy a motorcar for many reasons other than to provide transport or because his old one is worn out, and these reasons involve personal idiosyncrasies, personal taste, personal needs and personal emotions. He may deny himself other things to buy it; he will make sacrifices. He is usually not much concerned about its design or construction or about the material of which the craphcheft is reader.

material of which the crankshaft is made.

"The same man, in his capacity of purchaser of technical products, does not buy a gasholder, a light casting, a filter press or an automatic loom because he admires its lines. He buys only after a critical examination of his need for it, of its design and materials and construction, of what it will do, what it will save or earn in

hard cash.

"The buyer of technical products is usually at least as well-informed as to his own requirements as is the seller. In fact, the buyer frequently draws up a schedule of his requirements in the form of a rigid specification, with full knowledge of the import of each item and the reason for its inclusion, together with some tightly binding clauses as to output under speci-

fied conditions or efficiency expressed as a percentage

"Contrast this with a washing powder, where the housewife is completely ignorant of its composition, properties, true cost and efficiency, and is content to take these 'for granted.'

"With these pointers in mind, I can definitely say that, with normal markets and conditions of demand and supply, the more factual and informative a technical advertise-

ment the better.

"If the product be one of which a photograph gives the most informative idea, a photograph should be used; if an arresting (artist's) drawing of the product or its relationship to its uses is the best way of hammering home a specific point, by all means use the artist; if lengthy letterpress is necessary to tell the full story, then use plenty of 'copy' or an all-copy advertisement. Humour is not barred, but needs to be handled with a delicate hand; the facetious is always wrong.

"The point is that the prospective purchaser is looking for information and must have it before he buys; if much of this information can be given in an advertisement so that the buyer is familiar with the outstanding claims and constructional features before the seller's representative is called in, then the time elapsing between the first approach and the completion of sale is considerably shortened. This is the true func-

tion of technical advertising.

#### What of War-time Advertising?

"All previous comments apply to normal conditions; most of them still apply equally to war-time conditions. But, in time of war, other considerations intervene; many producers are severed by controls, etc., from their normal markets and customers; they have nothing to sell.

"To advertise to se'll nothing is much more difficult than to advertise something for sale. This is the real reason for the present spate of humorous, artistic and completely non-informative advertisements designed to sell nothing; prestige, 'house,' institutional (or whatever you like to call them) maybe, but really they are indulging in that old-fashioned pastime of 'keeping one's name before the public.'

"This is a perfectly legitimate function of technical advertising when circumstances, as they so often do to-day, tend strongly to divorce the producer from his normal customers, with whom he seeks to keep some kind-of touch.

"Whether this humorous or artistic advertising, giving little or no information about the product, and sometimes even leaving the advertiser's name obscure, is good advertising is a debatable point. My own feeling is that such advertisements irritate the man who wants to buy something now, but amuse and please many others who are very likely potential customers. Particularly do they irritate the technologist and the professional buyer, but they very frequently influence for good the director or administrator, who often is the man who says the last word.

the last word.

"To quote some specific examples: several series of 'institutional' advertisements for The United Steel Companies, Ltd., have created exceptional interest at home and abroad. The editors of journals in Australia and elsewhere

have reproduced them in editorial pages with commendations to the readers to look and do likewise. These advertisements are non-factual about products, illustrated 'artistically' by well-known artists, 'copy' and artwork are matched together; dignified, restrained, rather visionary, and scarcely mentioning steel. Similar, but somewhat more factual series by I.C.I.

are also noteworthy.

"Humour in advertising is two-edged. I, personally, intensely admire the advertising of one noted manufacturer of small tools, for its humour and for certain excellencies in advertising technique, and for the results which I know it must bring. But I know several engineers to whom these advertisements are enathema and who have gone so far as to say that they will not buy from a concern which engages in such 'silly' publicity. This prejudice, if further analysed, seems to be based upon a dislike of facetiousness and not of humour or wit, for some of the very same men admire the wit of the advertising of tubes by Accles and Pollock and subsequent advertisers.

"One point more about highly artistic presentations: I continually in my practice encounter this situation. A client will say that he has immensely admired a certain advertisement, it is marvellous artwork, and why can't he have something like it? So I ask him to show me; a search follows through a pile of journals (many of them American, perhaps), a search complicated by the fact that he can't for the life of him remember the name of the advertiser or what he advertised!"—Frank Rawlinson.

#### Time and Place for Humour

"Your Editorial and correspondence in the August issue of your journal prompts the

following:-

"What is the object of advertising? I would suggest that advertisements are used mainly to replace the human salesman and thereby to reach a far larger prospect than is possible otherwise.

"If this be so, surely an advertisement should embody all the qualities that your successful salesman possesses, or try to do so as far as

possible.

"Years ago I was taught to work to a formula; here it is—A.A.I.D.D.A.—Approach, Attention, Interest, Desire, Decision, Action.

Attention, Interest, Desire, Decision, Action.

"Now, the salesman, or the advert., must make a proper approach; this done, either must gain attention. These two qualities surely imply an understanding of human nature. If to reach this stage humour is employed, and it must be the right kind of humour, then there can be no objection to its employment, although what may be verbally humorous may not look so printed.

After this you will not interest your prospect unless you know what you are talking about, or rather, letting your prospect do the talking and show by your replies that you know your

subject in a way that interests him.

"Now this is where an advertisement is up against it, because although it may be full of information, it cannot, like the salesman, hear what the prospect is NOT saying; it cannot study him, it cannot bring into play a particular knowledge for that specific type of human nature. An advertisement is unable to

react, and although it may be a speciality advertisement, intended to interest only a certain type of prospect, it is limited as already

stated.

"Having reached the stage of interest, can the advertisement create a desire to possess or to use, or to obtain any details not so far disclosed? This brings us to a stage where it seems that the salesman and the advertisement now no longer take parallel courses, but this is also governed by other factors. Are you selling a highly specialized product, or technical service? Is it a general user demand product or service or is it restricted? We appreciate that what it is governs the type of advertisement in the first instance and also the type of salesman who at this stage where service is concerned may no longer be a salesman, but has become a highly technical representative.

"This matter is now becoming so involved that it seems to be beyond the capacity of a letter to elucidate, so I will try to reach my conclusion by saying that if your advertisement reaches the desire stage it is extremely unlikely that anything further will result unless the human being now appears, and yet a successful advertisement should be able to get to the

decision stage at least.

"We now reach the answer to whether humour is out of place or not and that is it all depends upon what you are selling, and it also depends upon the experience of your prospect. To give one instance-how many of your readers have experienced the difficulties of drilling holes in undrillable places—their atti-tudes and contortions—but surely on looking back this has something funny in it. Well, an excellent series of very humorous advertisements has appeared in the 'Daily Telegraph by a firm of lightweight tool (drill) specialists. The humour in this case immediately shows that the advertiser understands the problem that his goods are designed to overcome and appears to be about the best way in which to put this fact before the prospect. So far as I am concerned this has so appealed to me because of its obvious truth, that I know what and where to buy when I want such tools.

"Truth in advertising! Does this include humour? It would be serious if it didn't (for the advertiser)."—For Durston, Lang and Co., Ltd., HAROLD DURSTON, Technical Director.

#### Levity Misplaced

"Your editorial in the August issue of 'Light Metals,' with the relevant correspondence, deals with a subject very much in my mind at the present time. I have therefore read the opinions expressed with considerable interest.

"My own personal view is that these so-called

"My own personal view is that these so-called humorous advertisements are definitely out of place in technical and other specialized journals. They may be permissible in the popular and lay Press read in our more leisured moments, but for technical publications they merely give the quite unfounded impression of cheap-jacks trying to gate-crash into a sphere, the high standards of which they neither know nor really appreciate, in the hope of selling catchpenny lines.

"In this connection there is one point to be remembered and that is that no two people have the same sense of humour and what to one person would be amusing would appear as plain silly to another. Following on from this, we must also bear in mind that the English sense of humour is 'peculiar' and is not always

appreciated by even our best friends overseas.
"To my mind, therefore, a very considerable risk is run by adopting a frivolous attitude in advertising, for such humorous displays are more likely to annoy than amuse the home reader, and in any case they do not give that impression of reliability and a real desire to assist a customer, which is desirable in the technical journal primarily intended for home consumption and essential in overseas publications if we are to retrieve, let alone expand, our export markets. We have a certain prestige to maintain and pseudo-humorous advertise-ments certainly do not inspire confidence either in the goods advertised or the manufacturer, and are not the type of propaganda which will appeal to overseas buyers who wish to know more of the details of our undoubted achievements in the engineering industry.

Whilst not in quite the same category, I feel that the 'art for art sake' style, too, is to be deprecated unless the subject matter has a really tangible and not highly imaginary connection with the products advertised. It is quite likely that these works of art attract attention and may even be remembered as pretty pictures, but I doubt very much if the name of the advertiser or his products would also be remembered.

"Advertisements are the advertisers' shop window and there is something to be said for the old style lay-out which gave the name of the manufacturer in prominent type and a nearcatalogue description with, perhaps, an illustration of his wares. Such displays could hardly be said to be attractive, although they could, if suitably worded, fulfil the necessary function of arousing curiosity which leads to readers sending inquiries with the consequent opportunity for the advertiser to state his case more

fully.
"The ideal to my mind is a combination of for it is essential to have an attractive layout, to arouse the curiosity of the reader by illustration and skilful wording, and to give a very definite impression of reliability and solid technical achievement."—E.G.

#### SCIENCE, UNIVERSITY, INDUSTRY!

During recent months there body on spate of reports by one or other body on Universities and URING recent months there has been a the future of science in the Universities and Technical Institutes. The Association of Scienrific Workers, which has rapidly become an important force amongst scientists, has now added its views\* on the policies and reforms which should be carried out after the war if science is to maintain its position as the explorer and guide of industrial progress. On many questions, e.g., curriculum, government, and salaries, the report is very similar to that of the Association of University Teachers, but it is restricted in large measure to the physical and biological sciences, touching agricultural, medical and social science only in so far as they interlock with the principal subjects.

Within this framework the report offers an extensive discussion under the main headings of degree courses, teaching, research, applied science, extra-mural activities, and the post-war problem; a useful summary of recommendations is attached, together with appendices giving proposed salary scales for academic and

technical staff.

Degree courses, it is argued, should be emancipated from the scourge of over-specialization. There should be available a broader background upon which intending experts could, in later stages of the course, build up their specialized subject. The syllabus should be so arranged, too, that during his last year a student could tackle a simple research problem, so that selection of post-graduate students could be easier and more certain. Emphasis is laid on the need for science courses for non-scientists;

it is to be regretted that similar emphasis is not put on the need for non-scientific courses for scientists. Anyone who has to read scientific books and research papers cannot fail to realize the widespread lack of ability on the part of many scientists to express themselves in elegant and accurate language, a serious fault which might be mitigated by a compulsory course in literature, or perhaps history, for all scientists.

Though the report treats teaching and research in separate sections, they are so intimately connected that they should be reviewed together. The impact of each on the other is so important that it is essential that all teachers should have ample time (half-time is suggested) for research. When administrative duties are too heavy to allow heads of departments to take an adequate part in both teaching and research, assistance should be provided, as part of the accepted set-up, to help in purely administrative work. Selection, training, and remuneration of staff should follow the same general lines as suggested by the A.U.T., while the provision of a sabba-tical year and the opportunity of exchange of personnel between universities, research associations and industries are considered essential for the maintenance of a healthy, progressive spirit and a proper perspective. Research, which should be fundamental and not special to the problems of any private concern, must be fostered by adequate grants (£250 p.a.) to post-graduate students, and by the provision of research fellowships (£500 p.a.) for postdoctoral students who desire, and are fitted for, further research before entering industry or The importance of frequent interteaching. change of views and personnel between various institutions carrying on research is stressed, particularly between sciences where progress is being made on the border-line. The formation

<sup>\*</sup> Science in the Universities. Report submitted to the University Grants Committee of the Treasury. (Association of Scientific Workers. Oxonian Press, 1s.)

of a system of Research Committees responsible to a Universities Academic Council to co-ordinate the development of research is strongly advocated, these committees administering special Government grants for research. Attention is also drawn to the need for adequate training and remuneration of laboratory technical staff, whose functions are destined to become more and more important.

Departments of applied science and technology, as well as improved technical institutes within the framework of the universities, adequately and separately maintained by special Government grants, are suggested. The possibility of capitalizing on discoveries of potential commercial value should be left to a central body modelled on the U.S. "Research

Corporation."

Extra-mural, or extension, facilities should be available for adult education, run by joint committees operating under a Graduate Studies Board.

The post-war problem is studied from the angles of increased numbers, accommodation and staffing, and the consequent increase in expenditure is estimated in terms of 1939 money values. It is suggested that the Government grant should increase during five years from double to quadruple its present value.

Nuffield College Report on Industry and Science (Nuffield College: Problems of Scientific and Industrial Research. A Statement, Oxford University Press, 1944).

Yet another prominent authority has also seen fit to issue a report on industry and science, and to indicate the direction in which post-war development must proceed if the best advantage is to be taken of our native ability and aptitude for scientific and technical

progress.

Whilst a large and speedy increase in research workers is necessary, it is claimed that, in spite of no permanent shortage of trained personnel, our lack of vision in educational provisions has led to the loss of a considerable proportion of our potential skill. This lack of foresight has not been restricted entirely to our much-maligned Local Education Authorities, and emphasis is laid on the fact that even now, in spite of the great awakening of industry to the importance of research, a great many industrialists still have but a hazy conception of what research is and of how it can be instituted as an aid to industry. Furthermore, there is still a great void between the more academic research characteristics of our universities and the translation of the new knowledge so acquired into obvious improvements in the quality and speed of industrial output.

In general, the report continues, the research associations have not fulfilled the hopes that were held at their initiation. The reasons for their comparatively disappointing performance are many, but are to be sought mainly in lack of adequate funds for the projection of really large-scale researches. It may be necessary for the Government to provide for a much greater allotment of funds to research associations, including, it is suggested, a compulsory levy on all firms within the particular industries

affected.

One very important point which the statement makes is the desirability of interchange of personnel throughout a given industry, including firms, research associations and universities. It is in this respect, in fact, that the report touches most closely on one of the major causes of the gap between the research and application, between the academic work of the universities, including the near-academic work of the research associations and the more empirical ad hoc investigations carried out by independent industrial laboratories. There are a very limited number of universities and colleges at present whose teaching personnel have any really live contact with industry, and unfortunately there is a similar, though less marked, lack of interchange of ideas between the research associations and the firms which help to support them.

The function of patents in the enlightened new era which is coming is discussed at some length. The stultifying influence which very wide patents have in the past had on progress may, it is suggested, be modified if the Government or the planning authority is given power to grant licence to manufacture under any given patent to any approved firm if such action is deemed to be in the public interest. It is pointed out that this adjustment of patent rights might be of very marked assistance in carrying out the policy of full employment in

the post-war period.

The part which the universities are expected to play is not minimized, and the Nuffield report acknowledges the necessity for a vast increase in expenditure in these institutions. Not only equipment and accommodation, but also teaching staff must be considerably increased, especially in the newer universities. The technical colleges should be raised in status and be shown similar increased financial aid in order that scientists associated with them may be able to give of their best to the community. Great emphasis is laid on the importance of retracting scientific experts from the ad hoc researches which have forcibly engaged their attention during the war, and allowing them to go back completely to the freedom of action which they enjoyed previously. This freedom has encouraged the investigation of the funda-mental problems—" basic ideas"—which must always remain the basis of any applied research, and must consequently be always a few stages ahead of development.

There is a final and very interesting suggestion to the effect that a research corporation should be formed to act on behalf of all the universities and technical colleges in the matter of patenting discoveries which have arisen during the pursuit of fundamental research and which may be of commercial value. The proceeds from patents have led to the development of at least one very excellent research department in one American university, and the idea has been followed by others. It should be no deterrent that there was finally some question as to the validity of the patents in this case, since this only cropped up when the patent had almost

run its course.

This suggestion seems to form the basis of a very profitable source of income for our impoverished institutions, and is an eloquent commentary on our appreciation of the excellence of our academic researchers.—E. R. ROBERTS.

#### PAN-AMERICAN ANTI-CORROSION SCHEME

AN instructive article on corrosion protection of light alloys under arduous service appears in the American journal "Metal Finishing," dated February, 1944. The maintenance of seagoing aircraft is detailed by the Chief Chemist of the Pan-American Airways System in an account with d. "Clippers "Constituted".

in an account entitled "Clippers v. Corrosion."

Adequate corrosion protection is particularly important as these aircraft are exposed to salt water and spray during taxi-ing, take-off and landing. All the external surfaces of Clippers are of anodized aluminium alloy, to which the zinc chromate primer readily bonds. The specification is designated AN-TT-P-656a. It is sprayed in one thin coat on to the prepared clean surface and allowed to air-dry for a period of between 30 mins, and 3 hrs. The top coats consist of three films of a lacquer containing aluminium pigment in the proportion 2 lb. to 5 gallons of vehicle, to Specification AN-TT-L-51.
The entire structure is covered with this finish, except for the hull below the water line, which is finished after zinc chromate priming with a heavy coat of a black glyceryl-phthalate enamel applied by brush.

Internal structural members are coated with two light coats of the zinc-chrome primer to which is added a half-pound of aluminium powder per gallon. This is stated to be a highly effective treatment. At any position where sea water might collect, as, for example, between the cabin floorboards and the hull, cloth bags containing potassium dichromate are provided at the lowest point, in order that the passivifying agent will dissolve and constantly maintain

a corrosion inhibiting solution.

Routine inspection takes place after every trip. Careful examination is made for corrosion around rivet heads, corrosion due to abrasion from floating objects, and at the joining edges of hull plates. Slightly corroded rivet heads will be cleaned down to the metal, reprimed and finished; severely corroded rivets will be replaced. Abrasions affecting the paint film will be reprimed and finish coated. Blemishes in appearance are rectified by a light spray of top coat blended into the surrounding ground, Touch-up work must be rigidly controlled on account of weight considerations.

#### National Certificates in Metallurgy

IT had been expected that the scheme for National Certificates in Metallurgy in which The Iron and Steel Institute, the Institution of Mining and Metallurgy and The Institute of Metals are co-operating with the Board of Education would be launched in time to allow colleges and schools to start their courses in the academic year beginning September, 1944.

This has, unfortunately, proved impracticable. The scheme will now come into operation so that courses will begin in September, 1945, and the first examinations will be held in 1946 for the Ordinary Certificate. Colleges and schools are being advised to this effect by the Board of Education, so that as much progress as possible can be made in anticipation,

#### STOVING BY INFRA-RED

"The Application of Radiant Heat to Metal Finishing"—J. H. Nelson and H. Silman. Chapman and Hall, Ltd. 1944. Price 8s. 6d. THE time required for paint film drying has L been spectacularly reduced following the application of "infra-red" methods. For application of "infra-red" example, a synthetic-base zinc-chrome primer coating can be dried by radiation in about one minute as compared with the 90 mins, required by the more orthodox convection method. Time saving of this order is obviously attractive during intensive wartime production, regardless of whether the process itself be economic, or the equipment as used efficient. It will be known to those readers who have seen infra-red installations that they are often quite elemen-tary structures merely supporting banks of

In this slim book Nelson and Silman have made a critical survey of the infra-red process for paint and enamel stoving, and to the reviewer, at least, who has had some experimental acquaintance with infra-red, many points of great practical importance are suggested. The principles of heat transfer are critically considered and, whilst it is probable that little fresh ground is broken, there is a salutary freshness in being brought down to the fundamental physics of drying processes. All too seldom is this sort of analysis embarked upon in industry.

The recent theoretical treatment of radiant heating by Tiller and Garber, published in America, is referred to and the conclusions given at the end of the theoretical chapter, important from the point of view of equipment design, are summed up in three rules; the temperature difference between source of radiation and the work must be as great as possible; because the quantity of heat transferred by radiation depends on the fourth power of the temperature difference radiation in the poet. temperature difference, radiation is the most efficient method of heating; and, third, the air temperature in a radiation oven should be such that there is a minimum transfer of heat by other than radiation.

It will be seen that the realization of such rules implies powerful criticism of many infra-

red installations at present in production use.

A very full account of the preparation of reflectors used in conjunction with the infra-red lamps is given. Anodized aluminium is stated to be the best material.

In their consideration of plant construction and design, Nelson and Silman keep to the forefront of discussion the need for control of convection which, if ignored, leads to waste of power. Attempts at such control by means of canvas sheets are only a makeshift and are in no sense a substitute for carefully designed enclosed ovens.

X-Ray Technology INDER the title "X-ray Darkroom Practice," Ilford, Ltd., have recently issued an informative brochure of great value to personnel engaged in industrial radiography. In essence it constitutes an indispensable appendix to many standard textbooks already available on the

Darkroom procedure, chemical stock and

formulation, developing technique and the diagnosis of faulty radiographs are all adequately dealt with; in a separate leaflet the use of lead screens for industrial purposes

Even experienced radiographers, we venture to suggest, will find the section dealing with defects in radiographs of the utmost interest and value.

#### NEW PATENTS REVIEWED

560,881. Improvements in or relating to Die Casting or Injection Mould-ing. Patentee: William Edward 25.4.44. O'Shei, a citizen of the U.S.A., of "Fernwood,"

Alton Road, London, S.W.15.

The aim of the present invention is to provide a means whereby the necessary minimum pressure of metal injection may be certainly achieved and indicated in pressure die casting or similar injection moulding. The fluid metal under pressure is caused to act upon a yieldable wall inserted in the mould so that the cast material causes the movable portion to move, producing a test piece either separate to, or as part of, the casting proper, the dimensions of such test pieces giving an indication of the pressure used. Preferably the yieldable wall is arranged to project into the casting pressure, so that the spring adjustment may be so arranged that under the correct pressure the fluid material produces a flat surface having neither depression nor increased thickness of section.

561,046. Improvements in Methods of Granted: Cleaning Articles of Magnesium 3.5.44. or Magnesium Alloys. Patentees: Wingfoot Corporation, of 1144 East Market

Street, Akron, Ohio, U.S.A.
This invention has for its object the removal of surface impurities such as magnesium hydroxide, elemental sulphur, borax, and sodium silicofluoride without substantially attacking the magnesium itself and thus maintaining machine tolerances. The use of an aqueous solution of chromic anhydride is an effective cleaning agent but has the disadvantage of appreciably attacking the metal, magnifying surface pits and pores and destroying machine tolerances. The present invention consists in the addition of small quantities of chromic trifluoride to the aqueous chromic acid. The method of cleaning magnesium articles comprising treatment therefore with an aqueous solution containing 15 per cent, to 30 per cent. by weight of chromic acid and above I per cent, by weight of chromium trifluoride, used at a temperature of at least 150 degrees F. but considerably below boiling point of the solution, is claimed.

Process and Apparatus for the 561,651. Manufacture of the Alkaline Earth Series. Patentees: Motrac Granted: Motormaker and Tractoren A.G., Badenstrasse 323, Zurich, Switzerland.

This invention relates to the manufacture of metals of the alkaline earths, such as magnesium and the like. Oxides or carbonates in a heated container are subjected to the action of a

heated gaseous mixture of chlorine and carbon monoxide, this apparatus being positioned above a receiver of the molten anhydrous chloride which also acts as an electrolytic bath. Any gaseous carbon compound which acts as a reducing agent may be mixed with chlorine. The anhydrous chloride is electrolyzed in the known manner. The advantages of this invention are said to be that the homogeneously mixed gases have a substantially higher rate of reaction than does a gas reacting upon two solids, and that since the reaction of the oxide or carbonate with chlorine and carbon monoxide is exothermic and the electrolyte offers some electrical resistance, the electric power con-sumed balances the heat loss of the whole apparatus so that it is only necessary to heat the furnaces independently at the beginning of the reaction. Chlorine generated by the electrolysis is used in the system. The metal so formed is pure, as the iron or aluminium which may be present are volatilized as chlorides.

561,748. Improvements in or relating to Granted: Flux for Use in the Treatment 2.6.44. of Light Metal. Patentees: Magnesium Elektron, Ltd., of Abbey House, Baker Street, London, N.W.1, and Harry Rowland Leech, of 12, Rutland Drive, Salford, 7, near Manchester.

This invention relates to flux for use in the melting of light metals consisting of magnesium, magnesium base alloys and aluminium base alloys containing magnesium, and to the kind which is thinly fluid, or non-inspissated of low melting point, intended more particularly merely for protecting the metal against oxidation. It has been found that for this type of alloy a satisfactory flux may contain much less magnesium chloride than has hitherto been used, with consequent economy, since anhydrous magnesium chloride is the most expensive ingredient of such fluxes. One claim is for a flux having a composition within the following range:

Magnesium chloride not less than 4 and not more than 20 per cent.

Calcium chloride not less than 25 and

not more than 55 per cent. Sodium chloride not less than 5 and not more than 40 per cent.

Potassium chloride not less than 5 and

not more than 40 per cent.

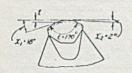
Magnesium oxide o to 5 per cent., the sodium and potassium chloride together amounting to between 30 and 60 per cent., the ingredients, excluding any impurities therein, amounting to at least 95 per cent. of the total.

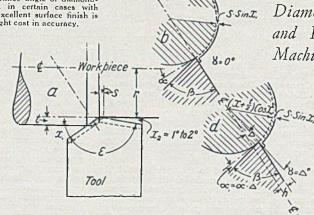
British Patent No. 539,023 is referred to.

# MACHINING OF LIGHT ALLOYS WITH DIAMOND TOOLS

Fig. 1 (right).—Cutting angles for turning tools. Clearance angle (a) lies as a rule between 5-9 degrees for turning tools, It has been suggested that the clearance angle of diamond-turning tools for light metals might in certain cases with advantage be reduced to zero; an excellent surface finish is obtained in this way at some slight cost in accuracy.

Fig. 2 (below).—Multiple facet diamond tool showing essential dimensions. (Compare with Fig. 4 below.)





SHAPED diamond tools have been introduced to an increasing extent into workshops as a result of the development of light metals, plastics and other specialized structural materials, because of more exacting demands for dimensional accuracy, and by reason of a demand for surface finishes of a smoothness which, some 10 years ago, were still beyond the range of measuring instruments.

compare available data relating to the machining of light metals with shaped diamond tools.

Diamond is especially suitable as a cutting material for turning and boring on account of

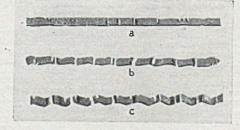
the following properties:—

(a) Great wear resistance and hardness

of the cutting edge.
(b) High polish of the surface of the

cutting edge.

Fig. 3.—Study of surface finish obtained on diamond-turned piston skirts: a, angle between axis of workpiece and rear edge of diamond tool I deg., surface finish satisfactory but somewhan matt; b, angle between—



-axis of workpiece and rear edge of diamond tool 6 degs., surface exhibits moderate gloss; c, angle between axis of workpiece and rear edge of diamond tool 15 degs., bad surface finish but high gloss.

Literature on diamond tools is somewhat sparse and deals mainly with their general application, with the form of tool edges, their adjustment, and so on. Tool and production engineers, however, are usually interested in the solution of a special problem relating to a certain material, such as the turning of lightmetal pistons or the boring of lead-bronze bearings, and here existing literature does not give much help. Therefore, in the following pages, an attempt has been made to collect and

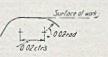
(c) Inertness, which prevents chemical reaction or welding between tool and workpiece.

These qualities of the diamond may be due to the way in which the carbon atoms are packed. The high polish of the cutting edge results in an easy flow of chip. Thus cutting pressure and friction are reduced. Welding of the chip to the diamond cutting edge has, generally, not been observed.

Wear of a diamond cutting edge is due, more



Fig. 4 (left).—Diamond tool with large circular edge (compare with faceted form in Fig. 2 above). Fig. 5 (right).—Faceted diamond tool with corners of facets rounded. This latter type of tool has been found to give optimum surface finish on aluminium pistons.



Summarizing the Advantages of ssmx. Diamond as a Cutting Material and Referring in Particular to the Machining of Aluminium Alloy Pistons

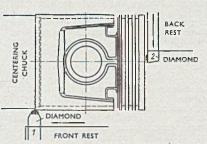


Fig. 6.—Machining of light-alloy pistons with diamond. The use of diamond tools for this purpose is very extensive, and for reasons connected with the structure of many commonly used aluminium-base piston alloys it appears unlikely that it will be superseded by any other material where highest grade finish is required.

or less, to minute chipping which is more pronounced when the diamonds are incorrectly orientated. Machining with diamond tools is the last finishing operation, no further grinding or lapping is necessary; a preliminary roughing operation is usually required. In a very few rare cases only has honing after diamond boring

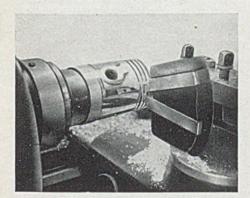


Fig. 7.—Diamond turning ring grooves in light-alloy piston. Special problems as to tool form arise here. (See Fig. 8 below.)

been applied, but, with modern improvements in surface finish, this second operation does not seem to be necessary and, indeed, may be even dangerous, owing to the risk of spoiling the machined surface. Cutting Angles for Turning Tools

For the production of geometrically correct surfaces it is essential that only one cutting edge be in operation at a time. The clearance angle a (Fig. 1) lies usually between 5 to 9 degrees for turning tools, and 8 to 15 degrees for boring tools. A variation in the clearance angle for boring tools is necessary owing to the correlation between thickness of diamond tip and diameter of bore, unless a secondary clearance be introduced. In this connection it has been suggested that the clearance angle of a diamond turning tool for light metals (Fig. 1) be reduced to zero so that the clearance face rubs slightly on the workpiece; thus a very good surface results, although precision may be impaired. The general practice is, however, to have a very small rear-adjusting angle of between 2 degrees to zero, which obviously produces a similar effect, and generally without disadvantage; this question is dealt with later. The point angle \( \xi \) is 120 degrees, if possible,

The point angle  $\xi$  is 120 degrees, if possible, for straight surfaces and for tools with one cutting edge, and 170 degrees for multiple facet tools (Fig. 2). Tools for stepped bores, shoulder turning and special profiles need point angles of less than 90 degrees, but owing to the weakening effect on the cutting edge and a probable influence on surface finish, the use of this tool shape should be confined to the applications mentioned.

The rake angle  $\gamma$  is from 0 to 3 degrees. A rake of angle of 0 degree considerably facilitates tool production and checking and has been long in use. Some materials, such as lead bronze, need negative rake angles.

The front adjusting angle x, is 45 degrees for

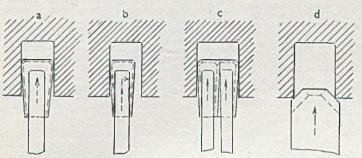


Fig. 8.—Diamond grooving tools (see Fig. 7 above): a tool of same width as ring groove, not recommended form; b, tool narrower than ring groove; c, tool with two diamonds; d, tool for chamfering the groove edge.

tools with one cutting edge, and 18 to 30 degrees for multiple facet tools. The rear adjusting angle  $x_2$  should be about 1 to 2 degrees.

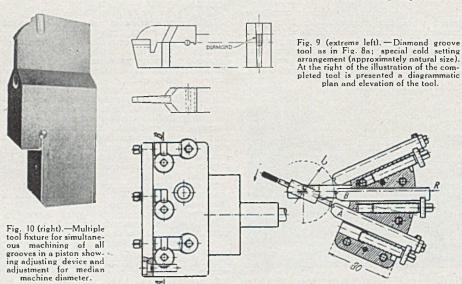
The influence of the rear adjusting angle x is clearly shown in Table 1 in connection with Fig. 3, referring to facet edge diamond tools. It is obvious from these investigations that surface quality is influenced by the rear adjusting angle, which should be chosen as small as possible.

A convenient tool shape is a large circular form providing for an infinite number of cutting facets (Fig. 4). Such circular forms were considered by some investigators as very suitable to avoid turning marks, and to obtain a high surface finish on aluminium. Improved technique in equipment and surface inspection showed, however, that optimum results in surface finish on aluminium pistons (down to

finish the feed must in no circumstances be more than a fraction of the length of the cutting edge. Small feeds and light cuts, after pre-liminary machining with other tools, preferably sintered carbides, account for good surface finish and are economical because they allow high cutting speeds. Feeds of 0.0008 to 0.004 in./rev. and a cutting depth of 0.008 to 0.025 in. are frequently applied.

#### Cutting Force

Small feeds, light cuts at high peripheral speeds and a highly polished diamond tool edge all tend to reduce friction, and the cutting forces are consequently quite small. Investigations carried out on turning aluminium with diamond tools showed that the main cutting force was sometimes less than I lb. This small load on the cutting edge, however,



I micro-inch = 0.000.001 in.) could be obtained with a tool form shown in Fig. 5 having facets with rounded corners.<sup>5</sup>

Economical Cutting Speeds

With diamond tools there is virtually no limit to the cutting speed, other than absolute freedom from vibration. Sometimes cutting speeds as high as 6.600 to 16.500 ft./min. are used. In this particular case feeds of 0.1 to 0.02 mm./rev. (0.004 to 0.0008 in./rev.) were employed and the diameter of the workpiece was probably comparatively large. As a general guide the following cutting speeds may be considered as economical:—

Work-hardening aluminium alloys (soft temper)—650 to 1,000 ft./min,

Unalloyed aluminium—1,500 to 1,800 ft./min. Magnesium alloys—1,000 to 1,250 ft./min.

Rate of Feed and Depth of Cut

Feed and depth of cut are, of course, dependent on the shape of the diamond tool edge, and in order to obtain a good surface

results in a specific pressure up to 200 tons/sq. in., a stress which no tool material other than diamond could be expected to stand for any respectable time.

Growth of the

Growth of the aircraft industries affected machining methods for light-metal parts to a large extent. Jointing faces on light-metal castings have to be carefully machined, small surfaces are sometimes diamond faced on a lathe, bigger areas being produced on special milling machines. The milling heads sometimes carry two to six diamonds in special holders, and operate at cutting speeds of about 1.500 to 3,000 ft./min. Diamond milling tools are more suitable than hard-metal tools for this kind of work, the latter, it is observed, tending to break more readily when faces with grooves, etc., are machined.

#### Machining Light-alloy Pistons

The most important present use of shaped diamond tools is that for the finishing of lightalloy pistons for internal-combustion engines.

(See Figs. 6 and 7.) It is claimed that 25,000 pistons can be turned without injuring the diamond tool. They are therefore more economical by far than hard-metal tools, especially for the machining of light alloys of the highsilicon type.7 The diamond turning tool is not influenced by slots and piston grooves.

For facing the piston crown a tool with a burnishing effect is sometimes used which is said to produce a smooth and dense surface to which gum and carbon deposits may not easily adhere. Piston grooves are first rough cut and then finish grooved with special tools, which are preferably held in special devices sometimes on the back attachment of the lathe. The shape of the diamond grooving tool is determined by the profile of the groove, the side of which must be very smooth to give the

smallest friction effects.

Fig. 9 shows a special tool evolved for this particular purpose. The cover plate fits into a wedge-like recess in order to prevent lateral and longitudinal movement of the diamond. If the facet width were to correspond to the width of the ring groove (Fig. 8a) the tool would be more or less useless once the edges become blunted. To overcome this difficulty two types of tool combinations have been developed. One is a single diamond (Fig. 8b) of width less than that of the groove to be produced. It faces at first one side, travels along the bottom of the groove, and then faces the other flank of the groove. The other type of grooving tool is shown in Fig. 8c. It consists of two diamonds, each of which machines one flank and a portion of the groove bottom. Both diamonds are fed of the groove bottom. Both diamonds are fed in simultaneously. In most cases, due to the narrowness of the grooves one diamond is arranged above the other and each is positioned radially with regard to the piston. For both types of grooving tool, very sensitive adjustments are provided. The groove edges after finishing may be chamfered (de-burred) with a single diamond having two cutting edges. (Fig. 8d.)

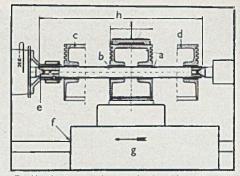


Fig. 11.—Arrangement for using hard-metal and diamond tool in the same set-up; the hard-metal tool has left the cut before the diamond enters it: a, hard metal; b, diamond; d, cut begins; c, cut ends; g, feed.

Instead of machining the groove successively with different tools, multiple tool attachments for mass production have been developed. By radial adjustment of the tool edges and tool holders in relation to the piston all danger of adjustment below or above centre line can be eliminated. Thus the operations of finishing a ring groove and chamfering it afterwards can be combined. By suitable arrangement the attachment may comprise, also, sets of com-bined tools, to machine all grooves of a piston at the same time. Such a device is shown in Fig. 10. Each groove is machined by two diamonds for facing the sides and one for chamfering the edges, each of the three diamonds being individually adjustable.

As already mentioned, diamond turning is the finishing operation and may result in mirror-like surface finish of about one microinch (0.000001 in.)

The exactness of dimensions is stated to be within limits of  $\pm 0.00012$  in. and the clearance

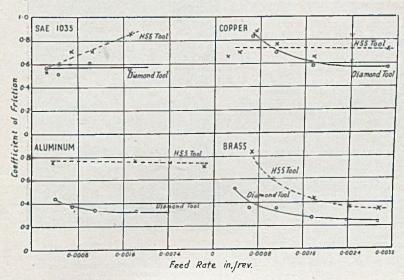


Fig. 12.-Cutting properties of diamond and highspeed steel tool compared on the basis of coeffi-cient of friction and feed rate.

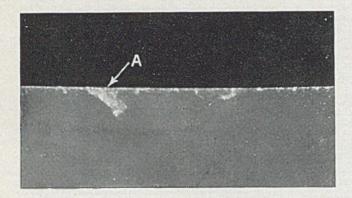


Fig. 13 (left).—Diamond cutting edge after run on aluminium. (Equivalent magnification in reproduction 75 diameters.) (Courtesy Cincinnati Milling Machine Co.)

Fig. 14 (below).—High-speed steel tool after run on aluminium. (Equivalent magnification in reproduction 75 diameters.) (Courtesy Cincinnati Milling Machine Co.)

between piston ring and groove is eventually more than 0.0006 in. precision cannot be improved by lapping or superfinishing and accounts for the long life of light-Recent metal pistons. investigations\* showed that when pistons have been in use for a long period, most of them still bear the turning grooves (or marks of the grinding operation). The wear does not take place on the piston skirts, but on the cylinder bore, piston rings or possibly the ring grooves. The surface finish is, therefore, considered to be "good enough" at 4 to 8 micro-

ins. for the skirt and 16 to 32 micro-ins, (or rougher) for the crown, especially when a protecting film (e.g., graphite) is applied to guard against corrosion during cold starting.

For certain sizes of piston and for certain alloys it has been claimed that sintered carbide tools give good results. An article which appeared recently in "Aluminium" (Germany) throws some light on this problem. Sintered carbide tools produce very smooth surfaces which are comparable with those produced by diamond, as shown in Table 2. However, the durability of sintered carbide tools is much less than that of diamond tools. If we compare the pistons which can be turned without readjusting the tool, we have 1,000 to 1,200 in the case of the faceted diamond tool and 80 to 100 in the case of the sintered carbide tool, i.e., a ratio of 12 to 1.

Again, if we compare the time after which the diamond tool has to be removed from the machine (after several readjustments of a new facet) with that of the sintered carbide tool, we obtain a ratio of 1 to 50.

The data referring to the regrinding of sintered carbide tools, after turning 2,000 to 3,000 pistons, are obviously incorrect, as it is not possible to re-lap these tool tips 25 to 30 times, without regrinding them. Nothing is known of the special cutting edge applied in this case.

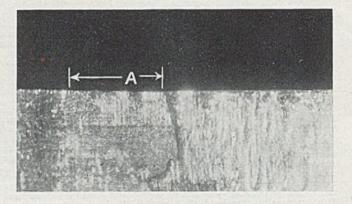




Fig. 15.—Sintered carbide tool edge not diamond lapped. (Equivalent magnification in reproduction 80 diameters.)

It may be added that, in comparison with a sintered carbide tool, the cutting time of which corresponds to a cutting length of about 18.7 miles, the cutting length of a diamond edge is about 1,250 miles, giving a ratio of diamond tool to sintered carbide tool of 67 to 1. This capacity is not reached at the present time by any other material and, moreover, there is practically no upper limit to the cutting speeds attainable.

Although the advantages of diamond turning tools for light metals seem obvious, it is felt that further comparative cutting tests of diamond and sintered carbide tools are highly desirable. These tests could perhaps be conducted on a line similar to those by M. E. Merchant of the Cincinnati Milling Machine Co., comparing a diamond tool and a high-speed steel tool. This investigation comprised speed and feed tests amounting to about 160 measurements. Coefficients of friction and cutting forces were plotted against cutting speeds and feed rates for workpieces of steel, copper, aluminium and brass. Fig. 12 shows as an



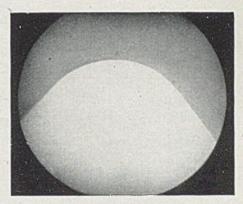


Fig. 17.—Diamond tool edge. (Equivalent magnification in reproduction 80 diameters.)

example the relation of coefficient of friction versus feed rate. For the whole feed range the diamond tool generated less friction on the aluminium workpiece than the high-speed steel tool. Photomicrographs before and after use presented additional information on what had taken place at the cutting edge. Figs. 13 and 14 show a diamond tool and an H.S.S. tool after the test run on aluminium.

It is of particular importance for test purposes and in practice that the sintered carbide tools have really sharp cutting edges. This can only be obtained by using diamond grinding wheels or laps. Unless sintered carbide tools are treated in this way they show a jagged edge (Fig. 15) and, in this respect, seem nearer in appearance to a H.S.S. tool which is not "stoned" (Fig. 16) than to a well-polished diamond tool (Fig. 17).

Fig. 16 (above). — Highspeed steel tool not stoned. (Equivalent magnification in reproduction 160 diameters.)



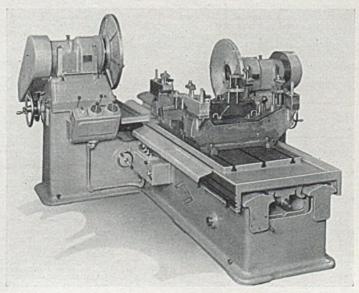


Table 1.-Diamond-turned Piston Skirts.

Angle between axis of work- piece and rear edge of diamond tool		Light-slot profile according to Schmaltz	Profile depth for 0.1 mm. feed†	Surface finish and appearance	
a	1 deg.		0.002 mm.	Satisfactory, somewhat matt	
ь	6 deg.		0.005 mm.	Moderate gloss	
c	15 deg.	*	0.011 mm.	Bad, high gloss	

\* See Fig. 3.

† Surface roughnesses of 1/40 to 1/80 of these values are now standardized in the British Industries. (See "Industrial Diamond Review," Vol. 4, 1944, pp. 29-32.)

Boring of Gudgeon Pin Holes

Gudgeon pin holes on light-metal pistons are finished on special automatic diamond boring machines. When the pistons come to the machine there is about 0.005 in. left in the bore for finishing, and the final size is held to a tolerance of 0.0006 in, for the size of the hole, which must also be true within a limit of 0.0005 in. per in. Speeds of about 5,000 r.p.m. are obtained and it is claimed that the finish is superior to internal grinding, whilst production is twice as fast.

No figures are available for comparing the economy of sintered carbide and diamond boring tools. Conditions, however, are probably similar to those described for turning tools.

A special problem arises in the setting, fine adjustment and balancing of the boring tools. The shank holding the diamond is inserted and clamped radially or at another suitable angle to the boring bar and adjusted by a micrometer which allows of fine radial adjustment of the diamond. Care should be taken to avoid direct contact between the measuring device and the diamond.

If hard-metal and diamond tools be used in the same set up for preliminary and finish boring, good care has to be taken that the hard-metal edge has left the cut before the diamond tool enters it. (Fig. 11.)

Table 2.—Precision Turning of Light-metal Pistons.

		The same of
Tool	Diamond	Sintered car- bide (Widia)
Form of cutting edge	Multiple facets	Specially ground
Cutting time (Standzeit)	4,000 to 5,000 pistons, up to regrinding. 1,000 to 1,200 pistons for each facet	80 to 100 pistons, up to relapping. 2,000 to 3,000 pistons, up to regrinding
Profile depth for 0.10 mm. feed and good condition of cutting edge	0.001 to 0.006 mm.	0.001 to 0.004 mm.
Reflection for the same profile shape and depth	Higher	Lower

Milling of Light Alloys

Milling of light metals with diamond tools for the production of flat surfaces or profiles has been successful and economical. In principle, the action of the individual diamond of a multiple milling tool is the same as the action of a turning tool. A recent development has been the Duplex Fine-milling Machine of John Lund, Ltd. (Crosshills, near Keighley), for machining two parallel and flat opposed surfaces in light alloy to extremely fine tolerances (Fig. 18). Two opposed milling heads are mounted on rigid bases which are bolted to the main bed. The positioning of the heads is obtained by means of narrow guides. The carefully balanced light-alloy cutter heads are 30 ins. in diameter and carry three equally spaced diamond tools on a 28-in. diameter circle. The peripheral cutting speed is 2.500 ft./min.

#### REFERENCES AND BIBLIOGRAPHY

REFERENCES AND BIBLIOGRAPHY

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# Light Alloys in Metal Rectifiers and Photocells

Concluding from "Light Metals," 1944/7/298, a Study of the Selenium Rectifier, and Introducing a Comprehensive Discussion on Photosells and the Role of Light Metals in their Construction

ETAILED study of the electrical charac-Deristics of the selenium rectifier is both interesting and intriguing. Space here only permits of the salient features being reproduced and therefore the attention of readers interested is drawn to the papers already cited, especially those of Williams and Thompson and Richards. Fig. 35 (after Williams and Thompson) refers

to instantaneous resistance characteristics for a

It is also interesting to note that Williams and Thompson state that rectification can be secured from properly made sclenium couples without electrical forming, although, of course, it is not so marked as with the formed ones. They give typical values graphically, as reproduced in

Fig. 37. E. Kipphan gives the curve in Fig. 38 for the static characteristics, forward and reverse,

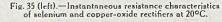
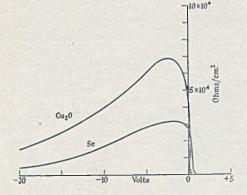


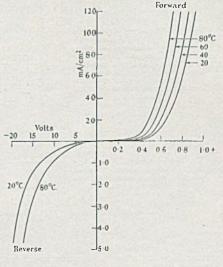
Fig. 36 (below). — Volt-ampere characteristics of selenium rectifier at temperature interval 20-80°C.



temperature of 20 degrees C. It shows curves comparing the resistance of the copper/copperoxide rectifier with that of the selenium rectifier as the voltage is increased, the voltages being applied only for sufficient time for measurements to be taken. The resistance shows a maximum value close to zero voltage in each case, higher for the copper/copper-oxide couple than for the sclenium couple. Fig. 36 (after Williams and Thompson) graphs the voltampere characteristics for the selenium rectifier for a series of temperatures; note the different scales for forward and reverse characteristics respectively. These should be compared with those given for the copper-oxide rectifier. It is seen that the forward curves are equally spaced for equal increments of temperature, whereas the effect of temperature upon the forward characteristics of the copper-oxide rectifier becomes less marked as the temperature rises. Regarding creep effects, Williams

Thompson state that these are generally negative with no recovery during rest. "Ageing" during prolonged service is exceedingly small,

but cannot always be neglected.



reduced to milliamperes/sq.cm. He states that tests indicate that the thickness of the barrier or blocking layer is of the order of 10.3 cm. No heating-up time is necessary to obtain out-put when the load is switched on because, contrary to the thermionic valve rectifier, electron emission is not dependent upon thermal effects. He claims no deterioration of the electrodes during service operation, and therefore the anticipation of indefinite life, claims which are, broadly speaking, confirmed in practice. Further, he states that the only change in service that occurs is a slight increase in forward resistance during the first 10,000 hours of operation. This is then compensated by an increase in the a.c. voltage by about 5 per cent, if necessary.

Fig. 39 (after Kipphan) shows the rectification ratio, for forward to reverse current at low voltages. In actual operation, of course, the

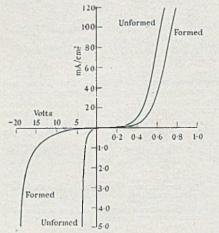


Fig. 37 (above).-Volt - ampere characteristics of formed and unformed selenium couples. (After Williams and Thompson.) It will be noticed that rectification, although more marked with the formed couples, nevertheless can be attained without electrical forming.

Fig. 38 (right).-Static characteristic of a sclenium rectifier disc of effective surface area 1 sq. cm. (After Kipphan.)

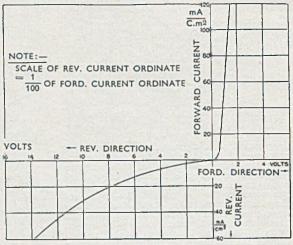
and under these conditions very inefficient operation results.

The recommended ultimate temperature limit for service operation of the selenium rectifier is 70 to 75 degrees C. Loads are usually specified, and designs effected, so that the operating temperature rise does not exceed 40 degrees C., giving the useful temperature of 35 degrees C, as the maximum ambient value permissible. Fan cooling, or convection cooling by design arrangement, as well as cooling fins, are methods resorted to to improve cooling as necessitated in particular equipments. Fig. 40 is given by Kipphan for short period overload, showing permissible time for overloads of various magnitudes, on the assumption that the interval between overloads is sufficient for the cooling of the rectifier, and at least 30 mins. Fig. 41 is used for short cooling periods.

Fig. 42 gives load ratings in relation to ambient temperatures to cover usage at values of the latter about 35 degrees C.

The forward resistance falls with temperature, and Fig. 43 shows this for the range - 30 degrees C. to - 75 degrees C. The variation in reverse resistance of the same range is given in Fig. 44. These are both from Kipphan's paper.

Regarding efficiency of the selenium rectifier, this is defined in several ways. Fig. 45 shows it at full load voltage for 3-phase and for single phase battery and resistance loads.



voltage drop at the load causes a large difference between voltages across the rectifier in the forward and reverse directions. The maximum usual voltage possible in the reverse direction is given at 18 volts. A continuous current density in the forward direction of about 50 milliamperes/sq. cm. is permitted, corresponding to a voltage drop of about 1 volt. Fig. 38 shows the reverse current for a reverse voltage of 18 volts is about 1 milliampere. This gives an effective ratio of 50/1 for forward/reverse current at full load current conditions and under full reverse voltage. At very low voltages, the rectification ratio approaches unity

Fig. 46 shows it as a function of rectified voltage.

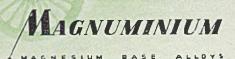
Figs. 47 and 48 are included as of interest in showing the use of the oscillograph for recording the dynamic forward and reverse characteristics respectively of the selenium couple; they are taken from Carole Clarke's paper.

The field of application for metal rectifiers is large and grows continuously; it is, in fact, almost unlimited. Battery charging was one of the first services satisfied. With a series resistance or choke of suitable magnitude, automatic tapering of the charging current to any desired final current is securable. Various

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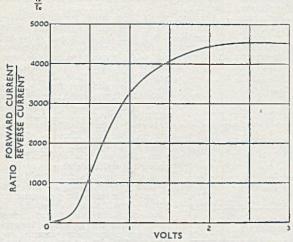
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devices for automatic switching off or transfer to a second battery set-up can be arranged. Other simple applications for eliminating need for batteries followed where direct current was required and could be taken through rectifying systems, with or without smoothing



devices, direct from a.c. mains, Electric motors, inductive loads as for lifting magnets, magnetic brakes, relay operation, switching systems, etc., are examples. For electro-acoustic systems, filters to remove or minimize residual ripple are necessary; applications of this kind fall within the fields of telephonic and radio communications.

Electroplating, and electrochemical finishing and metallurgical processes, perhaps represent the direction in which has development achieved during recent especially in this country. In of the electro-deposition cadmium, nickel, copper, chromium, tin, the precious metals, etc., it is very useful to have individual rectifier systems on each vat or barrel. Automatic plating can be neatly and econo-

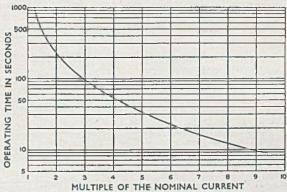
Fig. 39 (above).—Rectification ratio for selenium couple for forward to reverse current at low voltages.

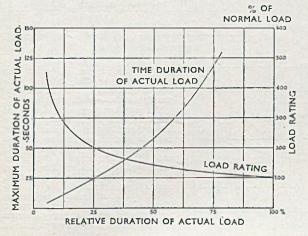
(After Kipphan.)

Fig. 40 (right).—Short-period current overload capacity of a selenium rectifier. (After Kipphan.)

Fig. 41 (below).—Overload rating and operating time for a selenium rectifier on intermittent operation.

(After Kipphan.)



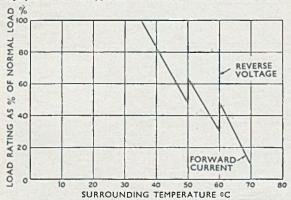


mically catered for in the same way. Electro cleaners and pickling processes, anodizing, etc., all fall into the same category. So do metal recovery processes from acid dipping, pickling and descaling operations, when these are operated electrolytically.

Fig. 49 (after Carole Clarke) shows an electroplating rectifier unit of 6-volt 1,500-amp. capacity, and demonstrates its neatness and compactness. The cabinet of equipment is self-contained, including ammeter and voltmeter, control handles and indicator lights.

Fig. 50 (after Richards) demonstrates the construction of an oil-cooled rectifier. It will be noted that the conventional assembly of the discs in stacks upon a spindle

has been discarded, and replaced by a method which comprises the mounting of the selenium couples flat on metal plates. The latter are of copper to promote rapid heat distribution for cooling by means of the oil. The copper plate could advantageously be replaced by aluminium or aluminium-alloy sheet for the same purpose, Fig. 51 (also after Richards) shows an auto-matic electroplating plant having rectifier equipment of this type mounted on an overhead



Eighteen 1,000 amp. units are runway. involved and they feed all the d.c. requirements of the plant for the preparatory cleaning operations as well as for the electro deposition

Oil cooling is also used for high-voltage rectifiers, and Fig. 52 (after Richards) shows the make-up of a unit for an output of 33 kv. at 70 milliamperes. The overall size is about 3 ft. cube, the tank housing the rectifier, con-

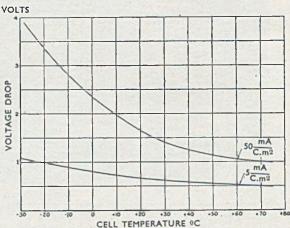
denser and transformer. It is the type used for electrostatic precipitation of dusts, spray, fume, smoke, Modern installations using generally such equipment are designed not merely to eliminate industrial atmospheric nuisances, but at the same time to effect a recovery of a product so as to more than offset the cost of installation, operation and maintenance.

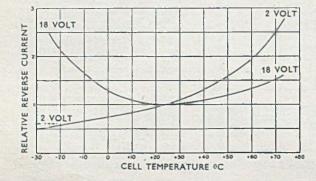
Another important application in a field closely allied to the foregoing is for cathodic protection of installations, especially in large scattered works and across Pipe line installaopen country. tions are a prominent example, and Fig. 53 (after Carole Clarke) shows an apparatus for this purpose. It



Fig. 43 (right).—Forward voltage drop and cell temperature for full load and 1 0th full load. (After Kipphan.)

Fig. 44 (below).-Reverse current and cell temperature for normal voltage and fraction of normal voltage. (After Kipphan.)



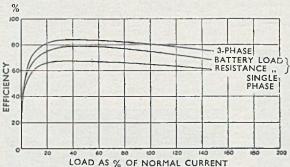


has an output of 14 volts, 100 amps., and is designed for pole mounting, being housed in a dampproof, weather-resisting cabinet.

Yet another large use for metal rectifiers is for starter-equipment for internal-combustion engines. is made possible by the low forward resistance of the selenium couple compactness of the and the assembly. Use of a rectifier starter, especially for difficult engines, means less wear and tear on bat-teries, and minimized recharging effort. Further, it gives constant output even when a heavy current is drawn from it for a comparatively

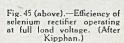
long time. Richards gives the data reproduced in Fig. 54 for a truck starter, comprising a rectifier made in two halves so that by means of a switch either 12-volt or 24-volt output at

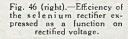
58 (for charging a 20-cell battery, adjustable from 4.5 to 7 amps.) and 59 (for charging two batteries with change-over from 40 volts 48 amps. to 80 volts 24 amps.).

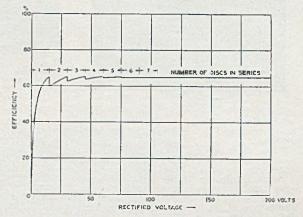


#### Photocells

Photocells, as the name suggests, are instruments for the detection or measurement of illumination, or variations in the latter. Two distinct types will be discussed, the rectifier and the thermionic varieties. In the rectifier photocell, the energy of the incident radiation becomes available as electrical energy in the closed circuit of which the photocell forms a part, no battery being necessary. In the thermionic type, which in its simplest form consists essentially of a diode valve, a potential is maintained







the same kilowatt rating can readily be obtained. A range of battery charging equipments (after Kippham) are shown in Figs. 55 (portable, 2 to 24 volts in 2-volt steps), 56 (watertight design, output 15 amps. 28 volts), 57 and

Table 7.—Sensitivity of Thirteen Selenium Photocells to White Light — Preston's Test Results.

Cell No.	μА	A/lumer
1	32	460
2	24	345
3	12	210
4	16	230
5	12	175
6	8	165
7	8	125
8	27	505
9	31	575
10	29	540
11	20	415
12	74	580
13	23	480

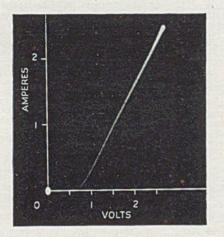
μA = microamperes. μA/lumen = microamperes/lumen. between the two electrodes to promote emission of electrons. One electrode is sensitized, and the emission of electrons varies in accordance with fluctuations in the intensity of incident light, thus rendering possible detection or measurement of the latter.

The rectifier photocells are represented by the copper-oxide and selenium types. The construction of these is not so very different from that of the corresponding rectifiers already

Table 8.—Preston's Test Results for Load Characteristics of Thirteen Selenium Photocells—ratio of photoelectric currents at 500 ohm. external circuit resistance and negligible resistance.

Cell No.	1500/10	Cell No.	1500/1 <sub>0</sub>
1 2	0.36 0.41	8 9	0.78 0.72
3	0.43	10	0.56
5	0.23	11 12	0.55 0.63
6 7	0.24 0.80 (.8)	13	0.77

described. The copper-oxide type does not directly involve the light alloys in the essentials of its construction. However, information will be given appertaining to it for comparison with the other types. The selenium type likewise does not essentially require the light metals, but can use aluminium or aluminium alloy for the base plate, and the more recent



practices favour this metal for the purpose. Information will be given therefore upon the construction and development of the sclenium photocell.

Of the thermionic types, the cæsium photocell is outstanding, and probably the only one produced commercially. One of the alkali metals is essential to its functioning, and cæsium is the one normally employed. Consequently, as much data as is available will be given upon this. The two types, rectifier and thermionic, will be dealt with separately.

#### Metal Rectifier Photocells

Much technical literature exists upon the rectifier photocells, and one of the outstanding papers published in this country during the past decade is that by J. S. Preston, entitled "The Selenium Rectifier Photocell: Manufacture,

Table 9.—Preston's Values for Current Illumination Characteristics for Circuit Resistance Values of 10 and 200 ohms.

Cell No.	R <sub>10</sub>	R200	
1	0.82	0,70	
2	0.79	0.67	
3	0.84	0.74	
4	0.94	0.81	
5	88.0	0.71	
6	1.00	0.95	
7	0.98	0.94	
8	0.95	0.89	
9	0.97	0.93	
10	0.95	0.83	
11	1.00	0.90	
12	0.96	0.75	
13	0.97	0.93	

Properties and Use in Photometry," "Journal of the Inst. of Elec. Engineers," Vol. 79, No. 478, p. 424, October, 1936. This deals in a very lucid manner with the field covered by the title. The same journal, page 435, presents an article entitled "The Selenium Rectifier Photo-Electric Cell: Its Characteristics and Response to Intermittent Illumination," by J. T. MacGregor-Morris and R. M. Billington. This article refers also to the copper-oxide photocell. A more recent contribution to the field is included in the paper on "Metal Rectifiers" already referred to by A. L. Williams and L. E. Thompson (J.I.E.E. 1941). Useful contribu-

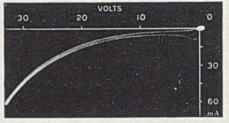


Fig. 47 (left).—Oscillogram of dynamic forward current characteristic of selenium rectifier. Fig. 48 (above).— Oscillogram of dynamic reverse current characteristic of selenium rectifier.

tions, especially with reference to methods of preparation and production of selenium photocells, are contained in the Russian technical Press, outstanding items being the following:—
"A New Method of Preparing Sclenium Rectifier Photo Electric Cells," by I. C. Frievert and N. B. Berdnikov, "The Journal of Technical Physics," Vol. 7, No. 13, 1937. "The Mass Production of Selenium Rectifier Photo-Elements Using Aluminium Metal Base Plates," by T. I. Moldaver, "Bulletin of the Academy of Science of the U.S.S.R.," p. 705, No. 5/6, 1938. All these papers contain a bibliography, that in Preston's article being particularly comprehensive. Abstracts and illustrations are taken from these authorities in the following. The selenium rectifier photocell will be discussed first.

#### Selenium Rectifier Photocell

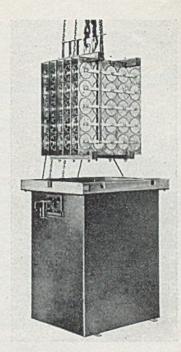
Briefly, the selenium photocell consists of a metal base plate covered with a thin, continuous and uniform film of selenium. This selenium is heat treated to bring it into the

Table 10.—Preston's Test Values on Selenium Photocells for Colour Sensitivity at 2,300°K. and 3,000°K., Indicating Uniformity over this Range.

Sensitivity for 3,000°K
1.07
1.09 1.07
1.18 1.05



right allotropic state, and in such a manner that it is converted into the optimum condition of crystal-The base plate serves as linity. опе connection to the closed The selenium surface is circuit. the one that is exposed to the source of light of particular concern, and across the selenium is developed the resultant potential difference, The other electrical connection to the closed circuit has to be taken from the selenium This is achieved by surface. covering it with a transparent metal film, usually precious metal (gold, palladium, etc.), or of aluminium, applied by cathode or evaporation sputtering This metal film vacuum. is obviously exceptionally thin, but is sufficiently continuous electrically to collect the "current." However, the actual electrical contact is reinforced by metal spraying a collecting ring of fusible alloy such as Wood's periphery. metal around the Obviously, masking is necessary because the transparent metal film must not extend to the edge of the disc for fear of short-circuiting to the metal base plate. Likewise, the sprayed metal ring



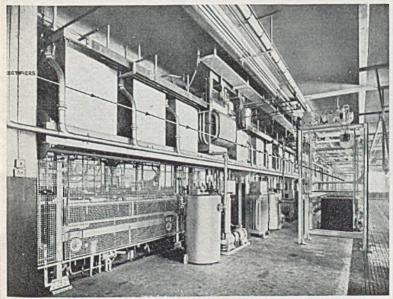
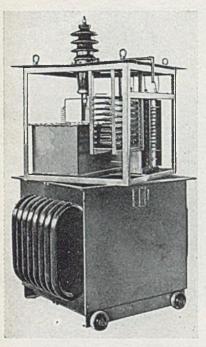


Fig. 49 (above, left).—A sclenium rectifier for electro-deposition, 6 volts. 1,500 amps. (Courtesy W. Green Electric Co.)

Fig. 50 (above, right).—Illustrating, after Richards, the construction of an oil-cooled sclenium rectifier. It will be noted that the conventional assembly of the discs in stacks upon a spindle has been discarded, the sclenium couples being mounted flat on metal plates.

Fig. 51 (above).—Automatic electroplating plant with oil-cooled rectifier of the type illustrated in Fig. 50, mounted on overhead runway.

must not contact the outer edge, yet it must make good contact with the transparent metal film without unduly reducing the effective surface area of the selenium film Finally, the transparent metal film is given mechanical protection by means of a thin spray coating of selected transparent lacquer or varnish, chosen to cause minimum loss of photo-electric efficiency, and to have no deleterious influence upon the metal or selenium This conlayers. struction is shown diagrammatically in Fig. 60. The base plate may be iron or mild steel, in which case it should be protected, preferably with a suitable metal coating, nickel-plating being usual for this. On the other hand, the more recent



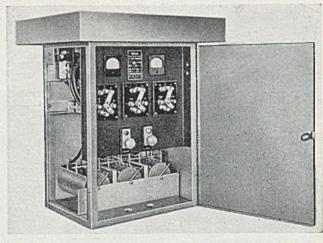


Fig. 52 (left).—High-voltage rectifier, after Richards, with output of 70 milliamps at 33 kv., overall size about 3 ft. cube with rectifier, condenser and transformer all housed in tank. Fig. 53 (above).—Selenium rectifier unit, output 14 volts, 200 amps., mounted in drip-proof, weather-resistant cabinet and designed for pole mounting. Equipment of this design is intended particularly for supplying current for the cathodic protection of plant installations, especially in large scattered works and across open country.

(Courless Electrical Facilities Inc.)

dency is to use aluminium, in which case it may or may not be nickel coated, according to the process adopted for applying the

selenium coating.

Examination of one form of selenium rectifier photocell representing modern commercial production in this country showed the following primary features. The plates were about 1/32 in. in thickness and, rectangular in shape, 1 by 1½-in. dimensions: The base plate was mild steel and the selenium had been applied directly without an intermediate electroplate layer. The front electrode was gold, visually not apparent. The collecting ring of peripheral spray metal was zinc. The reverse surface of the back electrode was also protected from rusting by means of a metal-sprayed coating of zinc. The transparent surface of the gold front electrode was protected by means of a thin layer of a hard lacquer of nitro cellulose base.

For efficiency of output, that is, maximum transformation of light energy into electrical energy, several fundamentals must be given full attention in practice. The same attention is needed for maximum stability, minimum drift and minimum ageing when not in use.

Surface perfection of base plate seems to be the first factor of extreme practical importance, The base plate should be perfectly flat and free from all biemishes. A smooth and almost polished surface is the ideal, providing adhesion of the selenium is not mitigated by excessive polish. Blemishes obviously mean lack of uniformity in the selenium coating, which must be the thinnest practicable in conformity with complete freedom from porosity, pinholes or lack of continuity. Pits, dents and even scratches in the base plate are reproduced in

the selenium coating. They promote porosity and discontinuities in the latter, through which the front electrode will inevitably pass, either during the process of its application or during Initial short-circuits, or potential are thereby caused. The purity operation. short-circuits, are thereby caused. of the selenium, or selenium mixture, must of course be maintained at the predetermined standard. Heat treatment to give optimum structure must be rigidly controlled. Regarding the front electrode, the application of a thin transparent film of good adhesion in intimate contact with the selenium surface evidently entails a scientific operation to be designed and controlled by experts; yet its operation can be reduced to simple control with the capabilities of an ordinary unskilled operator. The thickness of gold must be sufficient to give continuity and to carry the currents produced. Yet it must not be thicker than this, otherwise unnecessary light absorption occurs, and the sensitivity and efficiency of the cell suffers. Strict precautions must be taken during its application to avoid any short-circuiting to the base plate at its peripheral edge, that is, masking must be positive, accurate and effective. The same remarks hold when applying the collecting ring, with the additional warning not to contaminate the transparent gold surface. Over-heating, too, must be avoided during its spraying, otherwise the heat treatment of the selenium may be partially offset. It is for this reason that one of the lower-melting-point alloys, such as already illustrated in dealing with selenium rectifiers, is preferred to a metal such as zinc which, as just indicated, is sometimes encountered in commercial cells. Finally, the lacquering is not a mere finishing operation, but a delicate instrument-assembly process. It must be uniform and thin if the cell sensitivity is not to be adversely affected. At the same time, continuity must be provided and adhesion assured.

If mild steel be used as the base metal, special grades with respect to surface condition should be used. Great care in packing, transport, storage and handling is essential. Rusting must be avoided at all costs; this is by

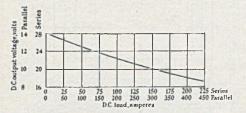
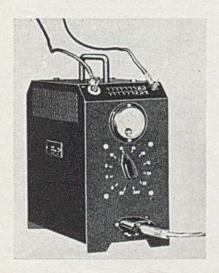


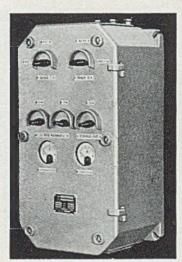
Fig. 54 (above).—Voltage and current of truck starter for internal combustion engine. Fig. 55 (below).—Pertable charging equipment for car batteries 2-24 volts in steps of 2 volts. Fig. 56 (right).—Battery-charging equipment in water-tight container: d.c. output 28 volts, 15 amps. Fig. 57 (below, right).—Equipment for charging or floating a 20-cell lead battery: adjustable from 4.5 to 7 amps.

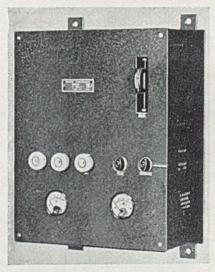


no means simple. Further, protection of the reverse side of the cell, with retention of electrical contact properties, is entailed. This necessitates electroplating in the uncoated stage, for example with a heavy coating of nickel, or metal spraying in the finished condition. With the latter care must be taken not to short-circuit over the edges of the front electrode.

The use of aluminium, or of aluminium alloy, greatly simplifies matters. These metals in sheet or strip form are regularly produced with

almost mirror-like finish; they are packed and protected for transport to safeguard against mechanical damage from grit or by scratching, as well as for protection from atmospheric corrosion. Deterioration is much less likely





than with steel and considerably more easy to prevent. Further, better attention is given to dimensional limits. The material may be used bare or, if desired, it can quite readily be protected by electroplating, as with nickel.

The aluminium-base light alloys thus have much to recommend them. Some of the patents already referred to in the rectifier section also appertain to photocells. Attention in particular is called to B.P. No. 476,790 that covers the use of light alloys of the aluminium series, as well

as the vacuum evaporation method of applying the selenium, B.P. Nos. 497,034, 532,221, 529,957 and 508,180 also appertain, and it will have been noted that they refer to aluminum-type base plates, vacuum treatments for them.

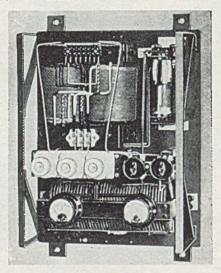
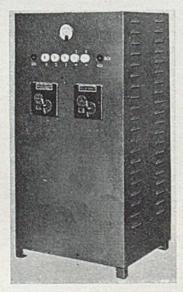


Fig. 58 (above).—Apparatus as in Fig. 57, showing internal details. Fig. 59 (below).—Charging equipment which can be switched over from 40 volts 48 amps. to 80 volts 24 amps. Designed for charging two betteries.



vacuum application of the selenium, and also mention aluminium as the front electrode. Two successive selenium coatings to eliminate weak or porous spots are referred to in B.P. No. 482,239. U.S. patent No. 2,203,328, referring to

selenium rectifiers and photocells, covers a mass method of heat treatment. The discs, comprising metal base plates covered with the layer of amorphous selenium, are stacked with interleaving discs of metal foil having a protective

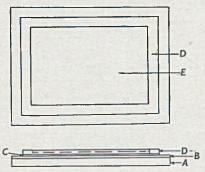
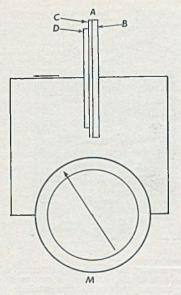


Fig. 60 (above).—Illustrating construction of a rectangle selenium rectifier photocell: A, metal base plate, iron or aluminium; B, thin selenium film; C, transparent metal film, front electrode, gold, platinum, silver or aluminium; D, low melting point cell spray, conducting ring; E, transparent protective lacquer or varnish. Fig. 61 (below).—Showing electrical circuit as in photocell above: A, photocell; B, back electrode; C, selenium film; D, front electrode with collecting ring; M, measuring instrument in series.



layer upon its surface to prevent damage to the selenium by chemical action. Pressure is applied, and heat treatment performed, with this pressure imposed. The heat treatment is continued until the desired degree of crystallization is secured. Thus the operations of perfecting the surface condition and heat treatment are combined in the one process. It is speculated,

too, that the superficially protected foil signifies anodically treated aluminium or light alloy.

It is proposed, now, to present brief abstracts from some of the technical publications in order to indicate the characteristics that are desired or obtainable in rectifier photocells.

Preston's paper reviews the knowledge on sele-

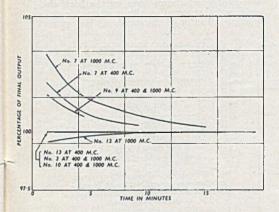
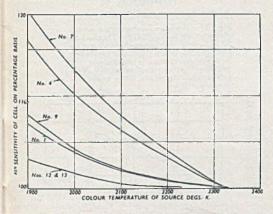


Fig. 62 (above).—Drift curves for selenium photocells.

Fig. 63 (below).—Colour characteristics of selenium photocells for tungsten light.

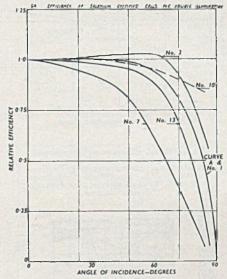
Fig. 64 (right).—Efficiency of selenium rectifier photocells for oblique illumination.



nium photocells available at that time, gives information from the examination of the construction of commercially produced units, describes methods developed at the National Physical Laboratory for making such cells, and gives the characteristics determined on the commercial and laboratory product. The characteristics are then discussed in relation to the requirements essential for accurate photometry.

In introducing the subject, the author points

out that in the selenium photocell energy from the incident radiation is rendered available as electrical energy in the circuit containing the cell, no battery being necessary. Conversion from radiant to electrical energy takes place directly in the cell, but the efficiency of conversion is quite low, being of the order of 0.5 per cent, or less. The actual conversion efficiency for any given cell naturally varies with the spectral distribution of the incident light, but it also varies with the electrical loading in circuit with the cell and the value of the illumination incident upon the cell. The conversion of radiant into electrical energy occurs at the boundary surface of a conductor and a semi-conductor, The conductor is usually a metal. Examples of semi-conductors are selenium and copper oxide. The conversion causes at least an initial transfer



of electrons from the semi-conductor to the conductor across the boundary surface.

In the absence of an external return path for these electrons, the transfer produces changes in potential which oppose further flow and, consequently the net current across the boundary falls almost instantaneously to zero. As a result, a difference of potential then exists between the conductor and the semi-conductor, and the value of this P.D. is a function of the incident illumination. If a return path is provided for the electrons, as through the external circuit, the transfer is maintained and the resulting current is dependent upon the incident illumination and the electrical resistance in the circuit. Provision is made in practice for the return path by means of a second metallic electrode in contact with the semi-conductor. The two metal electrodes are connected electrically in series through the external measuring instrument, as shown diagrammatically in Fig. 61. It is necessary to utilize the thinnest possible layer of semi-conductor in order to maintain the inter448 LIGHT METALS

nal resistance of the cell to a minimum possible

Preston states that these conditions are at best satisfied by a form of cell comprising a thin sandwich of semi-conductor between two metal plates. The "upper" plate can be in the form of a grid, the light penetrating through the holes or interstices to fall on the semi-conductor. Or it may be a translucent metal layer deposited upon the semi-conductor, as by cathode sputtering or vacuum evaporation. It is possible for structure and thickness best suited to the requirements defined.

Preston found little information to assist in the production of good-quality selenium photocells to be derived from published papers or patent specifications, but obtained limited data from commercial cells by a detailed examination of them. He found most manufacturers at that date used iron in some form for the back electrode, and that it was usually roughened in order to assure adhesion of the selenium. He assumed

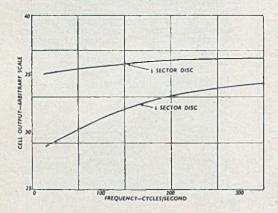
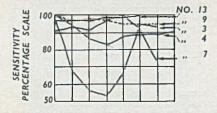


Fig. 65 (above).—Selenium rectifier photocell: frequency/current curves under intermittent illumination of constant mean value of approximately 100 M.C. Fig. 66 (below).-Variation and sensitivity of selenium rectifier photocells along a diameter.



the photo-electric action to occur at the boundary of the translucent electrode with the semiconductor, in which case they are classified as Vorderwand cell. If the semi-conductor is transparent, the photo-electric action can occur at the boundary of it with the back electrode; such cells are classed as Hinterwand type. If a particular construction of cell falls in both cate-gories, the net output of the cell is the difference between the two opposing actions.

The selenium-rectifier photocell is of the vorderwand class, and the capacity of even the thinnest useful layers of selenium preclude any possibility of light from reaching the back electrode. The chief requirements for the front electrode are properties of high electrical conductivity and of low optical absorption. efficiency in practice is attained from the sputtered or vacuum-evaporated metal films, produced under controlled conditions to give the

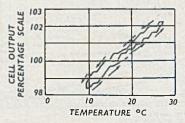


Fig. 67 (above).—Temperature/current characteristics for cell No. 9 with illumination of 50 M.C. and with external circuit resistance negligible.

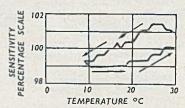
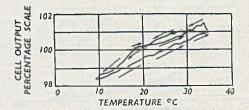


Fig 68 (above).—Temperature / current characteristic for cell No. 9 at illumination 50 M.C. and with external circuit resistance of 1,000 ohms. Fig. 69 (below).— Temperature current characteristic cell No. 9 at illumination of 400 M.C. and external circuit resistance negligible.



the selenium to be applied in the molten or plastic condition and then pressed or rolled to the desired thickness, but refers to the Russian work upon selenium evaporation in vacuo and condensation upon the electrode surface. With all methods, a heat treatment must follow in order to convert the selenium into the appropriate sensitive state. This thermal treatment causes a change in appearance from a glossy black surface to one that is matt grey, the actual appearance of the latter depending somewhat upon the degree of chilling to which the molten or plastic selenium is subjected in the earlier stages. Shrinkage of the sclenium occurs in the final heat treatment, and care has to be taken to avoid peeling of the sclenium film, or the formation of cracks or fissures. If the latter be present, continuity of the front electrode cannot be assured, and there may be the possibility of it passing through the apertures to short-circuit upon the back electrode.

Regarding the deposition of the front electrode, Preston points out that, in addition to the vacuum processes already mentioned, chemical deposition is feasible. He considers one of the noble metals is probably necessary because of the chemical reactivity of selenium, and that gold is frequently used, this one being distinguished by its distinctive colour. Contact to it is made by a sprayed peripheral ring of metal

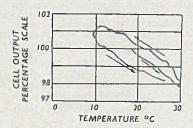
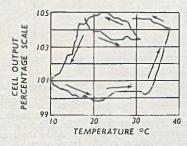


Fig. 70 (above).—Temperature/current characteristics for cell No. 9 at illumination of 400 M.C. and external circuit resistance of 1,000 ohms. Fig. 71 (below).—Temperature/current checked).—Temperature/current of 400 M.C. and external circuit resistance negligible.



near the edge of the cell, it not being obvious whether this is applied before or after the front electrode. However, in some cells, this sprayed ring is dispensed with, and instead contact is made by means of light copper fingers, but this type is usually mounted in a protective casing provided with a glass window. The other type is more general, and a protective coat of lacquer or varnish safeguards it against handling.

Various sizes and shapes of cell are available, the limitation being the resistance of the translucent metal front electrode. If this becomes too great it can outweigh the advantages of the larger light-collecting area. Finally, Preston refers to the possibility of admixtures of related elements to the selenium for the semi-conducting layer, sulphur and tellurium being possible.

Two methods of making selenium photocells have been developed by the N.P.L. They differ, first, in the keying of the selenium to the iron disc and, secondly, in the final state of the surface of the cell.

The first method was due to Barnard. He used a clean steel disc only slightly roughened; on



Fig. 72 (above).—Backwall rectifier photocell: AA, ring electrodes; B, semi-conductor (cuprous oxide); C, metal disc (copper); D, barrier plane, Arrow shows direction of electron flow.

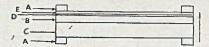
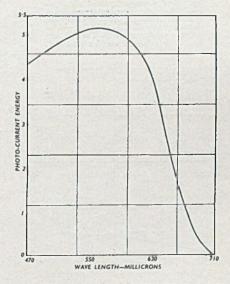


Fig. 73 (above).—Frontwall rectifier photocell: AA, ring electrodes; B, semi-conductor (cuprous oxide): C, metal disc (copper): D, barrier plane; E, metal film, gold or platinum. Arrow shows direction of electron flow. Fig. 74 (below).—Spectral sensitivity, selenium rectifier photocell, Freivert and Berdnikov processes.



this is spread the selenium mixture consisting of go per cent. selenium, to per cent. sulphur in a molten condition. To facilitate the spreading operation, the steel disc, used as a base plate, is held in a recess of suitable depth in a brass plate maintained at the necessary temperature. At the completion of the coating and when there is sufficient of the selenium compound to fill the recess, the surface is rolled over with a cold steel roller. The coated disc is then cooled rapidly for the selenium compound to solidify.

The next operation is heat treating to anneal the selenium, a period of three hours at 165 degrees C. being used. The presence of sulphur in the mixture prevents the latter peeling from the steel plate during the heat-treatment operation. The front electrode is next applied. Gold or platinum is used, and the method employed is cathode sputtering. A deposition period of

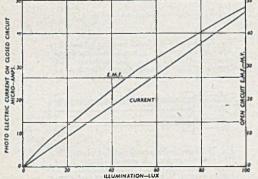
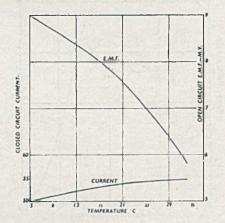


Fig. 75 (above).—Relationship between output and illumination for Freivert and Berdnikov selenium rectifier photocell. Fig. 76 (below).—Temperature coefficient of the Freivert and Berdnikov selenium rectifier photocell. Fig. 77 (right).—Temperature coefficient of the Freivert and Berdnikov selenium rectifier photocell.

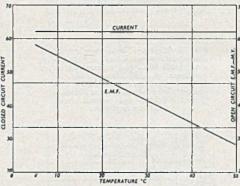


about three minutes with a current density in the discharge of about 10-4 amperes per square cm. is employed. The peripheral edge of the disc is protected by means of an aluminium ring.

The second method, due to Preston, uses clean steel as the base plate, roughened by treatment in hot dilute sulphuric acid. After this it is very thoroughly washed and heated nearly to red heat in order to drive off all traces of grease or moisture. The disc is maintained at an appropriate temperature and sufficient pure selenium

applied to give a thin uniform coating. A clean glass plate (such as a lantern-slide cover-glass), preheated on a hot plate at the same tempera-ture as the disc, is carefully lowered on to the selenium surface until it contacts the whole surface, care, of course, being taken to ensure that no air bubbles are included. Slight pressure is applied to expel excess selenium. The disc, with the glass plate adhering, is chilled by placing on a cold metal block, disc side down. thoroughly cold the disc is annealed for 1-1 hour at 200 degrees C. The glass plate is then split away from the selenium, which it leaves with a smooth specular surface. A ring of fusible alloy is next applied, and then wire leads are attached to this and to the back of the steel disc. The front electrode of platinum is then applied by vacuum cathode sputtering, and with the leads of the cell connected through an indicating instrument outside the vacuum enclosure. This enables the optimum thickness of front electrode to be applied. Finally, the cell is dipped in varnish or lacquer and dried. Matt variety is preferred for maximum response to oblique illumination.

Cells made by these processes have been compared with commercial cells, and it is not



claimed that they necessarily have a high standard of performance. Preston considered that the state of preparation of the selenium surface before application of the front electrode is a very important factor influencing the performance of the finished cell. Also, the conditions of deposition of the front electrode, for example, with reference to the presence of gas, are likewise very important.

In the summary of photometric requirements and properties a comparison is made between the cells made by the N.P.L. methods and commercial cells. They were all circular, and diameters referred to relate to the sensitive area and not to the overail size. In the tabulated and graphical data the various cells are referred to by numerals, thus:—

Cell No. 1.—N.P.L. manufacture, pure selenium, specular surface, platinum-sputtered upper electrode, coated glossy Frigilene lacquer, diam. 42 mm.

Cell No. 2.—N.P.L. manufacture as No. 1, except final lacquer, which was Ercalene

matt, diam. 42 mm.

Cell No. 3 .- N.P.L. manufacture, selenium sulphur, matt surface, platinum-sputtered upper electrode, coated Frigilene lacquer, which dried somewhat matt on the matt cell surface, diam. 38 mm.

Cell No. 4.—N.P.L. manufacture, pure

selenium, specular surface, silver-evaporated

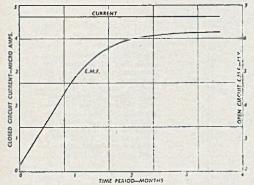
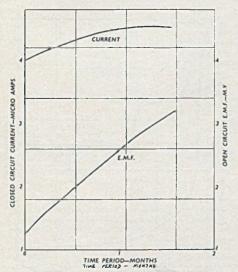


Fig. 78 (above).-Change in characteristics with time Fig. 78 (above).—Change in characteristics with time for the Freivert and Berdnikov selenium rectifier photocell. Fig. 79 (below).—Change in characteristics with time for Freivert and Berdnikov selenium rectifier photocell. Fig. 80 (right).—Moldaver's representation of selenium rectifier photocell: 4, aluminium base plate; 3, selenium evaporated film; 2, hypothetical barrier layer; 1, sputtered gold front electrode.



upper electrode, coated best paper varnish (turpentine), diam. 42 mm.

Cell No. 5 .- N.P.L. manufacture as No. 4,

diam. 42 mm.

Cell No. 6.—Weston Photronic cell in N.P.L. mounting nearly flush with no glass

window, diam. 35 mm.

Cell No. 7.—Weston Photronic cell in standard mounting with glass window, diam. 40 mm.

Cell No. S .- Electrocell, Feb. 20, 1935, diam. 37 mm.

Cell No. 9.-Electrocell, March 8, 1935,

diam. 37 mm.
Cell No. 10.—Electrocell, May 24, 1935, specially roughened surface, diam. 37 mm. Cell No. 11.—Infram cell supplied 1935, dated March 27, 1934, used in N.P.L.

mounting, diam. 35 mm. Cell No. 12.—S.A.F. cell (Large), diam. 57 mm.

Cell No. 13.-Tungsram cell S.41, No. 839. In standard mount, diam, 35 mm.

In this list, where no mounting is mentioned, the cell was used in the unmounted state with electrical connections made by means of small metal clips. The properties considered were as follow:

(a) Sensitivity to white light.-This is not considered of primary importance with respect to photometric accuracy, but the sensitivity of a cell to white light is a measure of the torque available in the measuring instrument and an indication of the type of instrument that should be used. Tests were made at an illumination value of 50 metre-candles (m.c.), using a tung-



sten light-source of colour temperature approximately 2,360 degrees K. Circuit resistance was negligible, and the current output of the various cells and the corresponding figure in microamps. per lumen are given in Table 7. It is noted that they fall in two groups, the first including Nos. 1 and 2 and Nos. 8 to 13, among which there is considerable uniformity, and the

second comprising Nos. 3 to 7, inclusive.
(b) Drift.—The term "drift" denotes change in the output of the cell at constant illumination during the period immediately subsequent to exposure to light, and the cell having been kept in total darkness for some time previous to exposure. Results are shown in Fig. 62. The curves demonstrate the cell output at a given time after the instant of exposure as a percentage of the final value. Curves for two values of illumination, 1,000 and 400 m.c. respectively, are included. For the tests the external circuit was kept closed, and its resistance in all cases was less than 10 ohms. In all cases the photocell was kept in the dark for at least 24 hours before testing. Usually, the rate of recovery in the dark is slower than the drift that takes place upon exposure. Tests were also made using filters to absorb the infra-red rays in order to determine whether the drift was due to the infra-red radiation or to heating Results were negative in both cases. Tests were also made to determine if drift were associated with current passing through the cell, again with negative results.

(c) Load characteristics.-The load characteristic is the curve showing the effect of introducing external resistance into the circuit containing the cell, while illumination is main-tained constant. It is not of direct interest in photometry except in so far as it indicates the effect of circuit resistance on the shape of the illumination characteristic. Table 8 gives the results, the figure given being the ratio of the current flowing when the external resistance is 500 ohms. to that when it was negligibly small. The illumination was maintained at 1,000 m.c. of selective sources or those giving line spectra. The colour characteristics for tungsten light sources are shown in Fig. 63. In this the sensitivity for a colour of 2,320 degrees K. was taken with 100 as the reference. It was observed in many cases that the curves continue

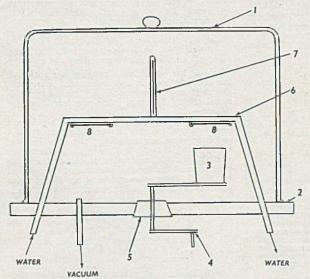


Fig. 81 (left).—Apparatus for application of sclenium by evaporation according to Moldaver: 1, glass bell jur vacuum chamber: 2, steel base plate: 6, hollow disc table to take cooling or heating water; 8, discs to be sclenium; 4, handle for rotating a stand upon which selenium container rests: 5, steel bearing for handle (4).

Fig. 82 (below).—Ageing of selenium rectifier photocells.

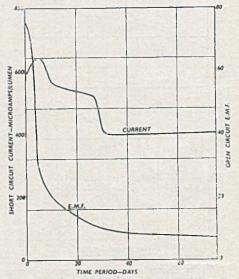
Cells giving the highest ratio are usually found to be the most satisfactory in other respects, such as smallness of temperature coefficient and linearity of response. The superiority of all the manufactured cells over the laboratory product is significant.

(d) Current illumination characteristics.—Current illumination characteristics of a cell are usually expressed graphically, but such curves do not clearly show deviations from linearity of characteristic. Preston, therefore, gives detailed figures in Table 9. This gives the ratio of sensitivities of the cell at two arbitrarily chosen illumination values of 1,000 and 400 m.c. The R<sub>10</sub> gives this ratio for an external circuit resistance of 10 ohms, and the column R<sub>200</sub>, calculated from:—

(Current output at 1,000 m.c.) (400). (Current output at 400 m.c.) (1,000).

For comparison of two unequal illuminations of identical spectral quality, the cell output should be proportional to the illumination to a sufficient degree of accuracy over the desired range. The smaller the range, the less stringent this requirement. The results given show the higher the illumination value, or the higher the circuit resistance, the greater is the deviation of the cell characteristics from the straight line. The best conditions, therefore, result when illumination values do not vary too widely, when they are not excessively high and when the resistance in circuit with the photocell is as small as possible.

(e) Colour sensitivity.—This is considered under two sections, namely, tungsten lamps at different colour temperatures and a comparison



to flatten out at higher colour temperatures, so that from about 2,700 degrees K. to 3,000 degrees K. the sensitivity remains almost constant. Results were also obtained on a number of cells for comparative sensitivities for colour temperatures 2,300 degrees K. and 3,000 degrees K. Results are given in Table 4. Information is given under this section for suitable colour cor-

rection, using a liquid filter containing cupric chloride and potassium dichromate.

In the case of selective and line spectrum sources it was found that different cells differ markedly in their relative sensitivity; a difference not only existing in the behaviour of cells of different types, but cells of the same type show marked dissimilarity. This rather suggests that experience with the technique of making photocells is of primary importance if a uniform and consistent product is to be obtained. The colour sensitivity of the selenium cell is by no means identical with that of the eye. The type of sensitivity curve shows a maximum in the yellow-green region and diminishing values toward the two ends of the visible spectrum. No two cells of one type can be assumed to be alike.

(f) The Cosine Law.—When considering oblique illumination, the effective sensitive surface of the cell should obey the cosine law.

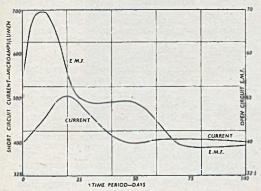


Fig. 83.—Ageing of selenium rectifier photocells; heavy gold front electrode.

According to this, exposure successively to light incident at various angles, the illumination E being adjusted in each case to bring the cell output to a constant pre-arranged value, the value of E should be related to the angles of incidence by the equation:—

 $\frac{E\theta}{\cos\theta} = E_{\bullet}$ 

In this equation  $\mathrm{E}\theta$  is the value for normal incidence and  $\theta$  is the angle of incidence. In practice it is found that for a simple cell with no correcting device the value of  $\mathrm{E}$  found to be necessary for an angle of incidence of  $\theta$  is always greater than shown by the equation. Fig. 64 for various cells shows comparative efficiency for light incident at various angles. The lack of efficiency at oblique angles is partly due, of course, to the increase in proportion of the light which is reflected at the surface of the cell by the glass window or protective varnish coating. Curve (a) is, therefore, included for comparison to show the percentage of incident light which will enter a single polished surface at each angle of incidence as compared with that which will enter at normal incidence (calculated for a refractive index of 1.55). The

identity of this curve with that for cell No. I is interesting. This particular cell had a highly specular surface on the selenium and was coated with a glossy cellulose lacquer of refractive index near 1.55. The efficiency of this cell, therefore, was almost independent of the angle of incidence.

(g) Applicability of Talbot's Law.—Talbot's law, as applied to photocells, states that the current output of a photocell when exposed to an intermittent illumination is equal to the output obtained when the cell is exposed to a steady illumination of the same mean value,

and the same energy distribution.

Preston states that the vacuum-type emission cells almost universally obey this law, but that rectifier cells do not appear always to do so. The NPL-produced cells consistently showed a rise in output with rise in the frequency of intermission of the illumination, the mean value of the latter being constant. The output appeared to approach a steady value for high frequencies, but in general the limiting value was not reached at a frequency of 300 per sec. On the other hand, the commercial cells, Nos. 7, 9, 11, 12 and 13, did not show any such variation in output. Fig. 65 shows the results on the NPL cells, giving frequency/current curves for the selenium rectifier cells when under intermittent illumination of a constant mean value 100 metre-candles. Values using ordinary sector discs of \(\frac{1}{2}\) and \(\frac{1}{2}\) transmission are given over the range of frequency of o to 300 cycles/sec. The increase in output is of the order of 20 per cent, and 7 per cent, for the two discs.

In testing the commercial photocells, sector discs of transmission [1, 2, 1, 1, 1, 1] and [1] were used. Cells 7, 11 and 13 were found to conform to Talbot's law within 0.5 per cent., which is the margin of experimental error. Cell No. 9 showed slight deviation, which was greatest for discs of lowest transmission. Thus for the sector, the deviation was 11 per cent. deficiency in output for the intermittent as compared with steady illumination. Similarly, cell No. 12 showed 31 per cent. deviation for the 1 sector disc. The tests were made at a mean illumination of 100 m.c. This means a steady illumination of 100 m.c. or an illumination of 400 m.c. interrupted by a 1 sector disc, etc., etc.

When using sector discs of this type the intensity of illumination on the photocell during the period of illumination is higher than the corresponding steady illumination of the same mean value. Consequently the cell will not be operating at the same point on the current/illumination characteristic as for this corresponding steady illumination value. It may, therefore, be expected that a deviation from linearity of the current/illumination characteristic will be associated with a deviation from Talbot's law, an expectation confirmed by the results found on cells Nos. 9 and 12. Both showed appreciable deviation from the linear current/illumination characteristic, cell No. 12 being the worse. Both show a departure from Talbot's law, again No. 12 being the worse. Further, the departure is in the direction expected, that of lower effective sensitivity for sector discs of low transmission.

The practical use of sector discs and the application of Talbot's law is only required when it is necessary to measure unusually high

illumination outside the range of the instrument. The tests results indicate that the procedure is sound provided that the cell in question has approximately linear current/illumination. The indications, too, are that when the latter quality is not linear, then the error that results is of the same order as that experienced when using a steady illumination of the same value without employing sector discs.

(h) Uniformity of Sensitivity over the Surface of the Cell.—When the whole surface of a photocell is used, lack of uniformity of sensitivity may not be of undue importance. If a restricted area or only a point be utilized, uniformity becomes of first-rate importance, This is even more critical if the local area or point is not definitely fixed, as may quite con-ceivably be the case. The use of photocells in spectrophotometry illustrates this point; in this sphere they form an integral unit of densi-meters, used for measuring the intensities of spectral lines on the photographic negative. Measurement of flux in the beam of light transmitted through optical systems is another

example.

Typical results from Preston's tests are shown in Fig. 66. The test procedure was as follows:-The cell was mounted on a traversing system whereby it could be moved through measured distances in its own plane behind a screen having a circular aperture of 5 mm. diameter. A constant illumination of 1,000 m.c. was maintained on the latter. The cell was moved in increments so as to traverse the spot of light across a diameter on the sensitive area. Results were expressed by taking the cell output in each position as a percentage of the highest value obtained in the traverse for that particular cell. From the curves it will be seen that one laboratory cell was exceedingly poor in this respect, particularly over its central area. On the other hand, commercial cells Nos. 9 and 13 showed up very well indeed on the tests.

(j) Temperature Coefficient.-A sound knowledge of temperature characteristics of a photocell is obviously important in most applications. It is particularly essential when using an instrument for quantitative measurements over a period of time, or from time to time. However, any study of temperature/output relationship must be extremely accurate, otherwise it can be very misleading. Preston points out the difficulties in making a practical assessment of this quality. He found that the cell must be mounted in an open ring mounting so that circulation of air to both back and front of the cell itself can be ensured. If this is not so, accurate temperature control of the cell is impossible. The cell temperature can then be determined by soldering a thermocouple to the back of the cell; fusible alloy is used for the soldering in order to avoid damage by over-heating. In the case of cells mounted in boxes, the light source must be outside the box so as to avoid its variable heating effect, and screens must be freely used to avoid illuminating anything other than the cell itself. This is necessary in case temperature changes or con-densation of moisture alters the reflectivity of the surfaces inside the enclosure, precautions which are not obvious at first sight, and which may not occur to the unwary.

Precautions respecting the conditions of use of the cell are also important. Considerations of drift render it essential to expose the cell to the test illumination for some hours before commencing the test measurements. circuit for measuring the cell output should be kept unbroken throughout.

Preston discusses his results from curves in which circuit output is plotted against temperature. Readings were taken over a complete temperature cycle, the arrows in the drawings showing the direction of the cycle. The illumination and circuit resistance are stated in

the diagrams.

Figs. 67, 68, 69 and 70 relates to cell No. 9. The following deductions can be made:—The introduction of resistance in the external circuit reduces the temperature coefficient algebraically; the higher the illumination, the greater is the reduction. At an illumination value of 400 m.c. the coefficient is about +0.1 per cent, per degree C. on a circuit of negligible resistance. It drops to -0.15 per cent. per degree C. on a 1,000 ohm. circuit. At an illumination value of 50 m.c. it is +0.15 per cent. per degree C. on low resistance, and about +0.08 per cent, per degree C. for a 1,000 ohm. circuit.

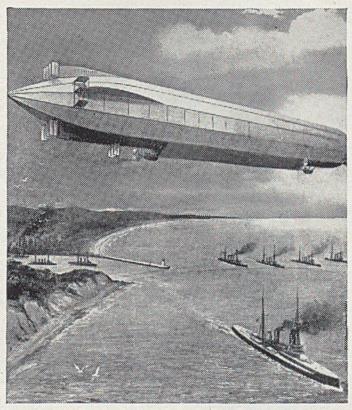
It appears, therefore, that there is an optimum circuit resistance to give zero tem-perature coefficient for any one given illumina-

tion value.

Preston says that the curves also show the presence of temperature hysteresis of some kind. Fig. 71 is for cell No. 6 with an illumination of 400 m.c. with negligible circuit resistance. It shows marked hysteresis and demonstrates the necessity for traversing the full temperature cycle when making tests. The hysteresis was much less marked when the circuit was 1,000 ohms. After studies to determine if the effect was caused by spurious thermoelectric effects external to the cell, Preston came to the conclusion that it definitely was not, and that undoubtedly temperature hysteresis is a characteristic of all selenium photocells.

Preston emphasizes that the results given must not be regarded as representative of particular makes of cell. Considerable variation is found from cell to cell, and a figure for temperature coefficient can only be given as roughly from 0.1 to 0.2 per cent. per degree C. for the better grades of cell when on short circuit.

From the entire research, Preston drew the following conclusions in relation to the product at that date:-The uniformity of characteristics of different cells of one type leaves a good deal to be desired. A small percentage proves unsatisfactory for accurate photometric purposes on account of large drift, high temperature coefficient, unstable output, and change of sensitivity with age. Selection from a batch is thus desirable for precision measurements, this being determined by the degree of accuracy required and generally by drift and linearity of response, but in particular cases by uniformity of sensitivity over the surface, temperature coefficient, or by the conditions of usage. Cells can be selected that satisfy requirements, but average quality is sufficiently distant from the ideal to render precautions necessary. must be taken to avoid misleading or valueless



The first airship built for the Navy, launched at Barrow-in-Furness, May 22nd, 1911

# WHEN WE WERE YOUNG

Nineteen hundred and eleven saw also the launching of Cellon; but that was not a matter of public interest. Yet though it could not be seen at the time, it was a matter of national interest, for Cellon is playing no small part in the country's war effort. The industrial progress of the past thirty-two years is reflected accurately in the development of Cellon.

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results; colour correction may be necessary. Nevertheless, the selenium rectifier photocell has proved its worth and indispensability in commercial practice, and much progress in its manufacture has been achieved since that date.

It is not proposed to make detailed abstracts from the paper by MacGregor-Morris and Billington, which deals with the characteristics and response to intermittent illumination; a few pertinent facts from the introduction, conclusion and discussion will, however, be recorded. A reference to the copper-oxide rectifier will be included, although it is out of place in this section.

The authors refer to the Lange cell, announced first in 1930, with a claim that it gave relatively large currents when exposed to the visible parts of the spectrum. This Lange cell consists of a copper anode and a light sensitive cathode of cuprous oxide. They are made by heating a strip of copper electrically for 20 hours in an atmosphere of oxygen at a temperature of about 1,040 C. The copper becomes coated with a film of cuprous oxide, and this in turn by a layer of cupric oxide. The latter is removed by means of aqua regia, leaving a thin layer of cuprous oxide. The ohmic resistance of the duplex combination in the direction from cuprous oxide to copper is several thousand times as great as that in the direction from copper to cuprous oxide. This unilateral characteristic is stated to be localized in the surface of separation between the semiconductor (cuprous oxide) and the metal. Lange refers to the interlayer as the "sperrshicht," now commonly termed blocking layer or barrier layer, and it plays an important part in the functioning of this cuprous-oxide/ copper photocell, and likewise in all rectifier photocells.

The authors state that the cuprous-oxide/copper cell functions as a rectifier because, under the influence of an electric field, electrons pass more readily from the copper to the cuprous oxide than they do in the reverse direction. But when exposed to light radiations, electrons tend to pass from the oxide to the copper. In short, they assert that when acting as a rectifier, the cuprous oxide is positive and the copper is negative, but when serving as a rectifier photocell, the reverse is the case; this direction of current flow holds good for all rectifier photocells.

When the oxide surface is exposed to light, the photoelectric action takes place at the surface of separation of the cuprous oxide and the copper disc, and the direction of electron flow is from the oxide to the copper, i.e., in the same direction as that of the incident light. The cell belongs to the "back wall" type, or Hinterwand class, because the incident light has to penetrate the semi-conductor to reach the active boundary which is formed on the "back" of the cuprous oxide. This is illustrated in Fig. 72.

The cuprous oxide may be coated by cathodic sputtering (or by vacuum evaporation) with a metallic conducting film, this usually being gold or platinum. This metal layer is designedly very thin, almost transparent, because the incident light has to penetrate this to reach the cuprous oxide. The boundary layer now exists between the sputtered metal

layer and the cuprous oxide. The photoelectric action thus occurs at the front face of the cuprous oxide, and the cell is said to be of the "front wall" or Vorderwand type. The electron flow still occurs in the direction from semi-conductor to metal that is in a direction opposite to that of the incident light. This is shown in Fig. 73.

The development of the selenium photocell followed and MacGregor-Morris and Billington refer to two types, distinguished by their internal resistance values. They are similar in construction and characteristics, one having a very much higher internal resistance than the other. The authors say that essentially they consist of a thin film of grey metallic selenium deposited evenly over the surface of an iron disc. Two electrodes in the form of copper rings are provided, pressing upon the iron disc and the selenium film respectively. The unit is mounted in a phenolic-resin case fitted with a glass window, the whole being evacuated and sealed for preservation against the atmosphere.

MacGregor-Morris and Billington investigated no-load and load characteristics, internal resistance, temperature effect, the Campbell-Freeth compensation circuit and the effect of applied external voltage. In their researches, they used the Weston "Photronic" cells, and the Everett Edgcumbe "Autophotic" cells, these having respectively 2.07 and 1.62 sq. ins. sensitive surface area. Briefly, their conclusions were as follow:—

(a) Current is an essentially more fundamental property of the rectifier photocell than the E.M.F.

(b) Total current generated (external and internal leakage) is strictly proportional to the illumination.

(c) Current in the external circuit is only proportional to the illumination provided that the external resistance is small compared with the internal resistance.

(d) This dependency for linear response upon the value of the external resistance can be compensated for.

(e) For the cells tested, the current output was of the order of 1 to 3 microamperes per foot candle.

(f) Current generated is unaffected by temperature.

(g) Internal resistance of the cell is the only property affected by temperature.

(h) Reduced sensitivity with increasing temperature is due to change in internal resistance and not to a reduction in the current generated.

(i) Response to intermittent illumination is poor because the output is reduced with frequency and the decay curve is delayed.

They suggest at that stage of development, that the rectifier photocell was inapplicable to sound-recording and television, due to reduction of output with increase in frequency, and to distortion of wave-form, but that it was suitable for photometric measurements. Extensive applications were being found in this last field, because of ease and simplicity in making measurements, and fair accuracy is possible if the resistance of the measuring circuit employed be kept low and constant, and if the necessary temperature correction be made. For precision photometry and intermittent sources of illumi-

nation, further development is required. The great advantage of selenium rectifier photocells is the absence of auxiliary apparatus such as a

battery.

Finally, with regard to nomenclature, MacGregor Morris and Billington use the expression "photo-electric cells" as a generic term applying to all devices in which light controls electrical energy and make the following subdivision:—

(a) Photo-emissive cells to include vacuum and gas-filled types of Elster and Geitel classes; these are sometimes referred to as the "alkali cells."

(b) Photo-conductive cells to embrace cells dependent upon the change in resistivity of selenium when illuminated.

(c) Rectifier types of photocell to cover all those dependent upon a semi-conductor

in intimate contact with a metal.

The two U.S.S.R. contributions referred to are of approximately the same date, but they differ with respect to the recommended method of applying the selenium coating to the base metal. Freivert and Berdnikov apply liquid selenium and press with a glass plate, whereas Moldaver describes the merits of evaporation and stresses the use of an aluminium base plate.

Dealing first with the work of Freivert and Berdnikov, these authors refer to the work at a large number of Russian centres on selenium photocells and, to contrast with their own methods, summarize the existing general procedure for producing such cells as under:—

(a) The application of a thin layer of selenium to a metal plate by sublimation of

the selenium in a high vacuum.

(b) The heat treatment of this selenium coating by heating at 200 degrees C. to

210 degrees C, for several hours.

(c) The application of a semi-transparent front electrode over the selenium layer by cathode sputtering of the metal in vacuum. They claim to produce selenium photocells of superior sensitivity by their method, which they also state is simpler for production practice.

Their base plate can be aluminium, iron or glass, metallized by a layer of metal such as The surface of the base plate is brought to a high condition of smoothness by finishing with fine abrasive. A pool of molten selenium is placed on the plate and is uniformly and evenly spread by means of a glass plate. amount of selenium taken and the pressure applied to the glass plate control the thickness of selenium layer. The sandwich consisting of metal-base-plate/selenium/glass-cover-plate heat treated at 200-210 degrees C. forseveral hours. The glass is then removed, coming away quite easily and leaving the selenium with a bright mirror-like appearance, and having perfect smoothness. The front electrode is applied by cathode sputtering in the usual way. For this they use gold, sputtering with air as the residual gas, pressure about 0.10 mm, of mercury, achieving this vacuum with an oil pump. For units having a surface area of 10 sq. cms., they claimed higher sensitivity than with the vacuum-evaporated types, the values being of the order of 400 to 50 microamps/lumen. In other respects, there was close resemblance of properties. Spectral sensitivity is shown by the typical curve in Fig. 74. In this, the photoelectrical energy in empirical current units is plotted against wavelength in millimicroms. The relationship between the photo-electric current on closed circuit with an external resistance of 0.63 ohms, and the illumination intensity in luxes is shown in Fig. 75; the corresponding photo-electric potential on open circuit is illustrated in the same drawing. The authors state that the curves in Fig. 75 closely follow those for selenium photocells made by the evaporation process, but that sensitivity shown in Fig. 74 is superior.

Temperature coefficient was also examined. Values on one cell were as follow when illuminated with an intensity of 20 lux:—On closed circuit, the change in photo-electric current was + 0.22 per cent. per degree for the range of 5.5 degrees C. to 32 degrees C. External resistance was 6.3 ohms. On open circuit, the change in potential was - 1.35 per cent, per degree for this temperature range. These results are shown

in detail in Fig. 76.

Values on another cell for a temperature range of 6 to 47 degrees C, showed a temperature coefficient of nil for the short circuit current and of — 00.67 per cent, per degree for the open circuit E.M.F. This is illustrated for

the full range in Fig. 77.

For maintaining sensitivity, Freivert and Berdnikov found it necessary to coat the sensitive surfaces with a thin layer of clear varnish. They found polyvinyl-acetate solutions and benzyl-cellulose lacquer suitable media. The effect of this varnishing was found to decrease the open circuit potential several fold, and to increase the closed circuit current from 15 to 20 per cent. These effects are explained by the decrease in the quantity of light reflected from the surface, i.e., greater absorption when varnished.

By taking measurements using a Taylor's sphere, the reflection before and after varnishing was 40 per cent. and 27 per cent. respectively. The reciprocal of the ratio of the corresponding absorptions (60 per cent. and 73 per cent.) is 1.22, which closely agrees with the ratio of 1.2 that they found for the photo-electric currents with and without the varnish coating. The decrease in the open circuit potential after varnishing, and its gradual recovery over a period of time, is explained by a penetration of the semi-transparent gold layer by the liquid varnish, this decreasing its resistance. Recovery occurs in time due to the drying-out of solvents.

Regarding stability, the authors give two sets of curves for closed circuit current and open circuit potential measured at intervals over a period of time. The cells upon which data were recorded were not varnished. It will be seen that current remains approximately constant and that potential increases, rapidly at first, tending to become constant after a time. The same phenomena are observed with varnish-coated cells. The curves are reproduced in Figs. 78 and 79.

Freivert and Berdnikov explain the improved sensitivity that they obtain as based upon the mirror-like nature of the surface and consequent lower inherent resistance of the gold front electrode. They give the short-circuit current of the photocell as follows:—

$$I = \frac{AER}{R + R_1 + R_2}$$

where A is a constant, E the illumination intensity, R the resistance of the barrier layer, R, the resistance of the selenium film and Ra that of the gold electrode. They substantiate their hypothesis by taking glass plates (area 20 mm. by 10 mm.) and coating with selenium, one by each method. After heat treatment, gold electrodes were fixed to the ends, and the resistance of the selenium layers measured. In each case it was greater than 10° ohms. They were then gold sputtered side by side, and the resistance of the gold layer determined. On the smooth surface of the selenium produced by their method, the resistance was 54 ohms, whereas on the more rough surface from the evaporation process it was 3,350 ohms. They considered the point established, and, even if not the full explanation, there is undoubtedly very much in the point.

Finally, the authors state that the same procedure can be employed when using selenium mixtures, such as those containing sulphur, tellurium or certain metals, for instance, aluminium. These mixtures are utilized to vary spectral sensitivity and to improve sensitivity generally. As an example, photocells made from selenium containing 2 per cent. of aluminium

are mentioned.

Moldaver's paper is concerned with the commercial production of photocells, it being stated that at that time 20,000 cells had been made by the process described. The paper also contains investigational results of a study into changes in closed circuit current and open circuit potential which occur with time. All the rectifier photocells concerned have an aluminium base

Moldaver considers that many of the troubles encountered in the manufacture of photocells are due to insufficient understanding of the essential semi-conductor material, selenium. Like sulphur, it has many allotropes, and these essential are probably more numerous and less well understood than those of sulphur. Normally, the selenium as applied to the metal base plate is in the amorphous, glass-like form of the vitreous allotrope. After heat treatment it exists as the metallic allotrope. Moldaver's laboratory experiments showed that the condition of the selenium could be profoundly influenced by the conditions of application if vacuum evaporation were employed. This statement holds good even for layers of selenium of identical thickness and the same visual appearance, after-operations, of course, being kept constant. Thus entirely different photo-electric effects were produced. The evaporation conditions that could be varied to produce these results included degree of vacuum, rate of evaporation and the temperature of the base plate upon which condensed. Moldaver was unable to explain these phenomena, finding them very obscure; nor could he explain the difference in behaviour between photocells pro-duced by the evaporation process and those made by the molten selenium method. He assumes them due to isomeric and polymeric differences in the selenium, due to variations in temperature and other conditions obtaining during the coating operation. He reminds readers that the same peculiarities occur with sulphur. Thus flowers of sulphur and rock sulphur are both rhombic allotrope, yet have different physical properties, e.g., solubility in carbon disulphide.

This is due to polymeric condition, the quickly condensed flowers not having had time to polymerize to the eight atomed modification.

Moldaver gives the sectional view in Fig. 80 for the diagrammatical representation of the Item 6 is in effect a table in the (Item 2). aluminium base plate, Item 3 the sclenium film, Item 2 the barrier layer and Item 1 the trans-parent gold electrode. Of various ways of applying the selenium, viz., pressing in the liquid condition, cathode sputtering, electro-deposition and vacuum evaporation, he chose the latter for large-scale production purposes because it

gave most consistent results.

Regarding the process of applying selenium evaporation, the vacuum equipment employed by Moldaver is shown in Fig. 81. It is simple in design and follows the usual lines for apparatus employed in metal evaporation. It consists of a glass bell-shaped jar (Item 1) that fits closely on to a heavy steel base plate (Item 2). Item 6 is in effect a table in the form of a hollow disc through which cooling or warming water can be passed. The discs to be selenium-coated are shown in positions 8, there being eight such holders positioned con-centrically around the disc. The temperature of the base plates can thus be controlled by the water-cooling or water-warming system closely to a desired value. The small container for the selenium (Item 3) is held on a stand by means of which it can be rotated from the external handle (Item 4) which passes through the steel bearing (5).

Actually, the crucible of selenium is heated electrically through a winding of 2 to 40 ohms., using a current of 4 to 6 amps. The crucible using a current of 4 to 6 amps. The crucible may be of silica, although iron can be used because any slight reaction products formed by heating with the selenium are non-volatile. In practice vacuum is reduced to the order of 0.5 mm. of mercury, and then the current is passed around the container of selenium. After a period of 10 to 15 mins, the base plate above the crucible is bright with condensed selenium. The crucible is then moved forward one posi-tion to the next plate, and thereafter moved on at intervals of 2 mins.; when under the second and seventh discs, the current is reduced by 15 to 20 per cent. The rotation is continued in this way for a second coating at 2-min. intervals. The mercury thermometer shown at 7 gives the temperature of the disc and therefore of the sclenium base plates. Temperature gradually rises, and when it reaches 39 degrees C., cooling water is circulated to maintain this

The selenium-coated plates are removed from the sublimation chamber and loaded into a muffle furnace. Temperature is raised to 206 degrees C., and a short heat treatment given. From this process the plates are returned to the evaporation equipment, a second application of selenium made exactly as in the first operation; they are then heat treated for one hour at 206 degrees C.

The peripheral edge of the selenium is next coated with varnish and allowed to dry. The ring of low-melting-point alloy is then applied by spray, but with the selenium-coated disc warm at a temperature between 70 and 75 degrees C. Then, they are gold sputtered in high vacuum, using an electrode voltage of

1,300 to 1,500 volts, and a cathode current of 1.0 to 1.5 milliamps/sq. cm. Finally, they are varnished for protection of the sensitive surface.

From the process description, the operations in Moldaver's process are lengthy and, at first sight, appear cumbersome. In contrast with this view is the fact that large quantities have been produced commercially in this manner. Undoubtedly the practical layout of the operations to hasten flow of work can assist, and the process can be made semi-automatic. Further, the description apparently covers the first version of the procedure, and much can be done to render it more fully automatic, along the lines of small radio valve machinery, a procedure that can eliminate manual control of heating rates and increase the selenium coating portion of the process. Again, tunnel-type ovens electrically heated are so developed to-day with respect to uniformity of heating that the final heat treatments need present no problems, but can be very reliably performed at low cost. The breaking of the vacuum and baking between the two selenium coatings is, however, rather surprising, but presumably essential to obtain a dense, pore-free coating, and one having a flat surface.

Moldaver states that the deposit on each disc is about 0.3 to 0.6 grams. This is a very large variation, and the need for closer control should have been anticipated. He does not mention the area concerned, but assuming from 1 to 2 sq. ins., the diagram of the apparatus indicates something of this order, then the actual thickness of selenium is relatively high, being of the

order of 0.006 in. or more.

The purity of the selenium employed is given,

		Per cent.
Tellurium	 	 0.137
Sulphur	 	 o.10 or less
Copper	 	 0.021
Bismuth	 	 0.059
Iron	 	 0.035
Silicon	 	 0.092
Silver	 	 Traces.
Thallium	 	 Traces.

This corresponds to an ordinary commercial selenium, high tellurium variety, and certainly

is not a special purity material.

Moldaver made a detailed study of the characteristics of photocells over the range of 20,000 produced. He found fairly good photoelectric properties, with short circuit currents in the range 300 to 600 micro amperes per lumen, but experienced rapid ageing. Consequently, he studied the latter with a view to determining the fundamental cause. Fig. 82 shows curves typical of this ageing propensity. The cells used for these tests were protected with polyvinyl acetate varnish after one day. Open circuit e.m.f. and closed circuit current were recorded over a period of 70 days. Constancy was reached after about a month.

To determine if ageing were associated with the occurrence of structural changes in the selenium film, Moldaver carried out an exhaustive X-ray examination of the cells used for the ageing tests. All the radiographs were identical, so that it had to be concluded that the selenium films were structurally identical, that is, no allotropic or crystallographic

changes occurred with storage.

The period at which gold sputtering was applied was studied for the range of three days to two months, then varnish was applied and a further study made over 14 days. No change in ageing properties occurred and, therefore, no clues to its causes were established, other than to confirm that it was a question of changes in the barrier layer. Exposure to chemicals in a limited way was studied, using chlorine, fluorine and acctone, all of which exerted a deleterious influence. Chlorine in one second's exposure reduced the voltage to nil and the current to a few micro amps./lumen. Changes upon exposure to moist atmospheres, dry atmospheres (calcium chloride desiccator) and under complete water submersion were investigated, with the following results:—

(a) Immersion in water over a range of temperatures up to 70 degrees C., for times from half to 5 mins., before or after gold sputtering—no deterioration in characteristics and no evidence of reduced stability.

(b) Immersion in water of varnished and unvarnished cells for periods of 1 to 20 days: some deteriorated in one day, some did not. Those which deteriorated corroded at the periphery, and this was probably the cause of damage. Further periods caused selenium to be attacked, amorphous red spots appearing.

(c) Desiccation immediately after manufacture: normal ageing occurred, and in no case did improved stability result.

Generally, it was concluded that moisture did

not cause the initial rapid ageing.

Finally, the effect of gold thickness was studied. The normal time for gold sputtering was 35 secs.; therefore three successive applications for 35 secs. each were made. He gives his results in the form of the curves reproduced in Fig. 83. These are rather different from the curve forms shown in Fig. 82, but marked improvement in ageing is apparent. Further work is being done in this connection, but the importance of the gold thickness is clearly established.

Moldaver's work is significant and exceedingly interesting. The vacuum evaporation has much to recommend it, in freeing the coating operation of the skill of the operator. The double coating of selenium, cooling of the base plate during coating and the use of aluminium base plates are commendable advances in production methods. He claims, too, greater speed of selenium coating than in any previously devised methods. Obviously much remains to be done, and can be achieved, to simplify these operations. At the same time, further work by Moldaver on higher purity selenium, and then upon the influence of admixtures of tellurium and of sulphur would be welcomed. Again, it is felt that he should consider the influence of thickness of the selenium layer, especially in the direction of much thinner layers.

The vacuum technique employed by Moldaver calls attention to the method of the General Electric Co. of America previously referred to, reference "Steel," September 9, 1940, Vol. 107, p. 49. In this process 100 discs are coated with selenium under the vacuum jar and presumably

given only one coating.

(To be continued)

## ALUMINIUM FOR BEGINNERS

In response to a recent request from an industrial concern for a very elementary "interest talk" dealing with the history and field of application of aluminium, we present here an account meeting all the necessary requirements of accuracy and brevity. It is suggested that it might form a basis for a schools' broadcast

LIFE, in war or peace, would be very different if we had no aluminium. This light metal has taken a big part in engineering production in the last 25 years or so. For example, aluminium has become a commonplace in domestic equipment, not only as pots and pans but as vacuum cleaner parts, in washing machines and the like; the aeroplanes we see in the sky are so obviously aluminium externally that we are often tempted to fall into the trap of thinking they are all aluminium. It is broadly true that the modern aeroplane is only possible because of aluminium, but the aeroplane is an example of how many metals, each selected for its own special properties, are combined by the skilful engineer to work together to give a degree of efficiency unobtainable by the use of any single metal.

Familiar as we are with aluminium these days, the story behind its development and application is not widely known; the story is often unknown to adults, and even many engineers could not tell you how aluminium is won from the earth's crust.

#### Producing the Metal

Ninety-nine years ago aluminium was first produced as a compact material. Before then, all that had resulted from the experiments of the German scientist, Wöhler, was a grey metallic powder. (In 1855 aluminium was sold at about froo per lb.; now it costs about is per lb.) Bunsen, the German inventor of the burner that bears his name, produced aluminium by electrical means in 1854, and the French chemist Deville checked his result later in the same year. Although aluminium was known to exist in extremely large quantities as chemical compounds with oxygen and other elements, no method was known of extracting the new metal from them. Bunsen and Deville succeeded because they used comparatively simple compounds formed in the laboratory. Their raw material was not found in nature; cheap production of aluminium could not come until a method was found of dealing with natural raw material.

In 1886 a young American, Charles Martin Hall, found how to do this, and then the aluminium industry was born. Hall discovered that aluminium oxide could be dissolved in molten cryolite—another natural compound of aluminium—and that when an electric current

was passed through the solution decomposition took place, giving aluminium and oxygen. The great advantage of Hall's process was that all naturally occurring materials were used. Suitable aluminium oxide occurs in North and South America, and France, and is known as bauxite. It is, at present, a strategic material that became in extremely short supply on the German occupation of France.

The industrial production of aluminium was one of the greatest advances of American science; as soon as quantity production could be obtained, the metal ceased to be a laboratory curiosity and became ready to be applied to engineering work. The present famous Aluminum Company of America is a direct descendant of Charles Martin Hall's weak child.

#### Birth of High-strength Alloys

Engineers and manufacturers were intrigued by the low weight and attractive appearance of aluminium, but the pure metal alone was too soft to be of much use. The addition of other metals to form alloys gave increase of strength. It was not until 1907, however, that any great advance was made in this subject. A German scientist, Wilm, produced an alloy containing a few per cent, of copper and under I per cent. of magnesium, and found that when it was heated to 500 degrees C. and quenched in water the alloy became progressively harder and stronger, reaching maximum properties in four on five days. Wilm's alloy, which has become known as Duralumin, was then approximately "as strong as steel," and engineers now began to take notice of the new metal. Incidentally, the subject of heat treatment began to be studied, the phenomenon observed by Wilm being studied by British metallurgists at the National Physical Laboratory in particular.

It is not too much to say that a large proportion of aluminium alloy application is based

It is not too much to say that a large proportion of aluminium alloy application is based upon Wilm's discovery, for similar heat-treatable alloys are universally used for forgings, sheet and extrusions. It is true that these methods of producing shapes in metal were only successful after metallurgists of many nationalities had studied the physical properties of aluminium, for each metal has its working peculiarities. The methods used for steel fabrication are not necessarily applicable to other alloys. In older industries science has often learned a lot from craftsmen, but in the case

of aluminium science had to show the craftsmen what to do to produce useful articles satis-

factorily

In addition to the production of metal shapes by mechanical working there is the other wellknown method which consists of pouring molten metal into a mould of suitable internal form. The mould may be of sand, of iron, or steel, and occasionally of plaster. The simplest casting is of complicated shape as compared with the cylindrical or rectangular block required for forging, rolling or extrusion. Sound castings can only be made if solidification of the molten metal proceeds progressively from point to point, and such even solidification is rendered difficult by change of section. Another difficulty is that many alloys have a long freezing range; that is to say, for a considerable period of the cooling time they are neither truly liquid nor solid: they are pasty. Because of this fact it is often extremely difficult to make sure that the spaces left after partial solidification are completely filled by still molten metal. Foundrymen graphically describe such alloys as "hungry," because castings made from them require a lot of "feeding" before they are full up. Castings that are going to be made into important aircraft parts—on which brave men's lives may depend-are always examined by X-rays before they leave the foundry. Inci-dentally, this radiographical inspection also prevents labour being wastefully used on machining operations.

#### Light Alloys for Casting

Light metal scientists have sought, and continue to search, for the perfect casting alloy. Duralumin might be called the historic alloy for wrought purposes, and, similarly an alloy known as Alpax is a well-established alloy for casting purposes. Alpax consists of aluminium and silicon in the proportions required to form a mixture exhibiting many of the properties of a chemical compound; in particular, the mixture has a definite freezing (and melting) point. Alpax has no extended freezing range, therefore, in the molten state it is very fluid and very intimately takes the shape of the mould form, and, further, very thin sections may be successfully made. It is probably the easiest moulding aluminium alloy for these reasons. Its strength, however, is only moderate.

Many stronger alloys are known, some of them strong enough to replace aluminium forgings on aircraft. The strength of a casting depends to a large extent on the speed with which the molten metal cools to solidification A die casting is stronger than a sand casting of the same shape because the iron of the mould conducts heat away so quickly that solidification is quick; sand moulds have much less heat conductivity. Metal crystals in die cast metal are small because they do not have time to grow, and, in general, the smaller the crystal the stronger the metal.

The biggest advance in foundry alloys resulted from the discovery that small quantities of titanium effectively controlled the grain size, so that as long as the moulding technique necessary to produce sound castings is observed excessive crystal growth is prevented. Castings produced in titanium-bearing aluminium alloys are thus very uniform in mechanical properties as the physical conditions due to different rates of solidification are minimized. Not more than one-fifth per cent. of titanium is required to obtain this advantage and, it is worth pointing out, this small titanium addition was a British invention.

#### Aluminium in Engineering

Aluminium alloys are now accepted as engineering materials. Alloys have been developed for such special purposes as maintenance of strength at high temperatures for use in internalcombustion engines, and pleasing untarnishable appearance for architectural structures and decoration. It is not too much to say that there is an alloy for every requirement, whether it is cheapness, strength or appearance.

The metals that are most difficult to extract from the earth are usually the metals that corrode most easily. It might be anticipated that aluminium would fall into this class, but the chemical expectations are modified, so to speak, by the presence of a film of great protective value which is spontaneously formed by the action of oxygen upon the metal. minium alloys do not corrode at all in normal

atmospheres.

Some alloys have been successfully developed for sea conditions; lifeboats are frequently constructed of them and, after the war, when aluminium is free for anyone to use again, or in the more distant future, it is likely that a large part of the superstructure of ships will be made from the specialized aluminium alloys,

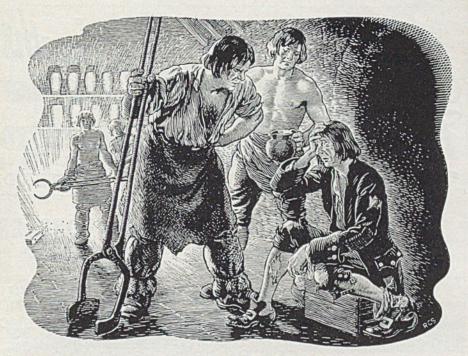
The natural oxide film giving adequate protection for many purposes may be increased in thickness by means of an electrical processing called anodizing, when greater protection is required. Anodizing, again, is a British invention. The anodized film is of a curiously attractive translucent appearance by itself, but it can be dyed simply giving further possibili-ties of intriguing finishes of any colour. The film is also of great assistance in promoting adhesion and conferring superior protective powers when painting or lacquering is specified.

#### Problem to be Solved

Many difficulties have been encountered and solved since Charles Martin Hall developed his method for aluminium production. one problem, however, remains for present or future metallurgists to work on, for molten aluminium alloys absorb hydrogen very readily, this gas being evolved on solidification. Great care must be exercised during melting, therefore, to prevent hydrogen pick-up, or pinholes caused by hydrogen will be found throughout the mass of solid metal. In spite of this everpresent difficulty, perfectly satisfactory castings and forgings in aluminium alloys are produced in immense quantities. The Air Forces of the Allies provide a confirmation of this, but lightalloy metallurgists are looking forward to the day when, the war won, they can extend the uses of their metal to the arts of peace.

In innumerable fields aluminium can play its part in reducing unnecessary weight and making

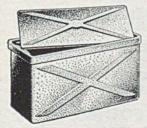
the world lighter and brighter.



## Mr. Huntsman loses his secret

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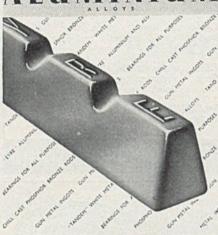
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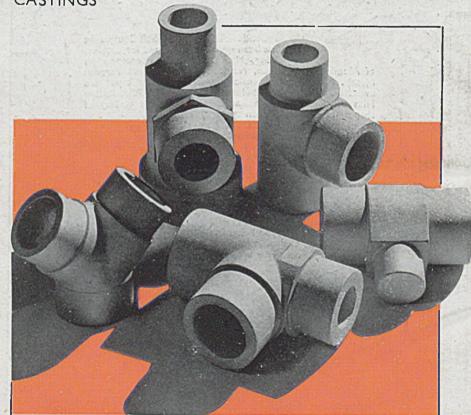
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