(5) 540300

(1A)

404485

AD No. 404485
ASTIA FILE COPY

(6) "PROPERTIES OF FERROMAGNETIC MATERIALS INSIDE THE MATRIX OF ANODIZED ALUMINIUM COATS".

(7) NA
(8) NA
(11) 31 Dec 6
(12) 32p.
(13) NA
(14) NA
(16) NA
(17) NA
(18) NA
(19) NA
(20) U
(21) NA

(10) by
Name of Contractor: Dr. J. M. Alameda.

(15) Contract ~~Number:~~ DA-91-591-EUC-2044.

Period covered: 1~~st~~ January ~~1962 to~~ 31~~st~~ December 1962.

(9) FINAL TECHNICAL REPORT

b.c.

MAY 21 1963

TISIA A

The research reported in this document has been made possible through the support and sponsorship of the U.S. Department of the Army, through its European Research Office.

ASTIA AVAILABILITY NOTICE
QUALIFIED REQUESTORS MAY OBTAIN COPIES OF THIS REPORT FROM ASTIA.

3.60

"PROPERTIES OF FERROMAGNETIC MATERIALS INSIDE THE MATRIX OF ANODIZED ALUMINIUM COATS".

(Contract Number: DA-91-591-EUC- 2044).

- SUMMARY -

Anodic coatings have peculiar structural, electrical and mechanical characteristics. In coatings obtained with acid electrolytes, a porous honeycomb structure develops that if filled with dyes are of use for ornamental or identification purposes.

Pores could be filled with semi-conducting, fluorescent or magnetic materials, possibly giving place to new applications for aluminium. If ferromagnetic materials were impregnated inside the pores, a parallel array of magnetic tiny rods could be obtained that in reason to its particular geometry, could become close in nature to the so-called ESD or elongated single domain particles. It perhaps should give place to a peculiar magnetic behaviour and perhaps to a material for magnetic memories or other related devices. The preliminar study of such a possibility is the main objetive of the present work.

Impregnation with solids has a number of limitations because of the small diameter of pores, in the order of 100 to 300 Å. A technique has been developed by the author doing possible an impregnation more easy and rapid than the classical ones, where the solid is formed only inside the pores. For ferromagnetic materials use has been made of solutions of organic or inorganic salts that by thermal demolition can give place, theoreticaly, to ferromagnetic oxides, carbides or free metals.

Unfortunately anodic coatings are very sensible to heat treatments, because of thermal shocks and develop, above 100°C, crazes and fisures deteriorating the samples. Some thermal treatment was carried out til near the melting point of aluminium (720°C) and while it was observed that magnetic susceptibility increased with temperature treatment no ferromagnetic phase was detected. Heat treatment with reducing atmospheres, that could develop such phases to lower temperatures, have been not carried til present.

Other experiences were carried out by using Kanigen solutions (Brenner process for electroless nickel plating) with no positive results with the propietary solutions used. Thermal decomposition of nickel carbonyls was not possible to be done because difficulties of procurement and transport regulations for this type of coumpounds.

From previous experience of the author, coatings were impregnated with semiconducting substances such as CuS, which impart and electrical conductive character to the oth otherwise very high isolant nature of such coatings. In these conditions they can be plated by using a suitable nickel bath.

Two different types of nickel films were obtained, depending if electrodeposition is done with or without a paint diaphragm lyed out on the anodic coating. In the later case, with no diaphragm, nickel is deposited on the anodic coating as a normal nickel film, with so scarce adherence that is very easy detached. No nickel is deposited inside the pores.

In the case that a diaphragm is used, a dark-grey nickel film is obtained which looks as forming a continous deposit from the top of the coating to the underlaying aluminium. Unfortunately it has been demostrated, that when the entire coating is removed from the aluminium support, two different layers are obtained : One, the nearest to the top, contains practicaly all the plated nickel and a second one with very few traces of nickel at all, being this a symptom that nickel deposits rather between the anodic coating and the paint film than inside the pores.

The magnetic behaviour of nickel films as plated on copper, brass or on conductive coatings was studied by doing use of a coarse version of a Neugebauer torsion magnetometer, whereby determinations on Ms, magnetic anisotropy and Curie Points were made. No fundamental differences were found between the studied samples.

In order to determinate values for Hc and Br of such films, an oscillation magnetometer was developed and hysteresis loops of several samples were obtained by this way. The distorted and out of value loops obtained are a clear symptom of the limitations of the measuring method or that a more sophisticated theoretical treatment is required in order this type of installation can be used for such purpose.

On the light of the results obtained up to present, the future work is being directed to insist in to find a suitable and reliable way to impregnate the pores with nickel or other ferromagnetic metals, by using metal electroless plating processes such as the Brenner or by thermal reduction under controlled atmosphere of suitable organic or inorganic salts.

European Research Office
U.S. Department of the Army.

FINAL TECHNICAL REPORT
Contract Number: DA-91-591-EUC-2044.

" PROPERTIES OF FERROMAGNETIC MATERIALS INSIDE THE MATRIX OF ANODIZED ALUMINIUM COATS".

Dr. J. M. Alameda,
Marconi Española, S.A.
Madrid. Spain.

Introduction.

Detailed study of the structure of anodic coatings on aluminium carried out by several workers (1,2,3,4,5) and specially by Keller, Hunter and Robinson (6), has shown that in anodizing electrolytes containing sulfuric, phosphoric, oxalic or chromic acids (which appreciably attack the forming oxide), the amount of oxide formed is usually a function of current and time and, that because of a process of simultaneous formation and solution of the coating, a cellular coating, with each cell having at its center a pore, a few Angstroms in diameter, is always produced (Fig. 1).

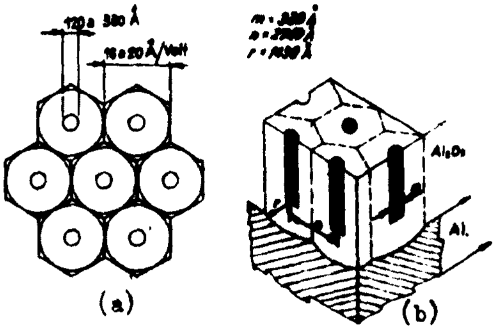


Fig. 1. Schematical view of structural cells in anodized coatings. (6).

The existance of such pores in the coating has made possible to dye the coats with different colours and to give, in conjunction with other physical characteristics of the coat (hardness, abrassion resistance, high adhesion etc.) a wide range of ornamental applications for aluminium and some of its more important alloys.

Keller and ad. (6) have been able to confirm qualitatively with the use of electron microscope and special replica techniques, that each cell is a hexagonal prism with an spherical shaped base containing a central star-shaped pore which does not penetrate the full lenght of the prism.

In other hand, quantitative measurements carried out by the same workers, about cell dimensions as affected by different operating conditions of anodizing with several electrolytes, established that cell size and barrier thickness are primarely a direct function of the forming voltage, and that pore diameter is only a function of the electrolyte and independient of applied voltage. In table I are given the obtained values for wall thickness and pore diameters with different electrolytes.

Table I. Pore diameter and Wall thickness of oxide coatings.

Electrolyte	Pore Diameter Angstrom Units.	Wall thickness Angstrom Units.
4% Phosphoric Acid, 75°F.	330	10,0
2% Oxalic Acid, 75°F.	170	9,7
3% Chromic Acid, 100°F.	240	10,9
15% Sulfuric Acid, 50°F	120	8,0

From these studies Keller and ad. were able to draw out a working picture of the structure of the anodic coat as shown in fig. 1 b, which gives dimensions for a coat obtained at 120 volts, with a 4% phosphoric acid electrolyte. From this model the cell size and the pore volume per cent of any particular coat can be calculated by the expresions:

Cell size = $C = 2W.E + P$ and Pore Volume in % = $V = 78,5\ P^2/C^2$,

where W is the wall thickness in Å/volts units for each particular electrolyte, E the forming voltage and P the pore diameter (assumed to be circular). It is clear from the above expressions that pore volume decreases with increasing forming voltage as it can be seen in fig. 2.

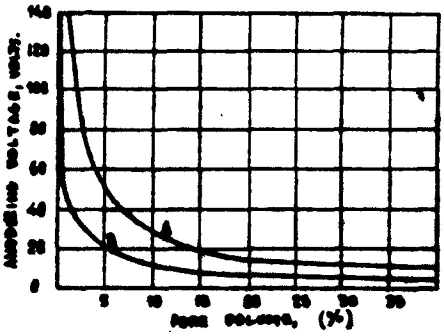


Fig.2. Relation between pore volume and forming voltage. (A) Phosphoric Acid.(B)Sulfuric Acid.(6).

It is interesting to notice that the bottom layer or blocking barrier, follows for thickness the same rule with applied voltage as the wall thickness of the cell. In both cases, it has been found that a superior limit of 14 Å per volt exists, the actual limit being less by a factor depending on the nature of the electrolyte.

Although the chemical nature of the anodic coating is rather complex and amorphous, it is known that is mainly composed of aluminium oxide which final crystal structure depends on the anodizing variables, the metal itself and the post-treatments after anodizing.

It is well known that the physical characteristics of anodic coatings are unique when properly obtained. Apart from hardness and high abrasive resistance, they present an high electrical isolant character, with resistivities in the range of $10^{14} - 10^{15}$ Ohms.cm and breakdown voltages in the order of 40-50 volts/micron. Pullen (7) has found that breackdown voltages for coats 5-10 microns thick, follow a lineal law, while in thinner coatings an exponential law is dominant.

The particular disposition of pores, in a parallel array, vertically disposed to the metal-base, in the same fashion as an honeycomb structure, the existance of a thin blocking barrier at the bottom of the coat, and the possibility to change , within certain limits, the parameters of the cell, makes this type of structure a very interesting one to study its behaviour when the pores are filled with different materials other than dyes as usually is made.

For instance, the author has been able to discover that the highly electrical isolant characteristic of the coating, dissapears when the pores are filled with substances like copper and silver sulphides. Fig. 3 shows the current-voltage curves for coats impregnated "in situ" with CuS by ussing different concentrations of copper sulfate solutions, and posteriously treated under the action of gaseous sulfhidric acid. The conductivity is no lineal depending on polarity. Direct and reverse values are given.

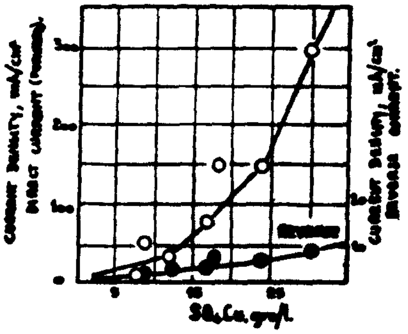


Fig. 3. Current-voltage curves for anodic coatings impregnated with CuS. Direct (anodic coat positive) and reverse currents.

Posterior studies shown that only a few compounds are able to impart this conductive character to the coat. The differences to CuS being of course considerable as shown in fig. 4.

The rectifying character found for CuS and AgS impregnations increases

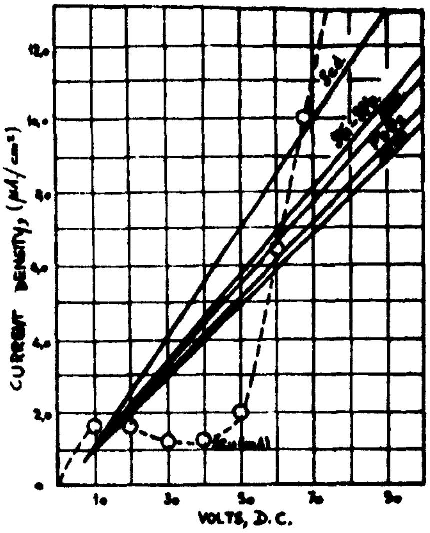


Fig. 4. Conductivities for different compounds impregnating an anodic coating. Note change of scale for CuS. Values for AgS are nearly a third of CuS ones.

after a previous electrical forming treatment as shown in fig. 5, the change from A to B taking normally place with a sharp burst.

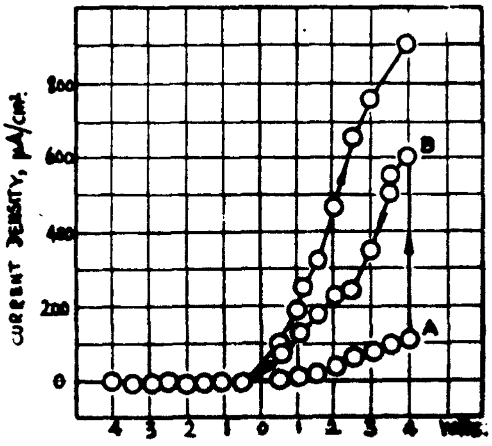


Fig. 5. Rectifying effect and formation process for an anodic coating impregnated with CuS. (Higher conductivity for impregnated coat as positive).

Fig. 6 is a record obtained on a milliammeter low speed Elliot recorder for a coating impregnated with AgS. On the right, side a current-voltage curve has been traced until 120 volts, in both directions, without breackdawn.

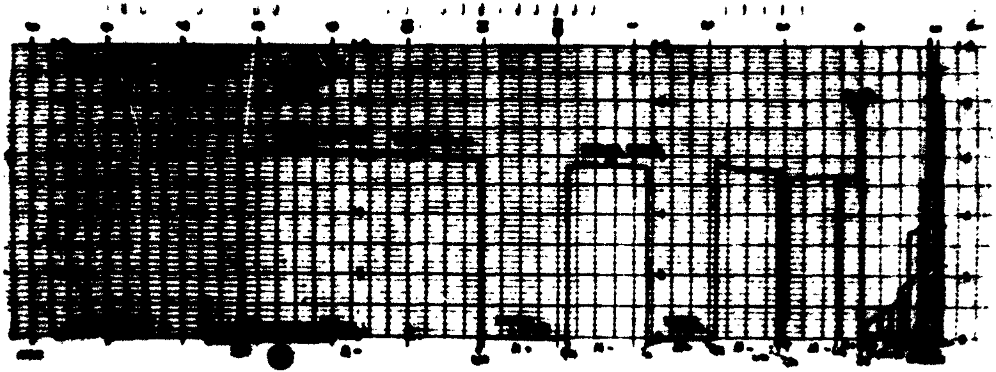


Fig. 6. D.C. direct and reverse values for an anodic coating impregnated with AgS. On the right side, current-voltage curves.

The high conductance imparted by this way to anodic coatings, makes it possible to electroplate, from suitable baths, nickel, copper, silver, etc. on the coat. The plate so obtained is normally very little adherent and can be easily detached, being this one a good method to obtain foils of metals .

On the contrary, if electrodeposition takes place through a suitable diaphragm, as for istance, by lying paint or gelatin on the anodic coat, the metal is deposited inside the pores, resulting a nickel coat with a very high adhesion. In both cases, the conductivity of the resulting coats is similar to that one of the bulk deposited metal, it is totally electronic in character, the rectifying effects being removed.

The performance of these complex coats, abrief resumeé of it has been given here, opens new fields of possible applications to anodised aluminium, the following being the most important:

1. Printed circuits for heavy-duty moving contacts. Fig. 7 shows a sample that has been working for more than five millions of cycles without appreciable deterioration.

2. Dry electrob capacitors of aluminium. Some work is now being done in this sense (8).

3. A printing method, without ink, by using suitable electrosensitive paper. Printing stencils to be prepared by photoetching the conductive coat. At parts where nickel, or copper, is removed, the anodic coating remains with its very high isolant character.

4. Electroluminescent panels by impregnating the pores with suitable materials.

5. Luminescent pictures by using the "Fotoanodizado" Process (9) or other similar and by impregnating the remaining empty pores with fluorescent materials. Pictures glow very bright when under ultra-violet light.

6. Ferromagnetic panels by impregnating the coat with magnetic materials. Because of the special estructure and disposition of pores, tiny rods

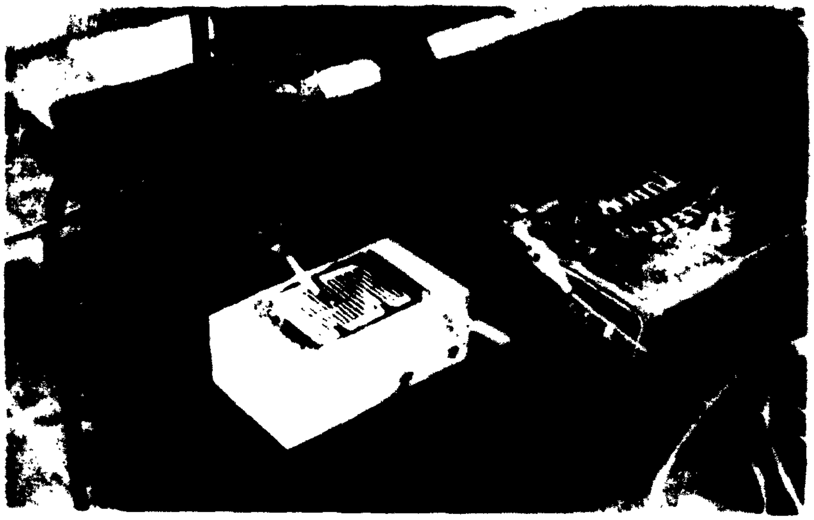


Fig. 7. Heavy-duty printed circuit done on an anodic coating impregnated with CuS and electrodeposited nickel.

of ferromagnetic materials could be obtained in a parallel array within the matrix of the oxide coat, which because dimensions, colud bring elongated single domain particles, that as a conjunt should be responsible for high coercitve values and square hysteresis loops. The main objetive of present contract, is to study these possibilities.

Part I -. Anodizing procedure.

Anodizing, as nearly all the electrochemical processes is subjet to a series of variables like temperature, time, voltage, current density, quality of metal, type of electrolyte, etc. that it is very important to keep all these variable within tight limits always that reproducible results are required.

An anodizing installation , able to keep under control the above variables has been built for this purpose. The cell used can hold any type of acid electrolyte and can be maintained within plus minus 0,5°C by using a thermostatic bath with a sensitive mercury relay who commands the heating and cooling system. Details of the anodizing installation can be seen in fig. 8.

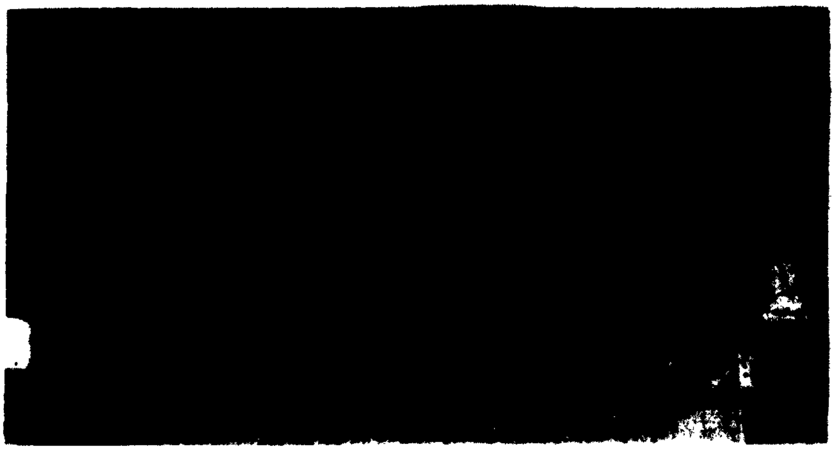


Fig. 8. General view of installation used for the work under this contract. On right side, the anodizing installation. Left side, torsion magnetometer. Center, oven and auziliar equipment.

A is the heating bath, B the mercury relay, C the solenoid valve controlling the flow of cold water, D a heat eschanger (not visible)to be loaded with ice when required and E the stirrer connected to the shaft of the motor by a flexible plastic sleeve closed at bottom with an small rod of glass. Air agitation is also provided.

Experience gained with this installation stablished that for anodising [illegible]peratures between 15 to 25°C and anodizing surfaces not greater than 1 [illegible] if proper setting of mercury relay is secured, a thermal equilibrium is [illegible]ched where temperature variations in the electrolyte remains within pl[illegible]nus 0,5°C, specially after anodising two or three dummy samples.

In order to keep the time of anodizing within the required values a time switch F has been incorporated, who at the end of anodising lights a lamp and excites a bell.

Control de current density is secured by recording current on a low speed Elliot recorder G, which gives also a permanent information of the exact time spent in anodizing each sample.

The quality of metal used has been 99,95% aluminium in plates of 100 x 50 mm. 0,8 mm thick. Also rods of 5 mm diameter, of a lower quality has been used.

The squences of anodizing are summarized in table II.

Table II.- Operative sequence for anodizing.

Step	Operation	Procedure	Product	Remarks.
1	Degreasing	Vapour	Trichloroetilen	-
2	Cleaning	Electrolytic	Na_3PO_4	Warm solution.
3	Rinsing	Dip	Running water	Cold.
4	Neutralizing	Dip	7% SO_4H_2	Cold.
5	Rinsing	Dip	As in 3	
6	Conditioning	Electrolytic	PO_4H_3,N-Butanol	60°C.
7	Rinsing	Dip	As in 3.	
8	Activation	Immersion	CrO_3, PO_4H_3	80°C, 10-20 min.
9	Rinsing	Dip	As in 3.	
10	Anodizing	Electrolytic	15% SO_4H_2	18-22°C.
11	Rinsing	Dip	As in 3.	
12	Neutralizing	Dip	10% NH_4OH	Cold.
13	Rinsing	Dip	As in 3.	
14	Conditioning	Dip	5% NaCN	Cold.
15	Rinsing	Dip	As in 3.	
16	Drying	Oven	Dry air	1 hour at 150°C.

In our anodizing procedure several special steps has been added to secure the best absorbing properties and a reproductible structure. Step 5, is a short electrobrightening treatment to remove the distorted surface layer of metal, always present from previous manufacturing processes. Step 7 is required to remove the pasivation left by the conditioning step. Other conditioning treatment is given at step 14 in order to remove any loose amorphous substance left in the pores by the anodizing process. Finally, step 16, heat treatment in absence of humidity, is given to improve the absortion power of the anodic coating and to promote its crystalisation.

During the time covered by this report, only anodised samples in 15% sulfuric Acid have been prepared. Anodizing voltages normally used has been 10 - 11 volts D.C. , temperatures from 18 to 22°C and an standard time of 45 minutes of treatment. The characteristics of cell structure obtained in these anodizing conditions, are aproximately, according the model of Keller and ad., the following:

Pore diameter............	120 Å.
Separation between pores.	180 Å.
Barrier layer............	80 Å.
Pore volume	10-20%
Total thickness (45min.).	10-15 microns.

With such structural dimensions it is theoreticaly possible, by impregnating the full lenght of each pore of the coating with a ferromagnetic material, to obtain a parallel array of numerous rods, aproaching the ideal characteristics of elongated single domain particles, with lenght to diameter ratios near 1000 where very particular magnetic behaviour could be spected.

Part II -. Impregnation Procedure.

Several methods can be used to impregnate the oxide matrix with magnetic materials. The fundamental problem is the difficulty, because of the very small diameter of pores, of putting any type of solid substances inside them.

To be succesfull it is neccesary to fill before the pores with a liquid substance by immersing the anodised sample into a true solution. Then each pore performs as a chemist tube of assay where, hydrolisis, thermal descomposition or chemical reactions, does it possible the formation of a solid substance "in situ". Details for a very suitable method for impregnation have been given by the author(9).

Unfortunatelly not all possible solutions are suitable for this purpose, because of attacking the coat or because in reason of causes not yet good understood they are unable to enter the pores, and if the impregnation with ferromagnetic substances is contemplated only a few possibilities can be considered.

Despite these limitations, several ways can be used, at least theoreticaly, to achieve the purpose, as for instance, the thermal descomposition of metal nitrates, nitrites, formiates, oxalates, ferricyanides or other organic metallic compounds as acetylacetonates and carbonyls. Fig. 9 is a collection of anodised aluminium rods containing iron ferricyanide obtained in situ by impregnating the coat with a mixture of solutions of amonium ferrous citrate and sodium ferricyanide, that after exposure to light and "development"with water, has been treated at different temperatures for two hours. This type of solution was selected because the amount of solid substance laid into the pores can be easily controlled with time exposure to light and because the final product of descomposition, at least when in bulk form, is constituted by a mixture of ferromagnetic oxides and carbides.

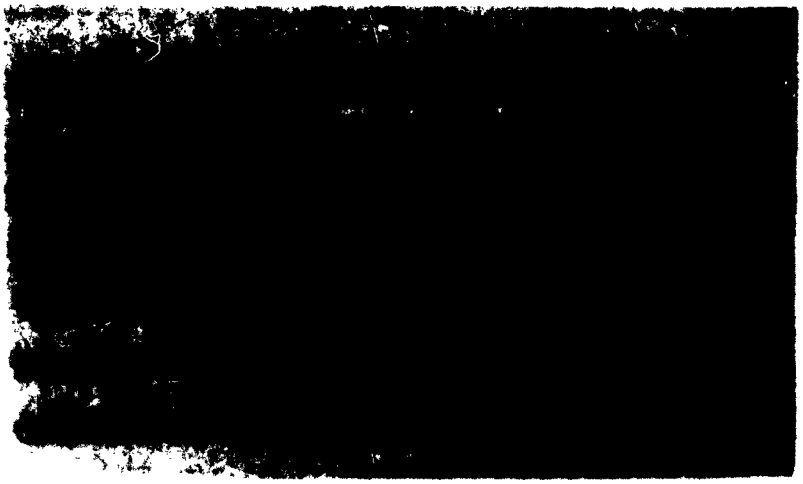


Fig. 9. Anodized aluminium rods impregnated with iron ferricyanide, treated to different temperatures for two hours. The two first rods are bare aluminium and plain anodised aluminium, respectively.

The rods were measured by a Guy method in a magnetic balance at Laboratory of Magnetism, Madrid University. Fig. 10 gives an idea about the variation of magnetic susceptibility with temperature of treatment. No traces of ferromagnetism was detected.

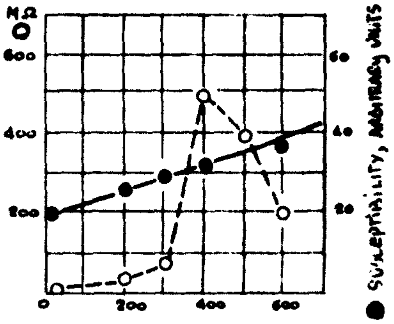


Fig. 10. Variation of magnetic susceptibility with temperature treatment for samples of Fig. 9.

Fig. 11 gives information about the variation of susceptibility with applied magnetic field for the sample treated at 500°C.

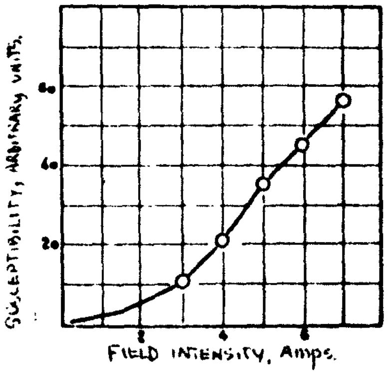


Fig. 11. Linearity of susceptibility with applied field for a sample treated at 500°C.

Unfortunately, heat treatments on anodized aluminium samples can not be greater that 700°C because of the melting point of the metal support. Moreover, treatments above 200°C (400°C by taking special care to avoid thermal shock), develops crazes and fisures on the coat, deteriorating the sample. By this reason, zones of temperature where ferromagnetism could develops have been not reached. It remains to check if longer time of treatment or treatment in a reducing atmosphere, as with pure hydrogen could bring out ferromagnetic phases. Reliable installation for heat treatment under pure hydrogen has been not available.

Because of these limitations, the impregnation with free ferromagnetic materials was considered advisable. For the purpose three different methods can be theoreticaly used: Chemical reduction of nickel by the Brenner process (Kanigen); direct electrodeposition or reduction of nickel carbonyls at low temperature. The last process being discarded temporaly by difficulties to adquire and transport the proper products. Preliminar work done with the Brenner Processhas given ultil present negative results, at least for the high pH propietary solutions used.

From early experience, electrodeposition of nickel was considered the most feasible for the means at hand. But in order to be able to obtain an electrodeposit on anodized aluminium it is required to make before electricaly conductive enough the coating. This can be done, as said before, by impregnating the pores with a conductive substance, such as CuS or AgS, the only compounds that between about other twenty sulphides, oxides and free metals tried, are able to impart this property to the anodic coat.

When a fresh anodized sample is immersed in a warm solution of copper sulfate or nitrate, for a few minutes, part of solution enters the pores. If then the sample is rinsed in clean water and immersed again in a weak solution of sodium or amonium sulphide, formation of copper sulphide takes place inside the pores and eventually on the top surface of the coat, as shown in fig.12b, because some of copper sulfate solution is not washed out by the rinsing and remains on the coat. It takes about 30 cycles similar to this one to obtain, with this classical way, a full impregnation.

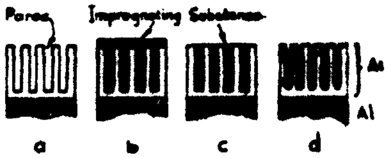


Fig. 12. Schematic process of semi-conductor impregnation in an anodic coat.

The method developed by the author (9) does that impregnation takes place only inside the pores, as in fig. 12 c. In this case, the rinsing step is eliminated and the surpluss solution is removed by wiping with a clean cloth. By this way only 4 to 8 cycles are required to obtain a full impregnation.

It has been found experimentaly that in the former case the exterior layer of copper sulphide really exist, because high conductivity is obtained when two electrodes are applied on the impregnated coat. In the second case, the high isolant character of the coat, remains after the impregnation. Of course, in both cases, good conductivity, if the proper polarity is used, positive for the coat), is obtained when the conductivity is measured through the impregnated coat, being the negative electrode connected to the bare metal-base.

These results seem to confirm that the process of conduction takes place only via the barrier layer existing on the bottom of the coat,near to the metal-base, well by tunnelling, by holes existing in the coat, or because ionic diffusion of copper ions. On the contrary, transversal conduction through the walls of each cell the thickness is great enough to allow any type of conduction.

The ideal impregnation for our purpose is schematized at fig. 12d. This can be achieved by controlled impregnation of the coat, in such a way that the semi-conductor only covers the wall and bottom of the pore.

Unfortunately during the development of this work, it has been discovered that not all the impregnations done with CuS are conductives. Sometimes a green variety is obtained which is not conductive at all. All the effort devoted to clear this problem has given til present no definite information. By this reason impregnation by chemical reduction in situ of silver nitrate with reducing agents has been experimented. The better results obtained have been after exposing the salt impregnating the coat to the light action and using a mixture of methol-hydroquinone as the agent to produce the reduction. Plain metallic silver impregnations have been obtained in this way but always with very low conductivity, similar to the other impregnants used other than CuS or AgS (see fig. 4).

Finally, the behaviour of these different types of impregnation (sulphides, oxides, free metals etc) to thermal treatment is rather complex. While for CuS first a decrease in conductivity takes place until about 400°C to increase afterwards as shown in fig. 13, where, for purposes of comparation conductivity of empty anodic coat is also plotted, in PbS or NiS, conductivity increases gradualy with temperature in a reversible process as shown in fig. 14.

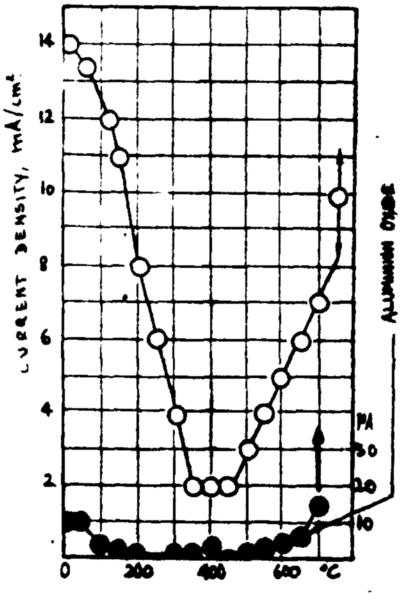


Fig. 13. Conductivity in function of temperature for a sample of anodic coat impregnated with CuS. The behaviour of a blank anodic coating is also plotted.

In other series of experiments with metal silver imprenating the coat, an irreversible change to higher conductivity takes place when samples are treated at 500°C for two hours.

From the above results, it is evident that a more intensive research on this subjet is required before definite conclusions can be drawn out from such a complex behaviour.

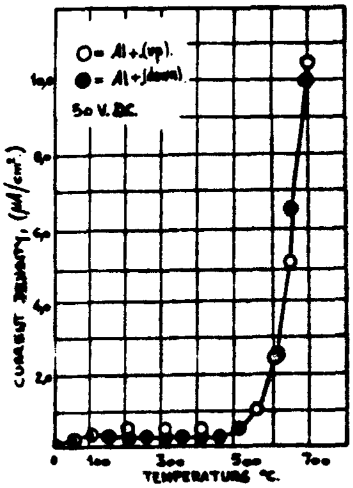


Fig. 14. Conductivity in function of temperature for a sample of anodic coating impregnated with NiS (Reversible process.

Part III -. Electro-plating Procedure.

Information has been given in Part II about the steps required for effective electroplating on an anodic coating. It remain to be discussed if plating action can take place inside the pores of such a coat.

The possibility of electro-deposition of nickel in narrow crevices or slots and the microthrowing power of nickel plating solutions has been studied by Garmon & Leidheiser(10) and they found that metal deposited in small-scale recesses is, in contrast to that deposited in large scale-recesses, virtualy uniform in thickness over the profile. Of course the semaller recesses studied by these authors were crevices 0,08 mm wide and 8 mm deep, i.e. with a lenght diameter ratio about 100 in place of 1000 as in the present case and with a very big difference in diameter, which does it difficult to ascertain if the results of these workers could be applied to a porous anodic coating.

In any case, when samples impregnated with CuS are immersed in an high nickel cloride nickel bath, a layer of nickel is obtained on the surface of the coat, normally requiring a working voltage of about 8 volts, if a normal nickel coat is desired. It was comprobated , by doing the electro-deposition in a Hull cell (see below), that for this working voltage the current density used is similar to that in use for nickel plating on clean bare metals. Lower current densities generaly deposits visible coats of nickel til a value about 0.05 Amp/sq.dm. where no visible nickel is detected, but the sample shows a feeble ferromagnetism.

It was also found that electro-deposition can take place if done through a coat of paint, applied on the impregnated coating by silk screen. After removing the coat of paint with a solvent, a surface with a grey-dark colour of high conductivityand ferromagnetic in character is obtained. Chemical and thermo-magnetic analysis shown that the substance in the pores was mainly free metallic nickel.

Photographic gelatine has been used also as diaphragm with similar results. In connection with these type of diaphragms attached to the coating, Sato (11) in Japan, has been able, while studying the mechanism of the permeation of ions through paint films, to find that ions actively diffus through paint films themselves rather than through possible pin-holes in the paint.

The behaviour of both types of nickel films on the impregnated coats(the obtained directly without and with diaphragm) is quite different not only in colour or aspect, if not in adhesion. While the nickel obtained without diaphragm is quite easy to detach, the dark nickel obtained under a paint diaphragm only can be removed if the entire anodic coating where is supported is removed from aluminium.

In other hand, when both types of nickel coats are immersed in a solution of sodium cyanide , the film obtained directly loss its conductive character when measured through the anodic coating. On the contrary, the dark one dont loss at all this metallic character.

It is apparent that in the last case nickel has entered the pores with a certain continuity through the full lenght of them. If this type of coat is now attacked by nitric acid, the nickel dissolves and the anodic coat remains unchanged and recovers the original high electric isolant nature.

That things are no so simple as here assumed is demostrated by the fact that in all the tentatives done to detach this composite coatings from the aluminium support, always two types of layers are obtained, dark in aspect the one nearest to the top of the coating , where practicaly all the deposited nickel is present, and a clear one mainly formed by aluminium oxide with feeble or nothing of ferromagnetism where nickel is practicaly absent. These factors point to suposse that when nickel is deposited through a diaphragm a layer of nickel develops between the anodic coating and the paint, rather than inside the pores.

The comparative study of both types of nickel films was considered of interest. To acomplish that samples were anodized, impregnated with CuS in the usual way and partially covered as shown in fig. 15, with white paint by silk screen. After electro-deposition on this samples, the paint is removed, and samples cutt out in pieces of 10 x 20 mm.

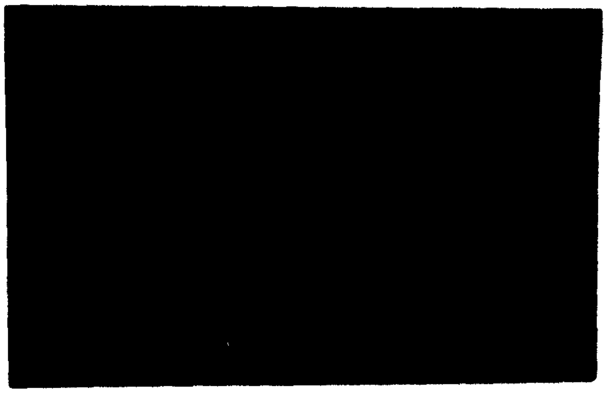


Fig. 15. Samples of anodized aluminium, impregnated with CuS and partialy covered with a paint diaphragm ready for nickel electrodeposition. The clearer sample has been already electroplated.

Apart of the normal plating procedures carried out in a classical electroplating bath, two other special electroplating cells has been used in connection with this work.

One, the Hull cell (12), because of the non-parallel disposition of both electrodes, fig. 16 a, presents on the surface of the cathode a continuous spectrum of current densities that gives place to an electro-plated film with decreasing thickness, whereby a collection of films with different thickness obtained under the same operating conditions can be by this way secured.

The visual examination of samples plated in this way, provides direct information about the influence of current density, bath composition and present impurities in the electrolyte on the final nature of the film. To avoid distorted values due to edge effects, only the central zone ABCD must be considered, fig. 16 b.

In our actual work, the plated samples at the Hull cell were properly divided in definite areas, as in fig. 16 b and cutt out in strips. The central

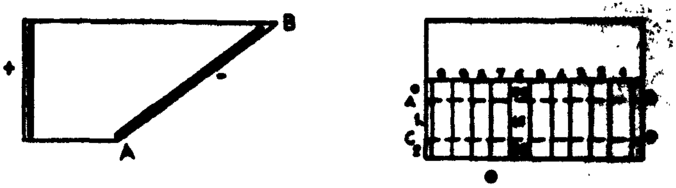


Fig. 16. Geometry of Hull cell. Preparation of samples.

strips were used for magnetic determinations and the side-band squares, top and bottom, used for thickness determinations, when possible, the average value taken as the true thickness of the correspondent strip in the central band.

While this procedure has given very good results when plating nickel on copper or brass, electroplating on conductive anodic coatings was in general iregular or deficient , because of surface differences in the conductivity imparted by the impregnating process with CuS. The most important facts detected in connection with this case were that film adhesion decreases with current density and that those areas where no nickel could be detected by the naked eye, sometimes a feeble ferromagnetism is present, being the late a symptom that some nickel has been electrodeposited inside the pores of the anodic coating. Chemical analysis of these areas detected traces of nickel.

Other type of electrolytic cell used is shown at fig. 17. This cell was

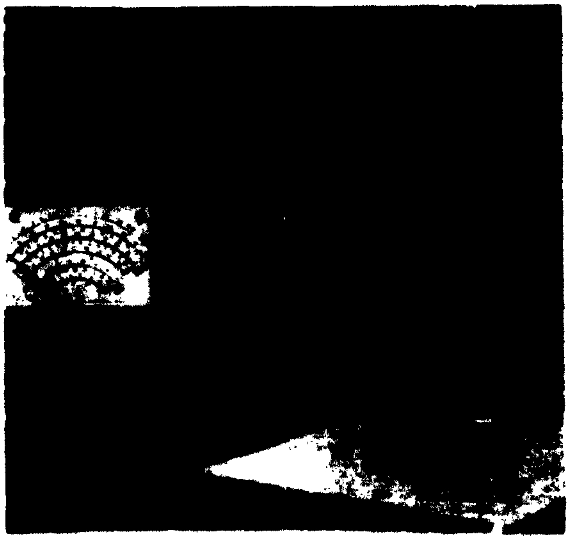


Fig. 17. Electroplating cell to obtain circular spots of nickel films on anodic coatings and for current polarisation studies.

done to be able to plate nickel films as small circular spots on the conductive anodic coatings and to study current polarisation curves of these complex systems. Also has been used to draw out current-voltage curves by using mercury as a full "adaptable" electrode.

Part IV -. Thickness measurements.

Always it has been possible use has been made of an electroetching method (Kokour Thickness Meter) to measure thickness of obtained films. This instrument gives accurate results, if proper care is taken, down to 0,1 microns. Results obtained by this method were eventualy checked out by direct weight determinations or with and electromagnetic method also available (Dermitron Thickness Meter). Both methods, while working well for films deposited on copper or brass give more or less erratic results for films of nickel deposited on conductive anodic coatings, which until present only can be measured by detaching the entire anodic coating from the aluminium support or by detaching the nickel film deposited on the anodic surface. In this late case , the film is transplanted to a calibrated mica sheet and measured mechanicaly with a CSIP Universal Measuring Machine for films thickness down to 0,5 microns as maximum.

Measurement below 0,1 microns, has been attempted on behalf of a Talysurf Profilometer, that in reason of possesing sensitivity enough to measure variations of an order of 0,01 microns, is of scarce use if the suport is not flat enough to avoid misinformation draw out from the inherent roughness of the sample, as is here normaly the case. By this reason, with this method only in a few occasions it has been able to give definite information for thickness below 0,1 microns. In fig. 25 a profil of nickel film obtained with and without diaphragm is given.

In other hand, other procedures for thickness determinations in the range of a few hundred of angstroms, as X-rays diffration or X-ray fluorescence spectrometric methods (13) were positively not available to the author.

This problem presented a serious limitation for the present work, until it was found that such thickness could be estimated, within a reasonable accuracy by doing use of Hull equations (12),

$$D = i\ (5{,}1019 - 5{,}2401\ \log . L) \quad (\text{for a } 250 \text{ c.c. cell}),$$

(where D and i are current density and total current respectively and L the distance from the particular point to the side of maximum C.D. Thickness is obtained by Faraday Law, assuming absence of cathodic polarization.)

always that the cell constants and the total current density on the sample were known and better if the thicker side of plated sample has thickness enough to be determinated experimentaly to be used as a reference thickness. With this method it has been possible to estimate thickness down to 500 A as shown in fig. 18.

The particular values of current density far each strip has been obtained from the above Hull equations for the particular cell used, as shown in table III, fig. 19.

Theoreticaly there is not limitation for the estimation of thinner films with this method and by using a greater cell able to plate longer samples, the author believes that an entire graduation of thickness from thick films to the thinnest ones could be obtained simultaneously by this way. As least this method looks as a suitable tool when no other are available.

Unfortunately, the above method has been used only with success for nickel on copper or brass. Its possible application to films deposited on conductive anodic coatings has been not possible until present because of the limitations above stated.

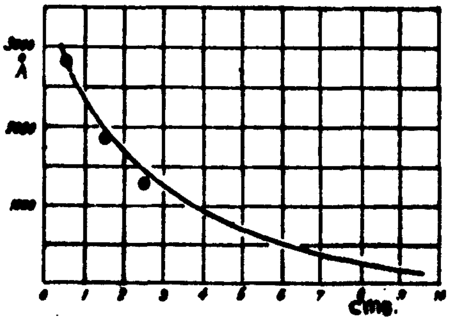


Fig. 18. Experimental values and stimated ones for thickness of plated samples on copper in a Hull cell.

Hull Cell of 250 c.c.

Amps/sq.dm.

										Total Current, Amps.
5,10	3,52	2,60	1,94	1,43	1,02	0 67	0,36	0,10	0	1A
10,2	7,04	5,20	3,88	2,86	2,04	1,34	0,72	0,20	0	2A
15,3	10,6	7,80	5,82	4,29	3,06	2,01	1,08	0,30	0	3A
20,4	14,1	10,4	7,76	5,72	4,08	2,68	1,44	0,40	0	4A
25,5	17,6	13,0	9,70	7,15	5,10	3,35	1,80	0,50	0	5A

0 1 2 3 4 5 6 7 8 9 10 cm

Fig. 19. Table III. Current density values obtained from Hull equations for a Hull cell of 250 c.c.

For the purpose of measuring thickness of anodic coatings, it was neccessary to detach the anodic coatings from the aluminium supports. Several tentatives were made to solve away the metal, but the solutions used attacked the film or the compound under the film. After several trials the better method found for this particular case was, first to mechanicaly detach an small part of the coat leaving the aluminium free and by immersing the sample in a solution of mercuric chloride where and small drop of mercury metal is present. The detaching process takes a certain amount of time but finaly the anodic coat is freed, the aluminium being not totally attacked when the coat can be extracted by using a mica support. After carefully washing, the coating can be dryed and ready to thickness measurement, done mechanicaly on the CERN universal measuring Machine.

Part V-. Magnetic Measurements.

Use of installations existing at Laboratory of Magnetism, Madrid University or built by the author at Marconi Española, S.A. Laboratories has been made in order to study the magnetic behaviour of samples of anodised aluminium impregnated with magnetic materials.

First it was necessary to check the possible presence of ferromagnetic impurities in the aluminium stock used for this work. An improved model of Curie-Cheneveau magnetic balance (14) was used for this purpose. Fig.20 shows curves obtained for selected samples of aluminium as compared with an standard solution of 15% nickel chloride. No traces of ferromagnetism were detected in the samples studied by this method or in other checked with a sensitive torsion magnetometer, lately found a more rapid and suitable method for this purpose.

In part II, details were given about the magnetic behaviour of anodic coatings impregnated with salts of iron, nickel or cobalt after decomposition in air under heat treatment. A guy method was used for these studies, but development of any ferromagnetic phase, as a result of thermal treatment could not be detected.

It was found lately that for feeble ferromagnetic materials, the available Guy balance was not enough sensitive and construction of a Sucksmith balance (15) was considered advisable for these type of materials where a wide variety in magnetic character could be spected. Unfortunately, after several attempts with different rings and materials, the method was discarded as unsuitable , mainly because or the system had not sensitivity enough to detect minute traces of ferromagnetism, or when sensible for this it was not possible to keep centered the sample in the gap when sustantial ferromagnetism was present. Both pole pieces and field mapping meet closely the requirements for the isodynamic gap required with such a type of magnetic balance , but the problem was mainly concerned with the shape and size of the samples.

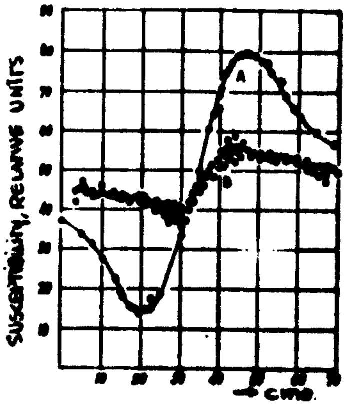


Fig.20. Calibration curve for a 15% solution of Cl_2Ni, $6H_2O$ (A) and dispersed values for a lot of blank samples of aluminium(B) as measured on a Curie-Cheneveau balance.

A coarse version of Neugebauer torsion magnetometer (16) was then built and tryed with success. Nickel films electrodeposited on copper, brass and made-conductive anodic coatings in the range of 5 to 10 microns were first studied by using a rather strong phosphor bronse ribbon (0,06 .0,6 100 mm. long).

A difficulty with this installation was an hysteresis effect related with the sense of measurement. Results obtained when increasing the magnetic field dont fit with those obtained by retourning to zero field. While part of these variations can be attributed to inexperience in measurement or to the special character of some studied films, the fact is that for any type or nickel studied, on different substrates, with different torsion wires and better measuring experience , the effect more or less always remains present in general in the form as show in fig. 21 obtained with a sample of 16 microns nickel film on copper. Although this hysteresis effect can perhaps have other signification that one of a mechanical character, no further enquiries were made about it because it was found that curves obtained by increasing the magnetic field gave always the values for Ms, imanation at saturation, in close accordance with the accepted ones in the literature. By this reason, all the values obtained in this work has been drawn out from the intial curves, as supposed is done by other workers.

As a representative example of results, fig.22 shows a collection of curves as obtained for nickel films of different thickness plated on copper (A) and made-conductive anodic coating. Curve (B) is for an anodic coating where nickel is assumed lying inside the pores. Curve (C) is the same sample before removing a 10 microns nickel film deposited on the oposite face of theanodized sample.

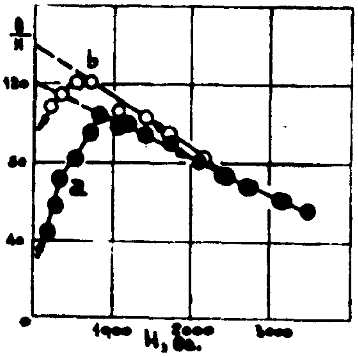


Fig.21. Hysteresis effect found by measuring at the torsion magnetomer, a) increasing field. b) decreasing field.

Because the thickness of nickel deposited inside the pores can not be experimentaly determinated, its "magnetic" thickness was estimated by assuming 508 emu to be the actual value of imanation at saturation of such a film. A thickness of about 2 microns was so obtained. It was lately comprobated, when the anodic coating was removed from the aluminium support that two coat could be distinguished, one mainly of nickel with a thicness of about 2 microns and a clear coating, mainly constituted by the oxide of aluminium matrix, about 6 microns thick. The fact demostrates that the film is deposited mainly on the top of the surface of the coating. That this is the case at least for the areas near the edges of junction for zones plated with and without diaphragm is demostrated by the profils obtained for these areas

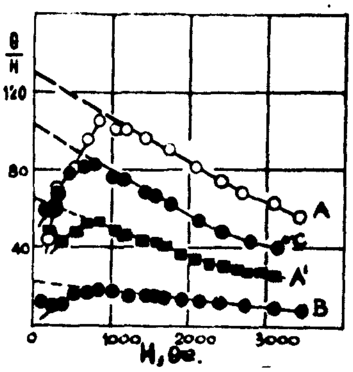


Fig. 22. Magnetic curves obtained for nickel films on different supports with the torsion magnetometer.

with the Talysurf Profilometer. In fig. 23, the left side correspond to to nickel film deposited on the anodic coat, the right side to nickel deposited through the paint diaphragm. The profil was taken after removing the paint and the jump corresponds exactly to the paint-non-paint junction. Notice the greater rugosity of film obtained under paint.

Fig. 23. Talysurf profil of a paint - non-paint junction as obtained for two films of plated nickel on an anodic coating with a a partial diaphragm.

In order to obtain more accurate information about these films, supposed to be inside the pores, further improviments were made on the torsion magnetometer. A new torsion head and thinner torsion wires were used, the actual one being of tugsten 0,0026 mm. diameter, sensitive enough to nickel films below 500 A thick for the area of samples used (2 sq.cm).

In fig. 24 curves are given as obtained with this new magnetometer for the same samples studied before (fig. 22). In fig. 25 a representative collection of curves is given for nickel deposited in gradualy decreasing thickness on a copper foil in a Hull cell.

The sensitivity obtained with this improved magnetometer present in other hand difficulties of measurement and it has been found necessary and advisable to increase the moment of inerce of the torsion system by adding suitable loads and by providing it with a proper damping. With these modifications, measurement are done with less difficulty and greater accurace.

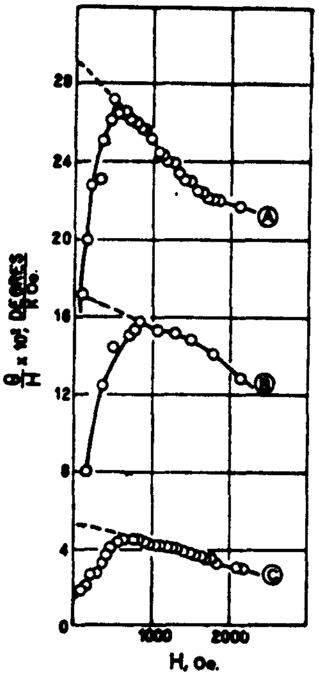


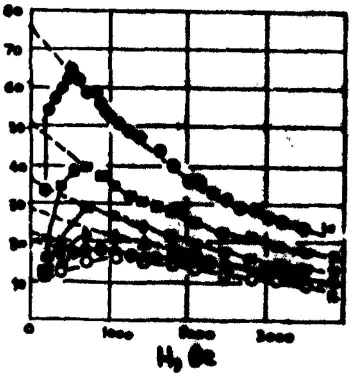
Fig.24. Magnetic curves as obtained for samples of fig. 22 with the new magnetometer.

With the experience gained, provisions are now taken to build up a new magnetometer. This will use a better electromagnet and shall be provided with air evacuation in order to improve conditions of measurement with temperature variation. The new installation will use the facilitie of Laboratory of Magnetism, Madrid Universty.

Finally, it has been found that the torsion magnetometer is a good instrument for Curie Points determination. Fig. 26 shows the thermomagnetic curves obtained by this method with several representative samples. By the experience obtained, the author is of opinion that the method, when properl developed, could become and excellent device to study with accuracy the "tails" of thermomagnetic curves, near the Curie Point, always difficult to measure.

While with the torsion magnetometer, information about Ms, magnetic anysotropy and Curie Points have been obtained for the nickel films under study, in order to have a full idea about the magnetic behaviour of these films, additional information about the Hc (coercitive force) and Br (remanence) is also required.

10 = 2820 Å
19 = 1960 Å
18 = 1400 Å
17 = 1060 Å
16 = 760 Å



Fig,25. Magnetic curves for nickel films obtained in a Hull cell in gradualy decreasing thickness (copper support).

Determination of Hc and Br can be secured through a B-H tracer like the electronic one developed by Crittenden and ad. (17)if sensitive enough for the very small amounts of ferromagnetic material present in each sample. Unfortunately the B-H tracer being developed at Laboratory of Magnetism, Madrid University that the author had in mind to use to measure the samples, has not reached til present to the sensibility required for this particular case, because of several difficulties with the circuitry and excitation coils geometry arising when greater sensitivity is forced out. At present the tracer works

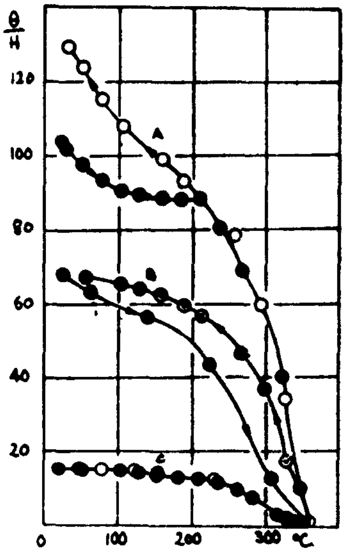


Fig. 26. Thermomagnetic curves as obtained in the torsion magnetometer, adaptated for this purpose. (nickel films).

quite well for amounts of nickel about 100 times greater than the normaly contained in the actual samples.

In order to by-pass this difficulty, a search in the literature gave as result, that despite several excellent methods were available, the feasible ones were out of author possibilities or not fitted for the size and shape of samples. In these circumstances a method, early used at Laboratory of Magnetism of Madrid for other purposes, was considered worth to be tried.

The method is based on the variation of natural frequency of torsion oscillations when the ferromagnetic sample is suspended from a torsion wire in an homogenous magnetic field, fig. 27.

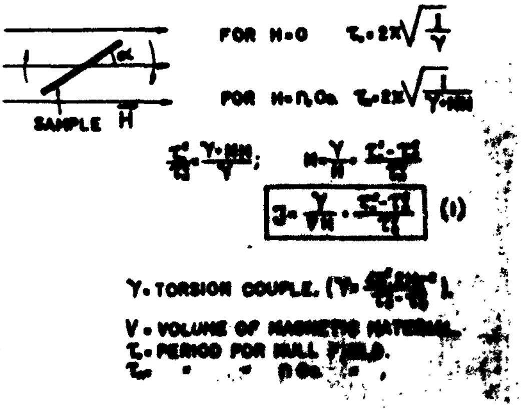


Fig. 27. Equations for intensity of imanation for an oscillation magnetometer.

In this way values for the instant imanation for each value of magnetic field from zero to saturation can be theoreticaly obtained by knowing in each case the values for both periods and the external magnetic field.

The method, of course, must meet several operating conditions. In first place a field as uniform as possible and same size and placement of sample is required. Second, the starting oscillation must be made from the same amplitude as possible. Third, the angles of oscillation must be keept between reasonable small values and fourth, the system must be capable to keep itself oscillating for time enough to provide for several determinations within the same stroke. Unfortunately, conditions 2 and 4 are difficult to be meet for different values of the field, specially if samples are substantialy ferromagnetic. The better results have been obtained with a combination of proper selection of torsion wire, additional inertia and a suitable slight damping.

Electrical pulses as obtained from a cadmium sulphide photocell has been found tha most suitable and accuracy method to determinate period values. These pulses can be sent to an oscilloscopy, recorder or electronic time-counter, whereby the value of semi-periods is obtained. We have used for this purpose an transistorized Admiral time-counter with good results, but a Hewlett-Packard 523B is also suitable for period measurement.

Details of oscillation magnetometer are given in figs. 28, 29, and 30.

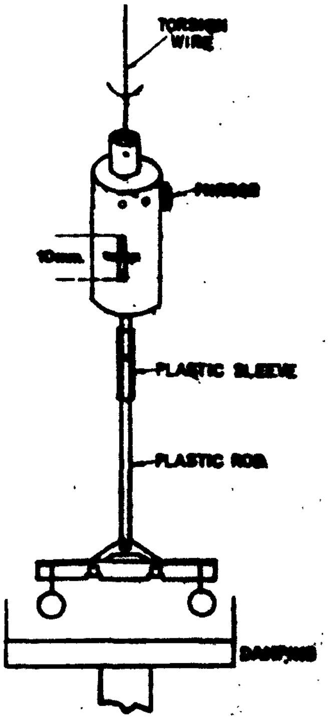


Fig. 28. Oscillation magnetometer. Front view.

A light beam is reflected from the mirror attached to the oscillating sample and gives electric pulses when passing for and back the cell, enough with this type of cell, to feed the counter without any amplification required.

In order to secure sharp and clean pulses, free of light modulation or spureous signals a series of precautions were taken. Light beam, after channeled through slits and lens, impinges on a cylindrical acrylic lens, being by this way sharply focused on the cell active surface. Pole piece faces, sample holder and any other objet able to reflect light was painted with dull black paint. Moreover the components of the electrical circuit, including the cell were optical and electricaly screened.

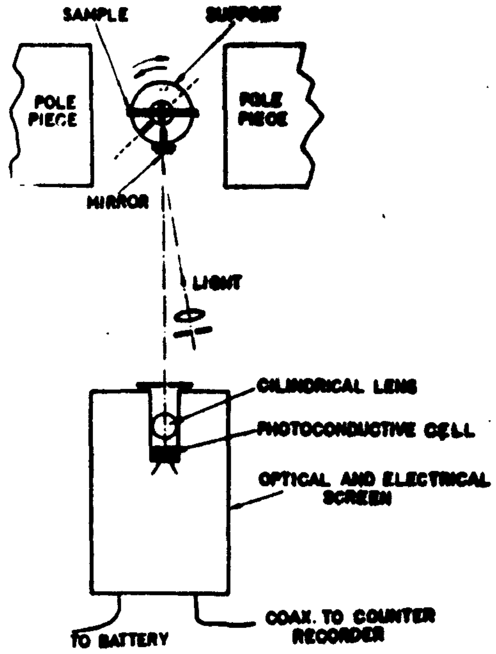


Fig. 29. Oscillation magnetometer. Plant view.

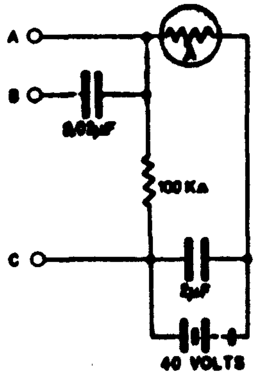


Fig. 30. Oscillation magnetometer. Electrical circuit.

Several attemptes were made to select the most suitable sample holder for the type of samples in study (strips 20 . 10 . 0,8 mm). The final solution was to use a moulded epoxy piece, where samples and mirror can be mutually positioned at rights angles at will.

At figs. 31, 32 and 33 results obtained with representative samples by plotting oscillation frequencies against applied field can be seen.

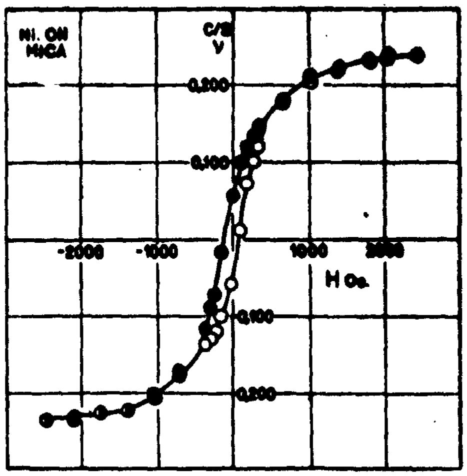


Fig. 31. Hysteresis loop obtained with the oscillation magnetometer. 10 microns Nickel film supported on mica.(Obtained on an anodic coating).

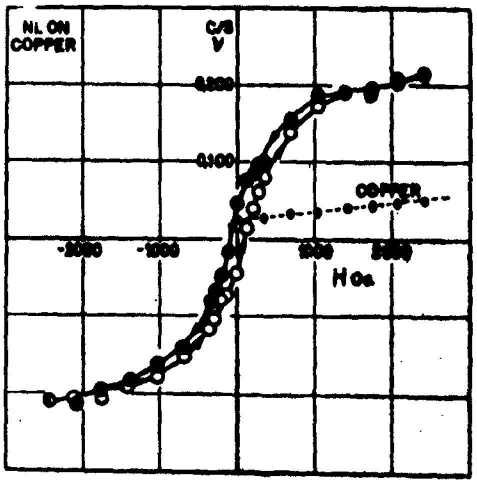


Fig. 32. Same as in fig. 31 for a nickel film plated on copper foil (8 microns).

In fig. 32, curve A shows the effect of the applied field on the oscillation periods (frequency) of a blank sample (copper foli, plus epoxy support and mirror, the effect being fundamentaly due to the epoxy support.

~~Several modifications to the equation have been worked out~~

Unfortunately, values for intensity of imanation J as obtained from equation 1 (fig27), with the experimental values of period, the hysteresis loops then obtained look quite distorted and the values are far of the habitual ones. See figs. 34, 35, 36 in compa ration with figs. 31, 32 and 33.

Several modfications to the equation 1 have been worked out without success. It is evident that because oscillations angles are greater

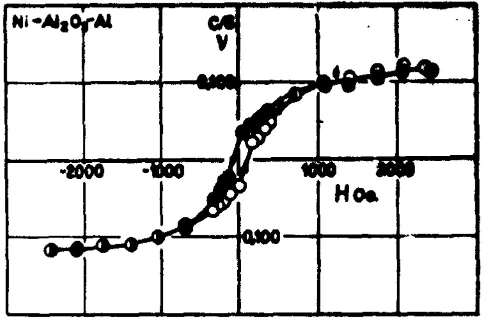
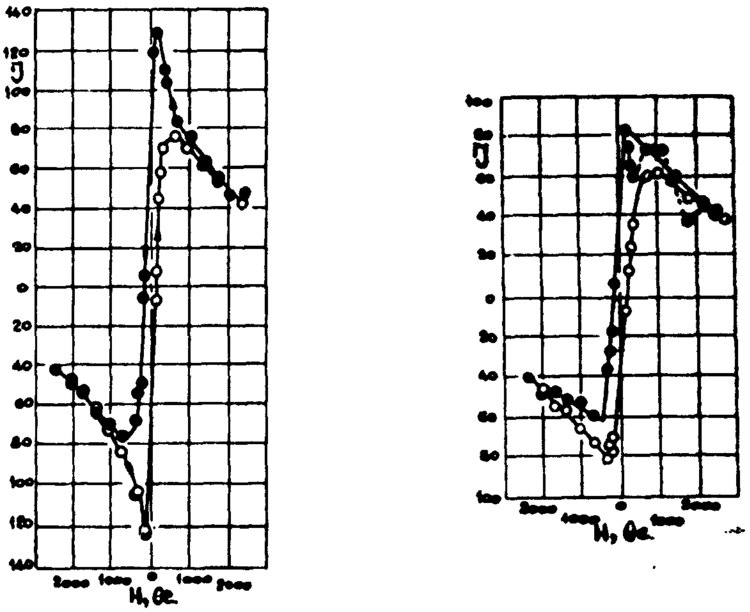


Fig. 33. Same as fig. 31 for anickel film deposited inside the anodic coating (2 microns).

than reasonably allowed (at least 30°C each side of central point) and the inherent difficulties to ascertain the true value of internal field in the sample, because of its size and shape, that the method is not very



Figs. 34 and 35. Hysteresis loops as obtained from oscillation magnetometer experimental values and calculated according equation 1 of fig. 27, for samples of fig. 31 and 32.

suitable for this purpose or at least requires other different treatment that the author has been unable to find until the present. The main failure is perhapsto assume and uniform value for J and H in every part of the sample, when this one is changing for and back constantly its position in the constant magnetic field where it is placed. Perhaps the method can be good there where the magnetic field is always keep constant, as for instance in determinations of Curie Points or magnetic anysotropies constants. The change of this late magnitude was studied by Zijlstra (18) by doing use of a similar improved device where oscillations were keept live electrically on behalf of a feedback system.

Of course, it has been observed that distorsion becomes less noticeable when the ferromagnetic sampleis weack, as for instance in the case of very thin films and possibly the method is to be usefull in the determination of strong super-paramagnetic structures where the influence of applied field is less noticeable.

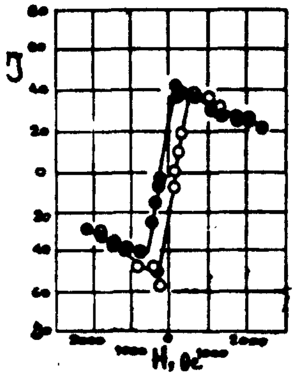


Fig. 36. The same as fig. 34 for sample studied in fig. 33.

As far as determination of Hc and Br values is concerned it remains to find a suitable method, and because of the difficulties found til present and the small possibility that the B-H electronic tracer reach in a near future to the sensibility required, a new revision of revelant technical literature is now being done, in order to find the most suitable method for this particular work.

Part VI -. Conclusions.

From the work developed til present the following conclusions can be made:

1. Anodic coatings can be made highly conductive by proper impregnation with copper or silver sulphide. No other compound from about thirty tried ~~have been~~ were able to impart substantialy this property to the coating.

2. The above results confirm that acid electrolyte anodic coatings, while in part porous, have an internal barrier layer at the bottom of the coating, between the aluminium base and the porous part.

3. The barrier layer can be made conductive probably in reason of one or a combination of the following processes: (1) by tunneling effect, if the barrier is thin enough for the voltage applied; (2) by electrolytic diffusion of copper or silver ions under the action of an electric field; and (3) by a doping action taking place at the barrier during the impregnating process.

4. The made conductive coatings can be plated with ferromagnetic materials, like nickel, well directly on the surface of the coat or inside the coat by plating under a paint diaphargm. In the first case no nickel is deposited inside the pores, the electrical connection with the aluminium support being done through the conductive CuS lying inside the pores This connection is interrupted, recovering the anodic coating its original high isolant character, when the plated sample is immersed in a solution of sodium cianyde.

5. When nickel is plated under a paint diaphragm it takes place not totaly inside the pores as first assumed. Only a short part of the length of the pores, near the top of coating, are quite filled with nickel. Of course, that some nickel is deposited through the entire length of the pores, reaching the barrier layer, is demostrated because immersion of sample in a solution of sodium cyanide dont destroys the high metallic conductive character that anodic coating got after electrodeposition. The process of layer growing looks as taking place in both ways: Nickel grows down towards the barrier layer and up through the paint coat. It is perhaps possible that with a greater time for plating, nickel could reach the bottom of the pores.

6. For any of both types of nickel , the magnetic behaviour was found substantialy the same, at least for the magnetic magnitudes studied, Ms, magnetic anisotropy and Curie Points. Values for Hc and Br has been not obtained because the required installation was not available.

7. As a result of these studies it has been found that impregnation with nickel by electrodeposition must be discarded by other more suitable method.

   The best alternatives are the impregnation with nickel iron or cobalt by electroless process now available (19) or by thermal reduction under controlled atmosphere of organic or inorganic salts.

- Bibliography -

(1).- Rummell, T. Z. Physik, 1936 99, 518.

(2).- Wernick, S. J. Electrodepos. Techn. Soc. 1934, 9 153.
(3).- Baumann, W. Z. PhysiK 1936, 102 59. 1939 111, 707.
(4).- Schenk, M. "Werkstoff Aluminium u. seine Anodische Oxidation",
A. Francke, A.G., Bern 1948.
(5).- Wernick, S., Pinner, R."Finishing of Aluminium". Draper Ltd. London,
1956.
(6).- Keller, F. Hunter, M.S., Robinson, D.L., J. Electrochem. Soc. 1953,
100, 411.
(7).- Pullen, N.D., J. Electrodepos. Techn.Soc. 1939 15 69.
(8).- Post, W. IRE Trans. on Component Parts, Vol. CP-9, June 1962.
(9).- Alameda, J.M. Electroplating and Metal Finishing, 1952 9 286.
(10).- Garmon, L.B., Leidheiser, H., 46th Ann Tech. Proc. Amer. Electroplaters' Soc. 1959 pags. 50, 360.
(11).- Sato, Y., J. Electrochem. Soc. of Japan, 1960, 28 E-224, 1961 29
E-142.

(12).- Hull, R.O. Proc. Amer. Electroplaters Soc. 1939.
(13).- Bertin, E.P., Longebucco, R.J., Metals Finishing, August 1962.
(14).- Cabrera, B. J. Phys. et Rad. 1938 9 209.
(15).- Sucksmith, W. Proc. Roy. Soc. London 1939, A 170 551.
(16).- Neugebauer, C.A., "Structure and properties of Thin Films",
John Wiley & Son, New York 1959, pag. 358.

(17).- Crittenden, H. Rev. Sci. Inst. 1951 22 272.
(18).- Zijlstra, L. Rev. Sci. Inst. 1961 32 634.
(19).- Saubestre, E.B., Metal Finishing, 1962 60, N6 67; N7 49, N8 45,
N9 59.

ANNEX 1

(to Final Technical Report, Contract DA-91-591-EUC-2044).

Personnel utilized during the reporting period..... **Principal Investigator.**
2 Collaborators (IAESTE,
engineering students guests
4 Assistants.

Number of hours expended during this period (Aprox.)..... **960 (PI).**
300 (C)
400 (A).

Number of manhours.................................. **1.660 (Aprox.).**

No important property has been adquired for the development of the work involved in this Contract. Main elements and installations used have been through the facilities given, without charge, by Marconi Española, S.A. and Faculty of Sciences, University of Madrid.