Development And Evaluation Of A Non - Destructive Adhesion Test

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SUMMARY

The object of this work was to further develop the idea introduced by Muaddi et al (1981) which enables some of the disadvantages of earlier destructive adhesion test methods to be overcome. The test is non-destructive in nature but it does need to be calibrated against a destructive method. Adhesion is determined by measuring the effect of plating on internal friction. This is achieved by determining the damping of vibrations of a resonating specimen before and after plating. The level of adhesion was considered by the above authors to influence the degree of damping.

In the major portion of the research work the electrodeposited metal was Watt's nickel, which is ductile in nature and is therefore suitable for peel adhesion testing. The base metals chosen were aluminium alloys S1C and HE9 as it is relatively easy to produce varying levels of adhesion between the substrate and electrodeposited coating by choosing the appropriate process sequence. S1C alloy is the commercially pure aluminium and was used to produce good adhesion. HE9 aluminium alloy is a more difficult to plate alloy and was chosen to produce poorer adhesion.

The "Modal Testing" method used for studying vibrations was investigated as a possible means of evaluating adhesion but was not successful and so research was concentrated on the "Q" meter.

The method based on the use of a "Q" meter involves the principle of exciting vibrations in a sample, interrupting the driving signal and counting the number of oscillations of the freely decaying vibrations between two known preselected amplitudes of oscillations. It was not possible to reconstruct a working instrument using Muaddi's thesis (1982) as it had either a serious error or the information was incomplete. Hence a modified "Q" meter had to be designed and constructed but it was then difficult to resonate non-magnetic materials, such as aluminium, therefore, a comparison before and after plating could not be made .

A new "Q" meter was then developed based on an Impulse Technique. A regulated miniature hammer was used to excite the test piece at the fundamental mode instead of an electronic hammer and test pieces were supported at the two predetermined nodal points using nylon threads.This instrument developed was not very successful at detecting changes due to good and poor pretreatments given before plating, however, it was more sensitive to changes at the surface such as room temperature oxidation.Statistical analysis of test results from untreated aluminium alloys show that the instrument is not always consistent, the variation was even bigger when readings were taken on different days.Although aluminium is said to form protective oxides at room temperature there was evidence that the aluminium surface changes continuously due to film formation, growth and breakdown. Nickel plated and zinc alloy immersion coated samples also showed variation in Q with time.

In order to prove that the variations in Q were mainly due to surface oxidation, aluminium samples were lacquered and anodised. Such treatments enveloped the active surfaces reacting with the environment and the Q variation with time was almost eliminated especially after hard anodising. This instrument detected major differences between different untreated aluminium substrates.Also Q values decreased progressively as coating thicknesses were increased. This instrument was also able to detect changes in Q due to heat-treatment of aluminium alloys.

KEY WORDS: Adhesion, non-destructive, vibration, damping, resonating.

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CHAPTER 1

INTRODUCTION

Since the very early days of the art, practioners of electroplating have been interested in determining how well a particular electrodeposit adhered to its surface. Many ingenious ways have been devised for this purpose. The simple techniques are still the most commonly used and indeed may be all that are needed for most practical purposes: burnishing, chiselling, filing, bending, heating, soldering etc. These methods are obviously destructive, although in certain instances heating the part may not deprive it of its further usefulness. Both heating and soldering methods have the disadvantage that they may change the strength or nature of the bond, thereby giving results that are not characteristic of the as-plated condition.

The adhesion of surface coatings to the substrate metal is of major importance in the finishing industry since, in general, poor adhesion leads to rapid failure. The adhesion of electrodeposits varies from the perfect adhesion of a deposit which continues the structure of the basis metal in such a way that to all practical purposes there is no boundary between the basis metal and the coating, to the almost complete lack of adhesion achieved in the deposition of detachable foils on greased or passivated surfaces.

A poor bond is produced not only when the basis metal has been inadequately cleaned, but also when mechanical polishing has produced a thin brittle surface layer which absorbs hydrogen during precleaning or during the deposition of the metal coating. This layer can be removed by etching or electrolytic polishing. Adhesion refers to bond, chemical and/or physical, between two adjacent materials, and is related to the force required to effect their complete separation. Cohesive forces are involved when the separation occurs within one of the materials rather than between the two. Adhesion is one of the most important properties of electrodeposits. Most of the functional characteristics of electrodeposits are dictated by their adhesion to the substrate, generally the base metals. Thus, the adhesion of the electrodeposits to the substrates dictates to a large extent whether or not the coating will perform its intended function irrespective of the objectives of applying coatings.

The tests commonly used to assess the integrity of the bond are qualitative; for example, bending, chiselling, resonance and heating. These tests are inadequate for a scientific type of study. A variety of quantitative tests has been used and discussed in the published literature, these involve shear, bending, torsion, tensile and fracture mechanics approaches to testing.

Considering the importance of adhesion, there is a definite need for a quantitative adhesion test for evaluating electrodeposits, and for investigating the factors in electroplating processes which determine how well the electrodeposits are going to adhere to the substrates. According to Mittal (1976) an ideal test for measuring practical adhesion should be : (i) reproducible, (ii) quantitative, (iii) non-destructive, (iv) easily adaptable, (v) relatively simple to perform, (vi) not very time consuming, (vii) applicable to a wide range of adherate thicknesses, (viii) independent of operator's experience, (ix) applicable to products and processes, (x) able to measure a wide range of practical adhesion strengths, (xi) free from interpretational complexities and (xii) amenable to standardisation. Furthermore, machining requirements for specimen preparation should be minimal and no specialised equipment should be necessary.

However, such idealisation is not realised in practice, as there is no technique which fulfils even half of the foregoing attributes. All commonly used tests for measuring practical adhesion are destructive in nature.

Quantitative tests for adhesion of electrodeposited coatings are mostly based on adaptation of devices which will provide a grip or handle to pull the deposit from the base metal. The force required to pull the deposit from the base metal is measured by various mechanical methods. None of the quantitative tests are really applicable to commercial applications, partly because it is difficult to translate the data obtained in the measurements to actual production practices. To obtain an absolute value of adhesion, the force should be resolved into its individual components but the majority of tests attempt to employ a single mode of stressing in order to avoid the complexities of this analysis. Few established methods resolve the applied force used for evaluating adhesion into its individual components and so absolute values can not be obtained. Direct comparisons can not be made between results obtained using different tests as the force applicable in that particular test is used as a measure of adhesion.

The "Modal Testing" facilities for studying vibrations are available within the department. This involves the striking with a hammer of a freely supported sample, also a special software package is available for retrieval and analysis of the vibrational data. This method has been used for studying vibrations/damping in an attempt to establish the difference between coated and uncoated specimens. This method was found unsuitable for this work and hence decision was taken to construct a working "Q" meter.

Because of these limitations any test which attempts to overcome them must be fully evaluated. The object of this work was to further develop the idea introduced by Muaddi, Izzard, Dennis and Bell (1985). The test is non-destructive in nature but it does need to be calibrated against a destructive method. Adhesion is determined by measuring the effect of plating on internal friction.

In this method an electromagnetic transducer was used to excite the sample bars at the fundamental mode. The vibrations were picked up by a microphone positioned very close to the vibrating surface. The resonance was found by displaying the drive signals on the beams of an oscilloscope. The nodes were identified by comparing the signal phase with the drive by moving the microphone over the vibrating surface. The sample bars were supported at two convenient nodes by small wedges of expanded polystyrene. The pick-up signal is fed to the Q-meter and the Q measured by counting the number of pulses between the two defined amplitudes. The level of adhesion influences the degree of damping i.e. Q.

However, it was not possible to construct an working "Q" meter using Muaddi's thesis (1982) as information contained was incomplete. Hence a modified "Q" meter had to be designed and constructed. Using the modified "Q" meter it became very difficult to vibrate the unplated aluminium bars which are non-magnetic. No problem was encountered in obtaining resonance peaks with the nickel plated samples. Therefore a reasonable comparison could not be made between the Q values obtained before and after plating.

Decision was then taken to design and construct a "Q" meter using an impulse technique by replacing continuous wave drive in which frequency needed to be tuned to resonance and was difficult to set. The impulse technique does not require tuning therefore is easy to operate. A regulated miniature hammer was used to excite the test piece at the fundamental mode instead of an electronic hammer and test pieces were supported at the two predetermined nodal points using nylon threads. Thus the problems of resonating the samples were overcome.

The results obtained from the new "Q" meter were consistent and also repeatable. Q decreased progressively as thickness increased ie. due to damping. It was not possible to distinguish between different levels of adhesion of the coatings, as the instrument has been found to be very sensitive to surface reactions.

CHAPTER 2

A REVIEW OF TECHNIQUES USED FOR MEASURING ADHESION

2.1 Introduction

Most of the adhesion tests which yield quantitative results can be applied only to relatively thick coatings on test specimen of a particular shape. Such tests are, therefore, unsuitable for testing production articles.

In this review, adhesion tests have been classified as mechanical and non-mechanical methods. The mechanical tests are separated into qualitative and quantitative tests. The main emphasis is on the quantitative techniques, hence a main section is devoted to these.

Adhesion, like abrasion resistance is a difficult property to measure. The simplest adhesion test, various modifications of which are incorporated into many Standards for electrodeposits and other coatings, is to burnish the coated specimen with a smooth implement such as a coin or disc made of copper, steel or agate (depending on the coating being tested) or even to rub with a file. If the coating adhesion is poor, blistering or lifting of the deposit will occur. British Standard 1224 : 1959 describes a test in which the coating is rubbed rapidly and firmly for fifteen seconds. The pressure shall be sufficient to burnish the film at every stroke, but not so great as to cut the deposit.

Poor adhesion is indicated by the formation of blisters, which increase in size as rubbing is continued. If the coating is brittle the blisters break and the coating flakes off.

BS 2816 : 1957 describes a similar test for silver coatings. In this case the test area is smaller and polishing is effected using a steel or agate tool.

The B.N.F. adhesion tester (Hothersall and Leadbeater 1944) makes use of an electromagnetically actuated hammer, operating at frequency of 1500- 6000 impacts per minute. Coatings having virtually no adhesion develops blisters and flake off within 10 seconds.

In the file test BS 1224 : 1959, the specimen is held in a vice and is filed, preferably at an edge or a corner, in a manner calculated to raise the deposit. This should not cause detachment of the coating if adhesion is good.

An indication of the adhesion is also provided by the behaviour of the specimens on heating, blistering often occurring when the bond is weak.

Strikkeling (1955) described a method of testing adhesion of electrodeposits which involves treatment with cathodically produced hydrogen. The test specimen is made the cathode in a 50% solution of caustic soda, and treated for 2 minutes at a potential of 8 volts. If the coating is still free from blisters 15 minutes afterwards, the adhesion may be regarded as good.

Heating of a specimen consisting of a basis metal and a coating can have different effects depending on the nature of the metals, the temperature to which they are heated and the rate of heating. If the coefficients of expansion of the two metals are very different and if adhesion is poor, heating may result in complete detachment of coating, i.e. flaking, or in the formation of blisters. Defects, which in service would develop only after an appreciable time, can be determined by short-time tests at higher temperatures. The severity of such tests may be increased by subsequent quenching in cold water. The test is non-destructive if the adhesion is good. Furthermore, this method can be used in cases where bend tests cannot be applied due to shape and rigidity of the article.The linear coefficients of expansion of different metals are shown in Table 1 below.

TABLE 1. Linear Coefficient of expansion of different metals (X 10^{-6})

Chromium	8.1
Steel	12.0
Nickel	13.0
Copper	17.0
Bronze	18.8
Silver	19.0
Brass	17.4-19.2
Aluminium	25.7
Zinc diecast alloy	27.7

It can be seen from the Table that chromium coatings, for example, on zinc-base alloy die castings would be subjected to very high mechanical stresses due to temperature changes. However, intermediate copper and nickel should cushion the effect to some extent.

The quenching test for adhesion is described in British Standard 1224 : 1959. It involves heating the articles to 350°C for steel, 250°C for brass or 150°C for zinc and quenching in water at room temperature.

Alloy formation can occur due to interdiffusion of adjacent metals. This may improve adhesion, though at the cost of greater brittleness. This occurs in zinc coating (galvannealing), and tin coatings on steel.

In general, oxidation will occur if heating is carried out in air. Thin uniform oxide films will be shown up by interference colours. Nickel and chromium are very resistant to oxidation. Copper is more readily oxidised. Oxidation of zinc causes the coatings to become matt and unattractive. The heating of electrodeposits causes the expulsion of hydrogen occluded in the metal. Recrystallisation and grain growth which can take place due to heating can affect the properties of the coatings very significantly.

2.2 Qualitative Tests

Numerous qualitative tests have been used for measuring adhesion of coatings. These have limitations depending on such factors as the geometry of the specimen, thickness of coating, initiative of the operator and the magnitude of the adhesion value. Operations which can be included in this category are bending, twisting, burnishing, buffing, abrading, heating and quenching, chiselling, filing, cupping and thermal cycling.

A brief description of the qualitative tests is presented in Table 2. Table 3 summarises the applicability of these tests to various deposits. A few comments worth mentioning regarding these methods are: (i) It is always advisable to use at least two methods as the interpretation of results is often subjective and also controversial, (ii) Each test has certain limitations as to its applicability to specific types of coatings, thickness ranges, ductilities or composition of the coatings and substrates, (iii) A suitable test simulating those requirements can be selected depending upon the functional requirements of the coated part, (iv) Numerical values of bond strengths cannot be attained but cases of very poor adhesion can be differentiated from the acceptable ones.

The bend test is popular since it is simple and at the most requires only the sawing through of the substrate, so that the specimen can be detached. Chiselling is used for thicker coatings where it is possible to chisel off the coating at one point and then peel it back with some type of grip. Burnishing and buffing are useful for thin coatings for which chiselling test would be unsatisfactory. Thermal cycling is particularly useful for complex shaped components which cannot be tested in any other way. One application of this method is for testing plated plastics, eg. between a maximum temperature of 80°C and a minimum of - 400 °C.

TABLE 2 A Brief Description of Qualitative Tests

Test Type	Principle and Comments
Bending and Twisting	Most commonly used, especially for thin deposits and to a lesser extent for thick deposits. This test is based upon the idea that the different lengthening of substrate and coating upon stretching side by side will result into forces tending to separate the two. Not applicable to brittle or hard coatings as cracks generally tend to develop. Ductile coatings can reduce the applied stress by plastic flow, poorly adherent coatings may not be detached.
Scribing or Scratch	Scratches are made through the coating in a variety of parallel or intersecting patterns. Lifting or peeling of the deposit between the scratches is the basis of evaluation. The tests are dependent upon many factors including the operator's experience , distance between scratches, thickness of the coating. Thick coatings are not suitable as a chisel or sharp knife is used to pry the interface and then it becomes a chisel test.
Chisel	Applicable to thick coatings and most severe of all adhesion tests. This is limited by the thickness of the deposits and the toughness of the chisel/tool used. Not suitable for soft and thin coatings.
File	The plated specimen is sawed and subsequently subjected to

	a coarse mill file across the sawed edge from the substrate toward the coating so as to raise it using 45° angle to the coating surface. Lifting or peeling indicates poor adhesion. Not suitable for soft or thin coatings.
Push-Out	A blind hole is drilled from the rear of the coated part and a hardened punch is applied at a uniform rate to push out a "button" sample. A microscopic examination is then carried out to study the button and the periphery of the crater in the substrate in order to evaluate the adhesion strength. Exfoliation and peeling of the film indicates poor adhesion. Suitable for a variety of basis metals, ductile or non-ductile, hard and brittle deposits. A minimum deposit thickness is required and not suitable for soft, very ductile and thin deposits.
Push-In	This is a variation of the push-out test. Small hemispherical indentations are pushed in to a predetermined depth on coated parts. It is a non-destructive test where adhesion is satisfactory. Poor adhesion can be easily detected by visual examination.
Cupping and Indentation	These tests depend upon the deformation of the deposit and the substrate in the form of a flanged cup or depression using a plunger. Peeling and flaking of the deposits is a measure of adhesion. Very satisfactory for hard and brittle coatings such as chromium and hard nickel. Ductile coatings which will deform easily are not suitable for such tests. Romanoff (1934) developed an improved modification called the flanged cup adhesion

test. Thickness of the deposit can affect the results. (Mittal, 1975).

TABLE 3 **Appropriateness of Qualitative Mechanical Tests For Various Electroplated Coatings (Mittal,1975).**

Adhesion Test	Ag	Au	Cd	Cr	Cu	Ni	Ni/Cr	Pb & Pb/Sn	Sn & Sn/Pb	Zn
Bend					*	*	*			
Burnish	*	*	*		*	*	*	*	*	*
Chisel	*			*	*	*				
Draw	*	*	*	*	*	*	*	*	*	*
File					*	*	*			
Grind & saw				*		*	*			
Heat/quench	*			*	*	*	*	*	*	*
Impact				*	*	*	*		*	
Peel	*	*	*		*	*		*	*	*
Push				*		*	*			
Scribe	*	*	*		*				*	*

2.3 Quantitative Tests

In this section the mechanical tests discussed include: tensile, shear, peel, flyer plate, knife and scratch, ultracentrifuge, ultrasonic and blister methods.

2.3.1 Tensile Tests

In these tests a force is applied perpendicular to the deposit-substrate interface and the amount of force per unit area necessary to disrupt the interface is a measure of adhesion strength.

For an ideal tensile test for measuring adhesion Schlaupitz and Robertson (1952) outlined the following requirements:- (a) the state of the stress should be identical on either side of the interface, and should approach hydrostatic tension, (b) symmetry across the interface, (c) absence of local stress concentration, (d) minimum plastic deformation, (e) failure should occur at the interface rather than in the deposit or substrate. These are stringent conditions and most of the tensile tests do not fulfil them. However, as discussed below Cramer et al (March 1970) have claimed that their design fulfils all of the requirements. Tensile tests can be arbitrarily divided into two groups: (i) tests based on the use of solders, adhesives and electroformed grips (Brenner nodule), and (ii) Ollard's method and its subsequent modifications.

2.3.2 Use of Solders, Adhesives and Electroformed Grips

Solders, adhesives and electroformed grips provide some form of grip to the coating through which the detaching force is applied. The electroformed grip is in the form of a nodule. The use of solders in determining quantitatively the adhesion of hot dip zinc coatings was pioneered by Burgess (1905). He soldered a copper plug to one surface of a galvanised sheet, cut excess solder from around the plug base and by a lever and spring balance arrangement determined the force necessary to detach the coating. Although the technique is quite simple and intriguing in principle it has several difficulties. The heating involved in soldering the plug can affect the coating, the coating and the substrate material must be considered, and depending upon the alloy properties, the adhesion strength may be enhanced or reduced. In case of porous coatings, the penetration of the molten solder can give rise to misleading and irreproducible results.

However, some of the undesirable traits of solders can be eliminated by replacing these with adhesives but the latter also suffer from certain disadvantages as discussed later. Ferguson (1948) proposed the use of high strength synthetic resins and cement bond strengths up to 4.2×10^7 Pa (600 psi) were obtained but he expressed the hope that under suitable curing conditions a resin strength of 1.75×10^8 Pa (25,000 psi) could be attained. Following these early uses of resins, and various adhesives, hard and cold cured resins have been used for the study of adhesion of flame-sprayed ceramic, organic and spray coatings respectively.

Mittal (1975) pointed out that although tensile tests using adhesives are commonly used and are relatively simple, the following points need to be considered (a) For these tests to be applicable, the bond strength between the adhesive and the coating must be higher than that between the coating and the substrate, (b) the adhesive should not in any way alter the properties of the interface, (c) in case of hot curing, one must be aware of the heating effect as discussed in the case of solders. Also, the variability in the degree of curing of the adhesive can lead to variable values for adhesion strength.

Catherall and Kortegas (1972) studied the bond strength of flame sprayed deposits using four different adhesives. They concluded that the penetration of adhesives can have a very substantial effect on the bond strength values. If the adhesives do not penetrate, then these tests are potentially the most attractive of the destructive tests.

Brenner and Morgan (1950) described a nodule method for measuring adhesion. This method involves electroforming of an adherent mushroom-shaped projection onto the surface of the electroplate to be tested to act as a grip for applying the detaching force. The bond strength is limited by the strength of the nodule. The specimen preparation requires "stop off" materials and plastic washers to control the shape and size of nodules formed. The basic arrangement is shown in Fig 1. In order to satisfy the requirements for an ideal tensile test, Schlaupitz and Robertson (1952) formed identical "mirror" nodules of nickel on both sides of silver plated thin copper sheets. A tensile load was applied through a specially designed grip to ensure axial alignment. This test is attractive, but the following requirements are all too critical to make this method of practical value: (a) the material of the nodule should have flow and fracture strengths considerably greater than those of the basis metal and the deposit to prevent the nodule failure, (b) the nodules are small in size (1.56 cm), so the axiality of the loading is extremely important. Furthermore, the rate of deposition of nodule material should be high and the adhesion between the nodule material and the coating must be more than that between the coating and the basis material.

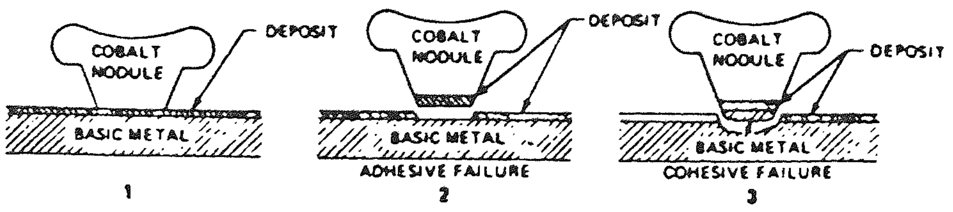
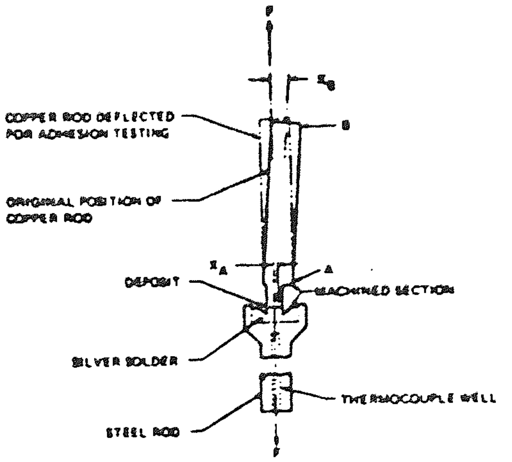


Figure 1. Basic Idea of Brenner Nodule Test.

Cramer et al (1970) have described a test which involves brazing the free surface of the deposit to a steel rod with silver solder, machining this specimen to a desired shape and then measuring the strength of the deposit-substrate bond by the application of tensile load. Adhesion test specimens were prepared using nickel electrodeposits about 50 µm thick on tough-pitch hard drawn copper rods of 1.3 cm in diameter. The author claims that this method gives precision comparable to the best techniques that were then used. It conforms in most ways to the mechanical conditions required of an ideal test. Fig 2 shows a schematic drawing of the test procedure. Misalignment of the rods leads to two potential corrections and they have derived these from the basic formulae describing the flexural behaviour of beams. They have also corrected the adhesion data for variations in testing procedure by the use of statistical methods with the result that the criteria for specimen preparation and for test performance are not severe. Using this technique the adhesion of nickel electrodeposit on copper substrates was 1.62×10^8 Pa with a standard deviation of 1.9×10^7 Pa. However, it should be noted that they have used silver solders and the same limitations outlined earlier apply, although they found that the absolute brazing temperature was not a significant factor.



X_A is the distance between the axes of the steel and copper rods at position A
X_B is the distance the copper rod must be deflected for the end to align with the axis of the steel rod

Figure 2. Schematic Diagram of the Adhesion Test According to Cramer et.al (1970).

2.3.3 The Ollard Method and its Subsequent Modifications

Ollard (1925) was the pioneer of this technique and it circumvents some of the difficulties discussed for the tests employing adhesives. According to Polleys (1963) this technique with its subsequent variations has become the best known of the quantitative methods for testing adhesion.

According to Davies and Whittaker (1967) the main objections to this test are: (a) stress concentration at the outer edge results in tearing action and therefore in low values for adhesion, (b) increasing the diameter of the central hole relative to the outside diameter gives higher results, (c) local stress concentration might result from too thin a deposit, which would also be difficult to grip, (d) the force on the coating is not always perpendicular and equally distributed over the area used to calculate the bond strength. Hence, this technique does not fulfil many of the requirements for an ideal tensile test and is suitable for thick films only.

In these tests a thick (2-3 mm) electrodeposit is applied at the end of a solid cylinder. The cylinder is then machined down to leave the nickel projecting. The detaching force is applied by gripping the coating itself and the stress is primarily tensile. Pushing or pulling is applied, however, pushing mode is preferred since pulling causes the outside of the coating to fail before the middle. This method is only suitable for measuring adhesion of very thick coatings, as thin coatings would not provide adequate means of support for the substrate to be pushed away. Consequently these specimen take a long time to prepare. The essential features of the method developed by Ollard are illustrated in Fig 3.

Several modifications of the Ollard test have been used. Roehl (1940) specified more precisely the dimensions of the test piece and the die holder so as to ensure separation by tensile rather than by bending or shearing. A ring and plug test method for measuring the adhesion of electroplated nickel to tin plated steel has been described by Hothershall and Leadbeater (1938). This technique has two advantages in that thinner deposits (0.037 cm) can be used and machining time is reduced in specimen preparation. Bullough and Gardam (1947) have discussed the objections to this method and they were the first to describe the tapered conical pin modification. This design was elaborated by Williams and Hammond (1954) giving a standard test piece for measuring the adhesion of chromium (0.025 cm thick) to steel. Fracture occurred in the chromium deposit in almost all the cases. It needs to be pointed out that the final adhesion values are strongly influenced by the thickness of the backing coatings, if used, cross sectional area and the material .

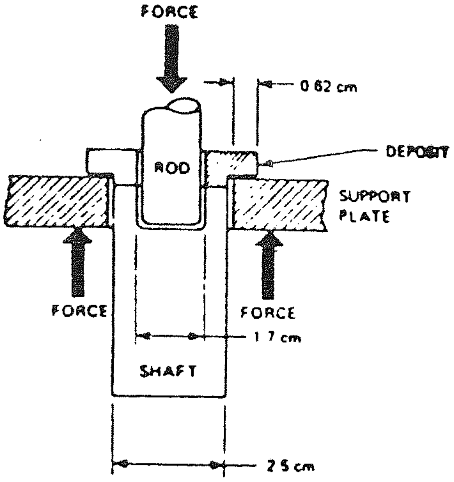


Figure 3. Ollard Test Using a Push Mode.

Gugunishvili (1958) and Domnikov (1961) have used a similar arrangement with a number of tapered pins fitting accurately into tapered holes in the substrate so that the ends of the pins and the substrate present a single composite face. A special jig has been used for gripping the ends of the pin and the force required to detach or withdraw the tapered pins in a tensile machine is recorded. This is shown in Fig 4. Polleys (1963) pointed out that the method is useful primarily for process evaluation of a research nature because of the careful machining required and specialised loading equipment needed to ensure axiality. This renders this technique unattractive in the case of parts or products.

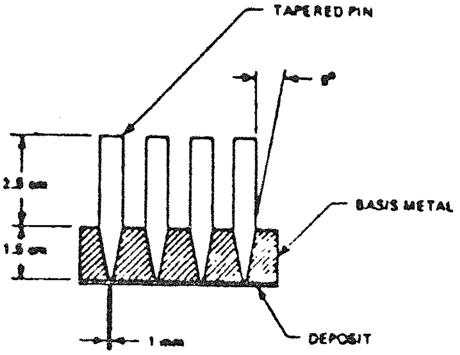


Figure 4. Tapered Conical Pin Modification of Gugunishvilli.

Knapp (1949) developed a sheet test modification which is valid for somewhat thinner deposits as well as more massive parts. The test specimen is a sheet material which has been electrodeposited heavily on both sides and subsequently machined in a pattern suitable for support in a die holder and jig arrangement (Fig 5). A steel plunger is inserted in the central opening so that the coating can be pushed off. Thin deposits must be overplated with a heavy adherent deposit for testing, otherwise cupping will result around the top edge of the hole giving low values of adhesion strength. This renders the specimen preparation a lengthy process.

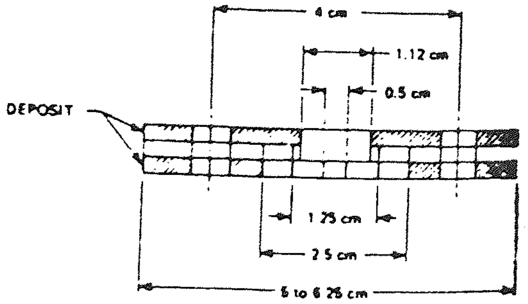


Figure 5. Knapp's Sheet Adhesion Test Specimen.

2.3.4 Shear Tests

In these tests, essentially a cylindrical rod is coated with separate rings of electrodeposits of predetermined width. This rod is forced through a hardened steel die having a hole larger in diameter than the rod but less than that of the rod plus the coating. The coating is detached and the bond strength, R, determined by the formula

$$R = P / \pi dt \qquad (1)$$

where d = diameter of the rod

t = width of the deposit

P = the force required for detachment

If P is in kg and d and t in cm then R is directly in kgf/cm^2.

Zmihorski (1947-48) originally used a ring shear test to measure adhesion between electrodeposited chromium and steel of thickness ranging from 0.020 to 0.006 cm. Zakirov (1965) used this technique for testing the adhesion of 0.25 mm thick iron electrodeposits on the inner and outer sides of steel. Dini et al (1972) used the ring shear test to study the adhesion of gold on stainless steel and nickel on various substrates. They have used rods of 12.7 mm diameter and 304 mm to 381 mm in length. Five 25.4 mm segments of rod spaced at 25.4 mm intervals were stopped off. This was done so that five separate rings could be machined from the rod, thereby offering the possibility of obtaining more than one piece of data for each test piece condition. The rod was coated with a deposit about 1.5 mm thick. A ring 1.59 mm wide was then machined in each plated segment. This ring width gave a convenient shear area of 64.5 mm^2. They proposed a masking off technique so that no machining would be required after plating in instances where there would be concern about damage due to machining or grinding and the difficulty of assuring a square edge. Their result showed that quantitative and reproducible data could be obtained by this technique and also revealed the best procedures to use for preparing particular substrates for plating.

It is important to note that they observed a strong dependence of the rate of loading of steel rod on the adhesion strength. Too rapid loading resulted in high adhesion values. Dini et al found a close agreement between the shear strength data for many substrate materials obtained by this technique with those reported in the literature, and this built confidence in the values obtained using this technique. Vaidyanath et al (1959) and McEwan (1962) have devised other variations of the ring shear test for certain applications.

McIntyre and McMillan (1956) have described a different technique for measuring adhesion in shear. This method is similar to the tensile tests employing solders, in that a plug is soldered to the coating and a shear stress applied to detach the coating. Evidently, this test has the same limitations due to solders as described earlier under tensile tests.

Zilberg (1958) in another version of shear test, has described two types of dynamic shear tests both involving a modified pendulum impact tester. In the first technique, the coating is sheared from the substrate by a knife arrangement using a special fixture in the machined groove on the specimen. The pendulum which is attached to the back of the assembly swings through the vertical position resulting in the detachment of the coating with the knife. The measured energy at the impact allows the adhesion to be expressed quantitatively. In his second version, the coating is stripped from the substrate by a more tensile stress. Here the specimen is machined with concentric or parallel grooves.

Krainov et al (1972) have developed a tangential shear test for determining adhesion of polymer antifriction coatings to metal bushings and bearings. This test should be more applicable in determining the adhesion of polymeric electrodeposits. Tangential shear has been successfully used to measure the adhesion of thin evaporated metallic films and reference can be made to the paper by Mittal (1973).

2.3.5 Peel Tests

In peel tests, basically the purpose is to grip the electrodeposit and peel it. There are two principal ways of achieving this. In the first technique which was first used by Jacquet (1934), an overcoat of electrodeposit is applied to the already coated specimen under test in such a way that part of it can be lifted from the specimen surface and used as a means of gripping the coatings. In the second method, the coating itself is in some way lifted sufficiently to allow it to be gripped.

In the Jacquet test and its variations, specimens can be prepared by dividing the sample into different zones, and applying some adherant materials which will reduce the adhesion of a further layer of electrodeposit, leaving a central uncontaminated zone. In the original Jacquet method, steel plate coated with nickel was the test specimen and copper was the overcoat. Adherents used included lacquer and protein solution.

Wittrock and Swanson (1962) proposed a modified Jacquet test for determining the peel strength of plated aluminium. The test was subsequently used by Such and Wyszynski (1965) to assist in the development of a modified zincate process for the plating of aluminium alloys. A Jacquet-type peel test has been used extensively since 1965 to determine the peel strength of plated plastics as has been discussed by Saubestre et al (1965) and McNamara and Sexton (1965). The direct peel test is applicable to relatively thick electrodeposits, however, in case of brittle deposits, the technique may not be useful.

Peel tests are commonly used for the measurement of adhesion of a variety of adherates, but the analysis of the forces involved is quite complex and the final value of adhesion strength is influenced by (i) angle of peel (generally an angle of 90^0 is used), (ii) rate of peel, (iii) width of the test strip, (iv) thickness of the coating, etc. For comparative purposes it is necessary to specify whether the values quoted are for the force necessary to peel the coating at a steady rate or the force necessary to initiate peeling. It can be added that the adhesion values for peel tests cannot be compared directly with the tensile or shear strength values, because the peel test values are given in force/length or energy/length whereas the latter are expressed in force/area or energy/area.

Theoretical aspects of peeling phenomena have been discussed by many workers, Lamb (1961), Jouwersma (1960), Kaelbel (1960) and Chang (1960). Saubestre et al (1975) used a modified Jacquet test to measure adhesion of electrodeposits on plastics and compared the results with those obtained from thermal-cycling tests. They have used pertinent equations in their paper and concluded that the width of the test strip, thickness of the coating, modulus of elasticity are all equally important in determining the peel adhesion values. Subsequently, Saubestre (1969) has specified the various test conditions needed to standardise the Jacquet peel test for electroplated plastics.

In principle, the Jacquet test is attractive and is frequently used, but the following points should be considered. (i) the technique is valid if the adhesion of the overcoat should be between the electrodeposit and the substrate, (ii) the thickness of the overcoat should be substantial so that it does not pull apart under load, (iii) the adhesive agents used should not, in any case, change the interfacial properties of electrodeposit-substrate combination.

Peel tests are also used to determine the adhesion of the electrodeposits to non-conductors, where the peel strength is usually a maximum of about 500 g/mm. A Hounsfield Tensometer is suitable for testing this system, but since adhesion is low, a sensitive beam of the Tensometer must be used. The detached end of the deposit is fixed to the chuck using an adhesive PVC tape which is capable of carrying the load. This technique has been used to determine the adhesion of electrodeposits to ABS and other plastics and to evaluate factors which influence the bond strength.

Gent and Petrich (1969) have measured the forces required to peel a thin layer of model viscoelastic adhesive off a rigid substrate at various rates of peel and at different temperatures. Their analysis is very pertinent to polymeric electrodeposits.

Golby et al (1981) pointed out that although peel tests are carried out under standardised conditions, quite a degree of scatter occurs, even when an attachment is used to ensure that the peeling force is always applied at right angles to the plated surface.

2.3.6 Flyer Plate Test

Flyer plate tests are used for quantitatively measuring the adhesion of plated coatings under dynamic loading conditions. The method was originally developed for shock wave testing materials, consisting of utilising magnetic repulsion to accelerate, flat metal flyer plates against the substrates in a vacuum.

Dini and Johnson (April, 1977) have described a "flyer plate" test for measuring adhesion under dynamic loading conditions. A magnetic repulsion effect is used to accelerate a thin flat metal flyer plate against a sample under test in a vacuum. When the flyer plate impacts the target specimen, a compressive wave is transmitted through the specimen. As it reaches the rear surface, it is reflected as a tensile wave which propagates through the specimen. This tensile wave combined with rarefaction waves from the front surface and waves from the impedance mismatch at the interface between substrate and coating , subject the interface to dynamic tensile stresses and if sufficiently large, separation occurs. This can be determined by a metallographic examination.

2.3.7 Ultracentrifugal Test

The direct pull-off methods ie. the tensile, shear and peel tests suffer from the basic problem of gripping the coating to apply a detaching force. If adhesives are used to attach some sort of device to the coating, then the undesirable effects may prevail. In the ultracentrifugal technique no adhesive or solder is used. Adhesion is determined by measuring the force necessary to detach a film by measuring the force necessary to detach a film normal to the surface. However, the equipment is both complex and expensive and special test pieces are required.

The specimen is in the form of rotor which is revolved at extremely high speeds to develop a high centrifugal force and if this is sufficiently high the coating is detached in one piece. Hallworth (1964) who appears to have pioneered this technique described it as a "whirl test". However, the real progress in the design of the equipment was through the efforts of Beams et al (1954). They suspended the rotor in a vacuum in a magnetic field to spin the rotor. At a later stage, Dancy (1970) designed a modern version of this system with angular speeds over 80,000 rps. Before Dancy's latest design, the main concern was that the rotor should be ferromagnetic and this had restricted the study of coatings to only a few substrates. Dancy's design enabled coatings on non-magnetic substrates to be investigated with the magnetic support system. Non-magnetic specimens must be rendered magnetic and this can be accomplished by the inclusion of a ferromagnetic rod that is aligned along the axis of rotation or by the addition of a ferromagnetic disc which is cemented to one of the test rotors. The possible stress distribution within the rotor must then be calculated considering the influence of this added body.

The maximum speed of rotation is governed by the mechanical properties of the rotor, or the weakest material in a composite rotor and for any given material can be increased only by reducing the overall diameter of the rotor. In the centrifugal system, the forces on the coating are given by:

$$T + \frac{Ar}{t} = \frac{4\pi^2 n^2 r^2 d}{g}\left(1 + \frac{t}{r} + \frac{t^2}{3r^2}\right) \qquad (2)$$

where T is the hoop stress

A is adhesion in gf/cm^2

r the radius of rotor in cm

n is the number of revolutions per second

d the density of coating in g/cm^3

t thickness of coating in cm

and g acceleration due to gravity (981 cm/sec^2)

The hoop stress, T, can be eliminated by making slits in the coating parallel to the axis of rotation. Under the conditions of $T = 0$, the above equation reduces to:

$$A = 4\pi^2 n^2 / g \qquad (3)$$

From this equation it is evident that the rotor size will be dictated by the degree of adhesion to be measured.

Ponizovskii (1967, 1974) has used this technique to study the adhesion of electrodeposited copper, nickel and chromium.This technique is quite versatile if the rotor materials are properly selected, then a variety of coatings can be studied.

2.3.8 Blister Tests

In this test a force is applied to the coating from beneath, at the coating substrate interface and the pressure is increased until the coating begins to detach ie. peel away from the interface. The beginning of the peel is usually indicated by a discontinuity on the pressure-volume plot. The force may be directed at the coating, eg. by gas under pressure (Hoffman and Georgoussis, 1959) or may be applied by the injection of a liquid under pressure between the coating and substrate (Dannenberg, 1960, 1961). The pressure at which the film was lifted was used as a measure of adhesion.

Most of the work using this technique has been done on relatively thick (25 μm) paint films. Dannenberg has described a blister test for determining the adhesion of dip and sprayed organic coatings to metals, based on the pressure required to cause the coating to blister when mercury or glycerine was injected under pressure between the coating and substrate. The amount of force required to detach a coating makes this technique unsuitable for use with metals, except where the coatings are weakly adherent. Williams (1969) had made a theoretical analysis of blister test and reference can be made to his paper.

As the work required to detach electrodeposits will be considerable more than the paint coatings, so only less adherent electrodeposits may be tested by this technique. However, the values of adhesion strength thus determined will be influenced by the thickness, ductility or brittleness of the deposited metal.

2.3.9 Ultrasonic Test

The ultrasonic test is quite promising but has not been extended to the quantitative adhesion measurements of electrodeposits. The effect of the thickness of the deposits on the adhesion strength values needs to be considered.

The main application of this technique has been for paint films and to a lesser extent for thin evaporated films. Ultrasonics can be applied in three ways (Davies and Whittaker, 1967): as high frequency vibration, as low frequency vibration and the combination of both. The first method is used to detect gaps or voids at the interface and is based on the principle that the efficient transmission of mechanical pulses in the ultrasonic range through a solid or substrate- coating combination is sensitive to gaps or voids. A gap at the interface of more than 1 μm can be detected by this technique. Myers and Schultz (1962) have used this technique to study the loss of adhesion of paint applied to a quartz bar. The sensitivity of this technique can be increased by the use of a microprobe and also heating the electrodeposited specimen.

An early original paper describing the second method in the study of adhesion is that of Moses and Witt (1949). In this method, the normal force is supplied by the inertia of the coating subjected to rapid reversals of motion at the ultrasonic frequencies. The method and apparatus utilise an electrodynamic system for producing longitudinal ultrasonic vibrations in a metal cylinder. When the force due to acceleration exceeds the adhesion strength at the interface, a coating deposited on the free end of the vibrating cylinder separates from the metal.

The force of acceleration is determined by the frequency and amplitude of vibrations and by the mass and area of the deposit. The amplitude of vibrations of the rod or cylinder is calculated from the input voltage. The maximum acceleration is given by :

$4\pi^2 f_o^2 a$, f_o being the fundamental frequency of vibration given by $\left(\frac{1}{2}\ \frac{E}{\rho}\right)$ where

(4)

E is the Young's modulus

l the length of the rod

ρ the density

At a frequency of 20 kHz, the maximum acceleration would be 2 x 10^5 and at 50 kHz it would be 5 x 10^5 times normal gravity. The mechanical restriction of the system limited the choice of the cylinder material to magnesium and aluminium alloys. In order to increase the versatility of this technique, screw caps have been used at the ends of cylinders, these screw caps can be of different metals.

Moses (1949) measured the adhesion of polystyrene films at a frequency of 23.6 kHz, to be 4.14 x 10^5 Pa. Using a frequency of MHz can raise the acceleration to 10^9 times gravity. This necessitates the use of a piezoelectric transducers and for fundamental operations of a quartz vibrator the limiting frequency is usually of the order of 12 MHz. Faure et al (1972) have used a modified arrangement to measure the adhesion of granular and fissured silver films. Whymark et al have extended the use of ultrasonics to ceramic/metal system employing three different modes of vibrations, which are (i) flexural excitation applicable to very low bond strengths, (ii) longitudinal excitation: transverse bond, (iii) longitudinal excitation: longitudinal bond. Milner and Tottle (1964-65) have suggested the applicability of this technique to the adhesion measurement between uranium dioxide and coating metal which constitute nuclear fuel elements.

2.3.10 Knife and Scribing Tests

These tests are indirect forms of peel test which do not require to grip the coating. Depending upon the mode of conducting these tests, they can be divided into two categories. In one case, the force required or the work done or rounded point across it is measured; and in the second case, load is gradually increased on a pointer which is dragged across the coating and the critical load. The first method is applicable for thicker coatings and the latter has been generally used for thin films eg. vacuum coatings. The second method is more commonly known as "scratch" or a "stylus" tests.

Green and Lamatina (1948) studied the adhesion of organic coatings to metal surfaces by measuring the force required to cut these coatings by dragging an ivory or hard-wooden knife across the surfaces. In the commercially available "Inter-chemical Adherometer" a test specimen is firmly clamped on a motor driven plate in such a way that it travels at constant speed under a weighted ivory knife and a definite width of the coating is stripped. A certain minimum thickness is required in this technique. The knife tests have mainly been used for organic coatings but have potentials for the study of electrodeposits in which case the effects of ductility and brittleness of the electrodeposits needs consideration.

The scratch or stylus test was first used by Heavens (1950, 1952) to study quantitatively the adhesion of thin evaporated metallic films on glass and the effects of chromium interlayers. Following Heavens, Weaver and Hill (1958) used this technique in their semi-quantitative study of adhesion of aluminium films on glass. Benjamin and Weaver (1960) analysed the test in detail. They formulated equations which can be used to convert the critical load into numerical values for adhesion.

$$F = \frac{a\rho}{\sqrt{r^2 - a^2}} \quad \text{and } a = \sqrt{\frac{W}{\pi\rho}} \tag{5}$$

where W is the critical load

r is the radius of the point tip

ρ is the indentation hardness of substrate material

F is the shearing force per unit area due to the deformation of the substrate.

Benjamin and Weaver concluded: (i) the critical load depended upon the nature of the interface without being directly related to the mechanical properties of either coating or substrate, (ii) the measured load became constant after the film thickness exceeded 80 nm. Slightly smaller loads were required for thinner films. The conclusions of Benjamin and Weaver are not too general as often workers have reported discordant findings. Chopra (1969) in his study of the adhesion of polycrystalline gold films deposited on glass, concluded that the critical load increased almost directly with the thickness above 200 nm.

The scratch test is particularly useful for :

(i) determining optimum adhesion parameters,

(ii) differentiating cases where adhesion of the coating is poor,

(iii) testing an area too small for other tests,

(iv)) studying the effect of aging or environmental degradation at an early stage,

(v) determining point to point variation

These tests are quick, reproducible, and require relatively simple equipments, so their use can be extended to the study of thin electrodeposits.

2.3.11 Groove Adhesion Test for Electrodeposited Chromium

Generally, thick, brittle deposits are not amenable to the scratch test unless a chisel or other sharp instrument is used in conjunction to expose the coating/substrate interface. The groove test was developed by Chen and Baldauf (1980) using the features associated with the hybrid scratch test. This quantitative test involves the cutting of parallel grooves across a plated surface using a small metal shaper equipped with a carbide tool. The grooves are cut at a depth just below the interface and shearing stresses are generated which can produce failure of the lands depending on the relative cohesive and adhesive bond strengths of the electrodeposited chromium. Energy dispersive X-ray analysis is used to map the distribution of residual chromium and obtain an intensity count (Fig.6). The ratio of count intensity normalised against a reference of 100% chromium coverage provides a quantitative measurement of adhesion. The groove adhesion test was found to be equally applicable for the evaluation of both hard and soft chromium deposits (Pan and Chen, 1986). However, the fracturing of coatings by grooving is a complicated process. The mechanism of coating delamination is beyond the scope of this study.

2.3.12 Microindentation Method

The possibility of using the microindentation method in assessing the adhesion strength of a coating to the substrate was examined by Berdikov et al (1978). The test was carried out using a PMT-3 instrument with automatic loading and recording, to study the bond of 6-20 μm chemically applied nickel coatings on a duralumin substrate (D16T and D16M). Figure 7 shows a typical diagram of indentation of a pyramid into a nickel coating.The loading part clearly shows the kink corresponding to the critical load P_{cr} at which the effect of the transitional layer between coating and substrate sharply increased the rate of plastic strain of the material.

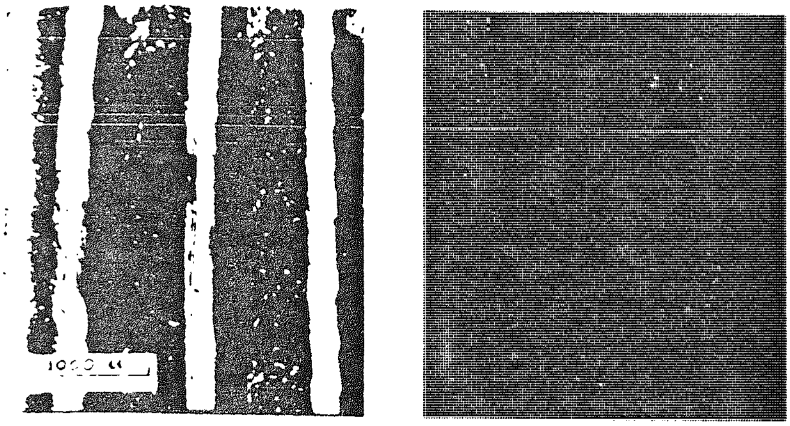


Fig.6.i.Photograph and chromium X-ray mapping of electrodeposited Cr showing good adhesion.

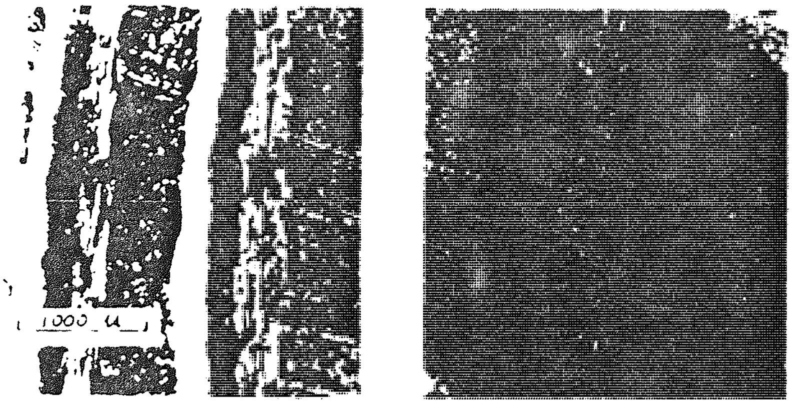


Fig.6.ii.Photograph and chromium X-ray mapping of electrodeposited Cr showing poor adhesion.

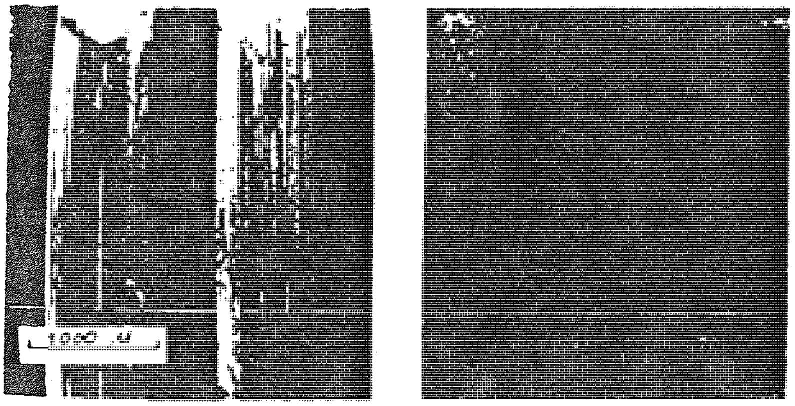


Fig.6.iii.Photograph and chromium X-ray mapping of reference.

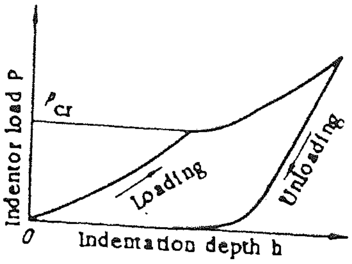


Fig.7. Typical Vickers pyramid indentation diagram obtained in testing chemically applied nickel coatings.

A link was established between the critical load and annealing temperature, t (Fig.8) and the maximum value of P_{cr} was observed at 300°C. Berdikov et al claimed that their test results showed this temperature represents an optimum for the adhesion strength of a nickel coating to substrate. They further showed that the value P_{cr} is connected with the strength of the transitional layer from coating to substrate, i.e. with their cohesion strength. This technique, based on microstrength determination of brittle materials, thus measures the damage zone in the region of the indentor including all the breakdowns (cracks, cleavage etc.) in the continuity of the material.

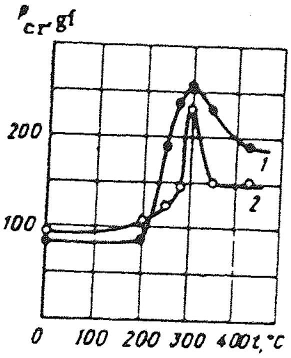


Fig.8. Dependence of critical load Pcr on thermostat (temperature t : 1, 2) nickel coating on D16M and D16T substrates, respectively.

2.4 Non-mechanical Methods

Ideally, one would like to have a test which yields numerical adhesion strength values without destroying the substrate-deposit combination. Such tests are described in this section. However, the following points must be borne in mind: (i) some of the tests are only qualitative, (ii) in some cases, specialised equipment is necessary, (iii) applicability may be restricted to only a few selected systems, and (iv) many of these simply detect the voids or gaps which are realisation of poor adhesion strength.

i. Cathodic Treatment

Although this is a relatively old technique, it has not gained much attention. The original references date back to 1930's by Hothersall and Leadbeater (1938) and Portevin and Cymboliste (1933). This method is similar to the blister method (discussed above) except here hydrogen is used as the fluid to cause blistering. In this method the coated part is made the cathode in an electrochemical cell and the hydrogen evolved diffuses through the coating to collect at the interface and causes blistering. It is evident that: (i) this technique has limited applicability as polymeric substrates may not be studied, (ii) it is qualitative in nature, (iii) the specific interaction between the coating and hydrogen evolved will affect the results and (iv) coating integrity is important.

ii.Electrochemical Method

This technique is based on the assumption that the degree of adhesion of an electrodeposited metal coating on a metal surface is related to the active surface of the cathode ie. where the metal is deposited. Vagramyan and Soloveva (1962) have shown that the area of the active surface can be determined from the value of polarisation at the moment of turning on the plating current. For this technique to be applicable the following conditions has to be satisfied: the current must be employed solely in the reduction of the metal ions to be deposited; the results will be invalidated if any side reaction occurs at the electrode at the commencement of electrolysis, especially where deposition occurs at a potential considerably more negative than that of hydrogen electrode. Most interfering side reactions can be due to surface active impurities and/or oxides present on the metals. Vagramyan and Soloveva determined the degree of adhesion from the polarisation behaviour as a function of time. Lipin (1959) found correlation between the results obtained from this technique for zinc plating on aluminium with the results of cyclic heating tests. Polleys (1963) has mentioned that other workers have utilised the electrochemical technique for nickel deposits on nickel and iron, and copper deposits on copper.

This technique seems quite effective in predicting the effects of both composition and other process variables on the degree of adhesion attained. However, it must be borne in mind that the extent of area on which the metal is deposited does not necessarily determine the adhesion strength. In electrodeposition, a smoother substrate surface yields better adhesion strength than a rough undulating surface which presents a larger surface than a plane surface of the same dimension.

iii. Pulsed Laser or Electron Beam Technique

This technique has been described by Anderson and Goodman (1972) in their study of adhesion of thin metallic films. This involves generating a compressive pressure wave in the solid object under test. The wave is then transferred by reflection into a tensile wave which stresses the interface to be tested. The main disadvantage of this technique is that it is experimentally exacting and can be very expensive.

In addition to the above tests, fluorescent, X-ray (Ferguson 1945, Weaver and Hill, 1958) and electron spin resonance (Campbell, 1970) have been described in the literature. The first two methods are primarily used for detecting defects, voids and gaps in the coating-substrate combinations. X-rays have been used to obtain qualitative information on the adhesion of epitaxial films deposited on single crystal substrates (Chopra, 1969). A capacitance measurement method has been patented in the Soviet Union (Nekrasov).

It is evident from this survey that a wide range of methods are available for measuring adhesion but there is no single technique which possess all the virtues of an ideal test. Many techniques can provide a suitable answer to the query, what is the adhesion of the substrate-deposit combination?, but due precaution must be exercised in the interpretation of the results. Very often the importance of the numerical values of adhesion is masked by the interplay of unwanted factors which are difficult to quantify. If the contributions of these are taken into account, the adhesion values can be misleading. If, however, no numerical values of adhesion are required then almost any of the techniques can be used to follow the increase in adhesion due to certain surface treatments or the decrease due to deterioration from weathering, corrosion, moisture etc. Qualitative adhesion tests are very much limited in their usefulness. These tests do not yield numerical values, the results cannot be compared with other techniques and the effects of process variables in the deposition process cannot be quantified, however, their virtue is simplicity.

Tensile tests using solders, adhesives or nodules are commonly used and are relatively simple to perform. However, the analysis of the forces involved is quite complex and to obtain reliable and reproducible results a very careful operation is required. Many modifications of Ollard's method are now available but are all difficult to perform, also they are of restricted utility.

Shear tests especially the ring shear method used by Dini et al (1972) have been shown to be reliable and reproducible. A range of thicknesses can be studied. Shear tests in which adhesives are used suffer from the same problems as the tensile tests.

The peel test is simple and requires modest equipment. The analysis of the forces involved is complicated and the angle of peel, rate of peel, width of the test strip and the viscoelastic properties of the adherate are all very important. Furthermore, peel values are expressed in force/length therefore cannot be compared with the tensile or shear values which are expressed as force/area. However, peel tests have been quite popular in measuring adhesion quantitatively.

Knife and scribing tests have not been used very often to measure adhesion of electrodeposited coatings. Knife tests are generally used for thick organic paints. The use of scribe or scratch tests has been confined to thin evaporated metallic films.

Ultrasonics are commonly used to detect voids, gaps or flaws at the interface. This technique has also been used to measure quantitatively the adhesion of relatively thick organic films.

Ideally, one would like to measure adhesion without gripping the deposit and the ultracentrifuge offers a solution to this problem. The applications of this technique to electrodeposits is well documented. With the advent of a solid-state ultracentrifuge (Dancy, 1970) this technique offered potential as a practical adhesion test method but not much has been done about this.

Unfortunately, the main disadvantage of all tests is exhibited by the above methods, that is they are destructive.

CHAPTER 3

Adhesion of Electrodeposited Coatings

3.1 Adhesion

The adhesion of electrodeposited metals/or alloys to three main groups of basis materials in which 'perfect' bond strength should be achieved is that in which the coating is deposited onto a cathode of the same metal. Under favourable conditions, the electrodeposit will commence its growth on the substrate in such a way that its crystal lattice aligns itself as much as possible with that of the substrate. In order that a satisfactory, well-adherent deposit should be able to form, the following conditions must be satisfied :

i. The lattice parameters of the deposit metal and substrate metal atoms must be within a given size relationship to each other (the deposit metal lattice must be within - 2.4 and + 12.5% of that of the substrate metal), and

ii. The substrate metal should not have suffered excessive distortion during preliminary machining, polishing, buffing etc.

Provided that these conditions are met, the electrodeposit will commence its growth on the substrate in such a way that its crystal lattice aligns itself as much as possible with that of the substrate. Such a mode of growth is known as "epitaxy". The extent to which epitaxial growth will continue depends on the degree of mismatch of the two lattices, the degree of distortion of the substrate, the operating parameters of electrodeposition and the electrochemical characteristics of the electrolyte.

If the substrate has suffered considerable distortion during preliminary mechanical treatment (but not tearing), attachment will occur preferentially by alloy formation eg.

zinc plated on highly polished steel surface.The alloy zone at the interface will be thin and will not adversely affect the properties of the coating adhesion under such conditions will also be satisfactory.

The metallographic structure of the growing deposit will be determined essentially by the changes occurring in the diffusion layer, which in turn are influenced by bath composition and operating parameters. High melting point metals (eg. nickel), in the presence of specific impurities or additives, tend to form a layered structure due to periodic adsorption of these substances, which cause cessation of growth, followed by fresh growth in a new layer.

Increasing the current density will result in an increased cathode polarisation and hence in an increased rate of nucleation; therefore a progressively finer crystal size will be obtained with rise in current density. Any factors diminishing the rate of increase in cathode polarisation, eg. agitation and/ or raising bath temperature, have the opposite effect. A high voltage usually results in the formation of columnar crystals, whereas a low voltage (as employed in certain simple salt electrolytes) tends to produce crystals of the equi-axed type, which often exhibit twinning.

This phenomenon of epitaxy which can also occur when the substrate is different from the electrodeposit has been discussed by several authors including Blum and Rawdon (1923), Finch, Wilman and Yang (1947), and Graham (1923). As the majority of electrodeposits are finely crystalline, physical evidence of epitaxy is the exception rather than the rule and epitaxy is not necessarily the only criterion for good adhesion. Using metallographic techniques Hothersall (1933) has shown that the grain boundaries of the substrate can be continued in the deposit. He deposited nickel from a solution that gave coarsely crystalline deposits onto a substrate of well defined grain structure. Finch et al (1947) used electron diffraction to examine metals deposited at low current densities onto substrates of known crystal planes. They have shown that the orientation of the substrate is continued up to thickness of 3 µm, but at greater thicknesses epitaxial growth no longer occurred.

In many commercial applications usually the coating and substrate are not the same metal, therefore epitaxy is unlikely to occur. In such cases, adhesion is represented by cohesive forces between metals. Hothersall (1935) claimed that discharged ions take up their positions immediately adjacent to the basis metal lattice and within the field of molecular attraction. Inter-atomic forces involved are van der Waal's forces, covalent forces, metallic bonding forces and ionic and polar forces. The structure of a dissimilar basis metal is more likely to be continued in the coating at low current density, and hence it is more likely that good adhesion will result from such processes. Evidence of epitaxial growth has been reported by Lashmore (1980) in zinc immersion films deposited on aluminium as an intermediate stage in the plating of aluminium. Results obtained by Golby et al (1981) indicate that the immersion processes used would not lead to good adhesion, although the situation is more complex than the direct electroplating of one metal onto another.

The third group of substrates are non-conductors. Non-conductors require the application of an initial conductive coating before an electrodeposited coating can be applied. Chemical reduction (electroless plating), or occasionally vacuum evaporation is generally used to provide the conductive layer. With this system, the three factors involved in adhesion are:

(i) Adhesion between the non-conductor and the thin conductive coating.

(ii) Adhesion between the thin conductive layer and the electrodeposit.

(iii) Cohesion of the outermost layer of plastic to the underlying bulk of the moulding.

Adherend is a general term used for solid substrate to which other materials adhere and Mittal (1974) has suggested that the term adherate to represent the material which adheres to an adherend. Obviously, in an adhering system of A and B, A adheres to B, and B adheres to A, but the thinner phase is called the adherate. Examples of adherates are thin films, thick films, paints and coatings. Adhesive is a special kind of adherate in that it adheres to two adherends instead of one (Mittal, 1978).

Essentially there are two aspects of adhesion study programme : understanding of the factors affecting adhesion and thereby improvement of adhesion strength, and the measurement of adhesion strength. The first aspect has been the subject of a symposia in 1976 (edited by Alner), Lee (1973, 1975) and the latter concerned primarily with the methodology of the measurement of adhesion in adhering systems has been the subject of another symposium in 1978 (edited by Mittal).

3.2 Adhesion Measurements

The measurement of adhesion is important for a variety of reasons : (a) to assess the effect of changes in the process variables or of substrate preparations, and thereby optimise the conditions which yield the required adhesion strength; (b) to discriminate parts or products which have poor adhesion strength from those which are acceptable; and (c) to gain fundamental insight into the mechanism of adhesion. So the need for reliable, reproducible, and quantitative methods for measuring adhesion is quite manifest.

The ASTM Definition of Terms Relating to adhesives (D 907-70) defines adhesion as "the state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking forces or both".

The various theories for mechanisms of adhesion have been discussed by Allen (1969), Raevskii (1973), Mittal (1975, 1976) and Huntesburger (1967) but there is no single theory or mechanism which can explain all adhesion behaviour. All these mechanisms are valid to varying degrees, but their relative importance depends on the adhering system in question.

In an adhering system, adhesion can be expressed in terms of forces or work of attachment, or in terms of forces or work of detachment. If expressed in the former manner, then the correct terminology should be "basic adhesion", "fundamental adhesion", "true adhesion", or "interfacial adhesion". Basic adhesion signifies the interfacial bond strength and should depend exclusively on the interfacial properties, without any contribution from any other sources. Basic adhesion is in the simpler term the summation of all intermolecular or interatomic interactions. These interactions could be electrostatic, chemical, or van der Waals type. Unless there is a well defined interface between the adhering phases, the term basic adhesion does not have any significance.

Experimentally, however, adhesion is measured in terms of forces or the work of detachment or separation of the adhering phases. The separation may take place at the interface, or in the interfacial region (also called interphase), or in the bulk of the weaker adhering phase. Separation in the bulk is termed cohesive failure and is related to the cohesive strength of that bulk phase. The cohesive failure of a thin coating or adhesive however, is unlikely to be the same as the cohesive failure of the same material in bulk. The two possible causes could be mechanical constraints by the adherends or differences in chemical composition or morphology due to the conditions of coating deposition or joint formation.

The interface is a mathematical plane and can only be realised in the case of a non-soluble/non-compound forming adherend-adhereate combination. On the other hand, an interfacial region or interphase possesses a certain thickness, and its mechanical properties are different from those of the contiguous phases. Interphases may be present on the adhering phases (for example, oxide on metal, oily layer on a surface), or they may be formed by interaction of the adhering phases, for example, diffusion type of interphase in a metal-metal system. The nature and thickness of interphases depends on the adhering phases involved Sharpe (1972), Chapman (1974). The presence of these interphases would give rise to additional interfaces.

So obviously, in real adhering systems, there can be many interfaces and interphases in addition to the two bulk phases, and separation could be at any of the interfaces or in any of the interphases or in one of the two bulk phases. If the separation occurs at an interface or in an interphase, then it is suggested that the measured adhesion be labelled as "practical adhesion)". Such suggestion is not entirely satisfactory as there are many unanswered questions.

However, it is suggested that unless the failure is deep in the bulk of the adhering phases, the measured stress required to effect separation of the adhering system be labelled "practical adhesion".

The forces required to disrupt the interface or interphase can be applied in various forms (tensile, peel, shear, etc) and the practical adhesion is expressed in terms of tensile strength, peel strength, or shear strength. Peel strength is expressed in terms of work or energy per unit length. Tensile strength is defined as the stress (force/area) required to remove a specific area of the adherate when the entire area of the adherate is pulled in a direction perpendicular to the adherend surface.

Forces of adhesion and the work or energy of adhesion can be related only if assumptions are made about the changes in force with distance of separation, so that an integration can be performed. In other words, ω, the work of adhesion is:

$$\omega = \int f(x)\, dx \tag{6}$$

According to Bikerman (1967, 1971) true interfacial failure hardly occurs in a "proper bond", that is in a bond where intermolecular interaction between the adherate and the adherend has been achieved. He further suggested that what is taken for interfacial failure is actually a separation in a weak boundary layer. Bikerman (1978) has also cited some examples of non-interfacial failure to bolster his previous views. However, according to Good (1972) what Bikerman calls "weak boundary layers" are actually the interphases between the adhering phases.

In any case, visual inspection is inadequate to ascertain the locus of failure in a separated system, and techniques like electron spectroscopy for chemical analysis, Auger electron spectroscopy, or secondary ion mass spectrometry are necessary for this purpose, and these have been used by Baun (1976), Wyatt et al (1974).

In order to establish a relationship between practical adhesion and basic adhesion it is necessary to look at some of the characteristics of both. Basic adhesion is strictly an interfacial property and depends exclusively on the surface characteristics of adhering phases. Basic adhesion should be independent of the thickness of adherate, thickness of adherent, specimen size, geometry of specimen, temperature, measurement technique, manner of applying external forces, manner of performing test, test rate, bulk properties of adhering phases, etc.

However, the adhesion measurement techniques measure practical adhesion, which is affected by all these factors. For example, practical adhesion in terms of peel strength depends upon the rate of peel, angle of peel etc. Tensile strength depends upon the manner of performing the test and the rate of pull.

Basic adhesion can be theoretically calculated or indirectly determined. In the case of thin-film deposition, basic adhesion between the film and the substrate can be determined by the nucleation methods, ie. by observing the formation of these films Campbell (1970). On the other hand, if the adherate is in liquid form, one can calculate the thermodynamic work of adhesion in terms of its wetting behaviour Mittal (1975). In essence, basic adhesion is calculated by taking the summation of adsorption energies of individual adatoms. The nucleation methods of determining basic adhesion are of limited applicability and are quite tedious.

An approach based upon the molecular models was taken by Taylor and Rutzler (1958), but was not extended to a stage where it could be used to quantify basic adhesion in a system of interest.

The relationship between practical adhesion and basic adhesion can be expressed as follows:

(i) If a sharply defined interface exists between the two adhering phases and the separation is clearly at this interface, then:

Practical adhesion = f (basic adhesion, other factors)

(ii) On the other hand if the separation is in the interfacial region, then

Practical Adhesion = f (interatomic or intermolecular bonding within the interfacial region, other factors).

These other factors include intrinsic stresses (which depend, among other things upon the adherate thickness), presence or absence of sites of easy failure, the mode of applying external stress, the technique of measuring practical adhesion, the failure mode, etc.

The testing for adhesion of coatings is an area in which many different tests are available but they are all destructive and usually require the production of a specially prepared test piece if quantitative results are needed. They all have other limitations such as requiring a thick deposit, for example, in tensile and shear tests or the production of a tab in order to start the test eg. peel tests. Few of the established methods resolve the applied force used for evaluating adhesion into its individual components and hence absolute values cannot be obtained. Direct comparisons cannot be made between results obtained using different tests as the force applicable in a particular test is used as a measure of adhesion.

As there are so many factors which affect practical adhesion, the experimental results while quoting values of practical adhesion must specify the experimental conditions, specimen size and geometry , and other relevant parameters. For example, unless the rate of peel and the angle of peel are kept constant, different experimenters will measure different peel strengths for the same adhering system. The choice of the test for measuring practical adhesion should be based upon the type of stress the test piece is going to encounter in practice.

Because of these limitations any test which attempts to overcome them must be fully evaluated. The object of this work is to further develop the idea introduced by Muaddi et al (1985) which enables some of the disadvantages of earlier methods to be overcome.

The method developed in this work involves the use of a "Q" meter and is based on the principle of exciting vibrations in a sample, interrupting the driving signal and counting the number of oscillations of the freely decaying vibrations between two known preselected amplitudes of oscillations. Adhesion is determined by measuring the effect of plating on internal friction. This is achieved by determining the damping of vibrations of a resonating specimen before and after plating. The degree of adhesion between substrate and coating influences damping characteristics.

CHAPTER 4

Plating on Aluminium and its alloys

4.1 Introduction

Due to the microstructure of aluminium alloys, the alloy surfaces do not respond uniformly to the various pretreatments applied. It is due to many different responses of various alloys to the same pretreatment sequence which has led to the wide range of pretreatments recommended for the numerous aluminium alloys. It is possible using aluminium to produce a range of adhesion values depending on the alloy and or pretreatment used. Hence in this work aluminium alloys were used to produce different levels of adhesion to provide a means of evaluating the Q meter technique.

However, electrodeposition onto aluminium alloys poses a number of fundamental problems due to their reactive nature. As soon as aluminium is exposed to the atmosphere a thin oxide film forms rapidly. In order to accomplish successful adhesion between an aluminium substrate and electrodeposited coating this oxide film must be removed and stopped from reforming by being replaced by a more receptive film for satisfactory plating. Since the electrochemical behaviour of aluminium alloys varies with composition and metallurgical structure, it has been difficult to find a preplating procedure that will be equally satisfactory for all types and tempers of aluminium alloys.

Aluminium being a very reactive metal, demands special consideration as the reaction products on the metal surface interfere with the formation of metallic bond between the basis metal and the electrodeposited metal. Although it should be possible to form a metallic bond between aluminium and the plated metal because a stage must exist in the dissolution of the oxide where the clean metal surface is exposed, in the normal pretreatment sequence the oxide reforms on the surface before the metal can be made cathodic in the electroplating solution. Therefore the metal needs some form of protection in the transition stage between the removal of oxide and subsequent deposition.

4.2 Immersion Zinc Processes

The well-known zincate process is the most widely used technique for preparing aluminium for plating. The zincate process has been developed into a relatively simple, cheap and reliable technique for plating on aluminium and a wide range of its alloys (Wernick et al 1987). The zinc immersion process was first developed by Hewitson in 1927 in the USA but was shortly to be found in use in Germany (Altamannsberger 1931, Elsner 1935) and Britain (Brand and Sutton 1935). This development was soon followed by the double dipping technique introduced by Korpiun (1939).

The simplest form of the zincate solution consists of zinc oxide dissolved in sodium hydroxide. The caustic dissolves the surface layer of oxide from the aluminium and zinc is then deposited onto this fresh surface by galvanic action. This thin layer of zinc prevents the oxide from reforming and acts as an adherent base onto which other metals - most frequently copper or brass can be deposited .

The metals which have been deposited by immersion processes are Zn, Sn, Cu, Fe, Ni, Mn etc. These metals have been used as undercoats prior to electrodeposition and have offered positive adhesion of subsequent deposition to aluminium, but the adhesion was not always satisfactory, especially on aluminium alloys (Wyszynski, 1967). In order to electroplate on aluminium, it is a standard practice to first apply an immersion deposit of either zinc or tin, of these zinc has been the most common.

Straumanis and Braks (1949), Streiche (1949) and Petrocelli (1950) established that the dissolution of aluminium in alkaline solution is electrochemical in character. Hydrogen evolution may take place to some extent at the cathode, this is usually not important. It has been shown that the ratio of zinc oxide and caustic soda in the zincate solution has a profound effect on the subsequent electrodeposits (Wernick et al 1987). The physical conditions, time of immersion and temperature, can also affect the degree of adhesion.

4.3 Mechanism of Zinc Deposition

The mechanism of deposition of zinc from zincate solution is very important as the adhesion of a subsequent plated coating depends on the form of the initial deposit. According to Bullogh and Gardman (1947) the adhesion between zinc and aluminium depend on the degree of epitaxy between the substrate and deposit.

The lattice constant of aluminium is 0.404 nm compared with 0.266 nm for zinc (Table 4), the zinc immersion deposit is formed by replacement of aluminium atoms by zinc atoms, on the (110) plane as an atomic layer with little distortion. The X-ray and electron diffraction study of immersion zinc coated aluminium by Bailey (1951) showed the zinc film was covered with separated small crystals of zinc. He also presented evidence to support the existence of small amounts of zinc hydroxide on the surface.

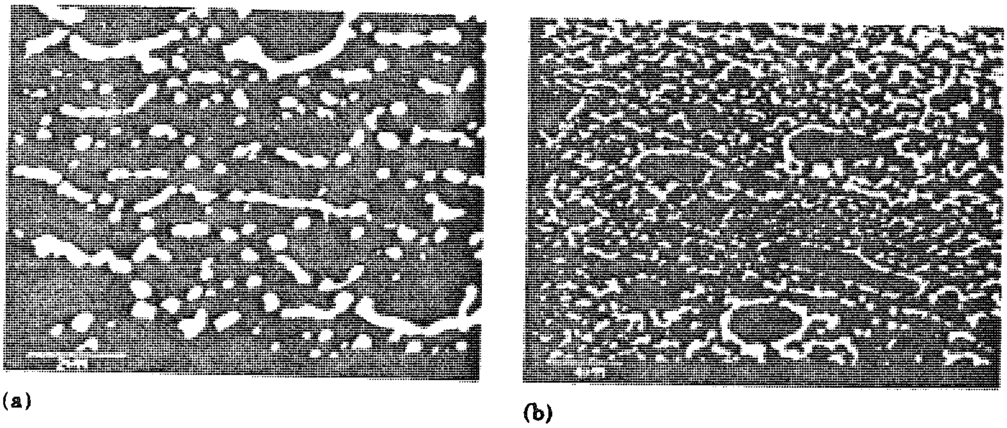
Lashmore (1980) made an extensive study of the zincating of aluminium. Using electron microscopy and electron diffraction he found that zinc initially forms epitaxial semi-continuous films on all the principal aluminium lattice planes. The subsequent zinc growth continued in the form of separate crystallites (200 nm diameter) which grew upon the initial film while continuing to maintain the epitaxial relationship.

Table 4. Metals for possible direct deposition of aluminum (Based on Schwartz and Newkirk, 1972)

Element	*Crystal structure*	*Lattice parameter* A	*Atomic diameter* A	*Valence*	*Solid solubility in Al*	*Plating process*	*Adhesion of plating on Al*
Al	fcc	4.0413	2.8577	3	–	–	–
Cu	fcc	3.607	2.551	1,2	0.1%	I*	poor
Ag	fcc	4.077	2.883	1	1.0%	–	–
Au	fcc	4.070	2.878	1	nil	–	–
Zn	cph	2.660	2.660	2	2.0%	I & E	good
Cd	cph	2.973	2.973	2	nil	I	poor
Sn	diamond tetragonal	6.476 5.830	2.804	2,4	nil	I	fair
Pb	fcc	4.940	3.493	2	nil	–	–
Cr	bcc	2.879	2.493	3,6	0.07%	E	good
Fe	bcc	2.861	2.477	2,3	nil	I	poor
Ni	fcc	3.517	2.487	2	0.005%	I	poor
Alloys							
Cu-Zn 70-30	fcc	3.693			0.2%	I	good
Zn-Ni 94-6	cph					I	good
Cu-Sn 70-30	fcc & orthogonal					I	good
Cu-Pb 80-20	fcc					E	–

*I = Immersion; E = Electroplating

Dennis and Golby (1981) published scanning electron micrographs of commercial purity aluminium after 5 and 30seconds immersion in zincate solution. In the first 5 seconds zinc crystallites had nucleated preferentially around etch pits, while after 30seconds (Fig.9) more of the surface had been covered with zinc and the growth centres had started to coalesce. They further found that even after 2minutes immersion the surface was still not completely covered though the preferential growth round etch pits was not as obvious.


(a)

(b)

Fig.9. Scanning electron micrographs of the surface of commercial purity aluminium pretreated by alkaline cathodic cleaning and etching for 1 minute in 5%HF,50%HNO_3 :

a) after 5 seconds immersion in modified alloy zincate solution at room temperature,

b) after 30 seconds immersion (Dennis and Golby, 1981).

According to Bailey (1951) a dilute zincate bath containing 5g/l ZnO and 45g/l NaOH produces thicker, large grained zinc deposits (1000 crystals/cm^2) with tree-like structure 10^{-3} cm diameter x 10^{-5} cm high which may correspond to single crystals. Bailey calculated the crystal size from theoretical grounds and found that in the concentrated solution was approximately 1/100th that in the dilute solution, with a corresponding large increase in adhesion between the zinc and aluminium in the former. However, the findings of Keller and Zelly (1949) are in contrast in terms of the grain structure. They found deposits from a more concentrated solution i.e. 100g/l ZnO and 500g/l NaOH are finer grained and more compact.

Wyszynski (1980) found that in a solution containing 20g/l ZnO and 120g/l NaOH the deposit obtained was irregular, while from a solution containing 100g/l ZnO and 500g/l NaOH a uniform but coarse deposit was formed with a tendency for the development of a dendritic growth.

The results described so far indicate that there is a lower limit to the concentration of the zincate solution below which adhesion is generally poor. Bailey (1951) measured adhesion of zincated sheet samples 100mm x 50mm x 4.5mm with 50µm thick nickel after which the samples were heated until the aluminium fractured. If the deposit could be separated by hammering with a chisel, 'medium-weak' or medium strong ratings were given according to the force required to to pull off the coating. Where no separation could be effected the adhesion was termed 'strong'. Figures 10-12 show that 1/2 minute zincate treatment was not sufficient to produce good adhesion. The adhesion after 3 minute was approximately similar to that after 5 minutes. Therefore, a suitable solution may be based on a ZnO/NaOH as below:

ZnO	40- 50g/l
NaOH	400 - 450g/l

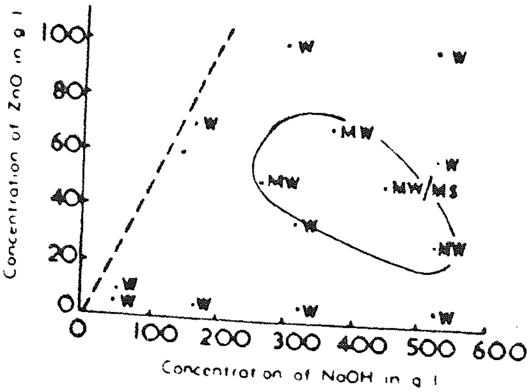


Fig.10. Effect of solution concentration on adhesion of zinc deposit obtained after 1/2 minute immersion in zincate solution. Adhesion ratings :

W = weak, MW = medium weak, MS = medium strong, S = strong.

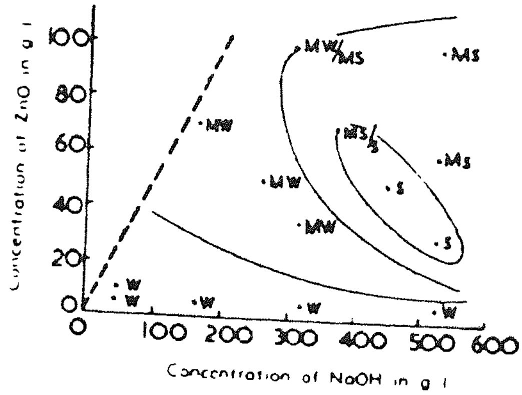


Fig.11. As Fig.10. but after a 3 minute immersion.

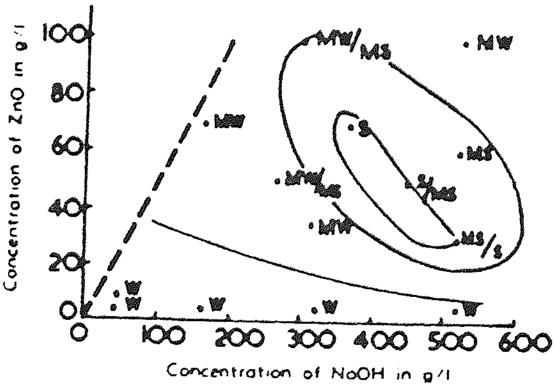


Fig.12. As Fig. 10 but after a 5 minute immersion

Wyszynski (1980) had carried out an evaluation of the adhesion of nickel onto aluminium which had been treated in a range of zincate solutions using a qualitative peel adhesion test. Wyszynski concluded that treatment in the concentrated solution generally improved the adhesion of the plate to the substrate and the treatment in the very dilute solution did very little to improve the adhesion between the plate and aluminium.

The effect of alkali concentration of the zincate solution on the weight of the deposit formed shows that the higher the caustic soda concentration, the lower the weight of zinc initially deposited (Keller and Zelley 1950).

Several suggestions have been made regarding modifications to the basic ZnO/NaOH solutions with the object of producing a thin, uniform, firmly adherent layer of zinc which will promote adhesion of plated deposit to aluminium and its alloys. Korpiun (1939) found that the addition of copper and sodium and potassium tartrate ion to a zincate solution containing 80g/l ZnO and 400g/l NaOH, improved the adhesion of various electrodeposits on zincated aluminium.

West (1946) indicated that copper ions in the zincate solution reduced the rate of zinc deposition and made the process more controllable. Zelley (1953-54) proposed three modified solutions which were claimed to give uniform zinc coverage of aluminium and many alloys, and improve the adhesion of a number of deposited metals. The solutions proposed are the following :

Table 5 Modified zincate solutions proposed by Zelley

	Solution 1	Solution 2	Solution 3
Sodium hydroxide	525g/l	50g/l	120g/l
Zinc Oxide	100g/l	5g/l	20g/
Ferric chloride	1g/l	2g/l	2g/l
Potassium sodium tartrate	10g/l	50g/l	50g/l
Sodium nitrate	-	1g/l	1g/l

Small amounts of ferric chloride in conjunction with the tartrate ion improved the adhesion of deposits. Sodium nitrate present in the dilute solutions limited the weight of zinc deposited. Solutions 2 and 3 are recommended for plating complex shaped components where rinsing and 'dragout' are likely to cause problems. Solution 3 is a compromise between dilute and concentrated formulations to give the large zinc reserve needed for high volume production with only slightly increased drag-out.

Such and Wyszynski (1965) have indicated that the presence of nickel in the zincate solution is beneficial in promoting adhesion of nickel plated directly on to the zinc immersion film. A certain amount of copper added to the modified solution was found useful for zincating certain alloys. Excess quantities of copper, however, caused unsatisfactory adhesion. Metal additions were maintained within a range of concentration and the ratios between the metals kept within certain limits. The work of Such and Wyszysnki resulted (British Patent 1961, 1965) in the formulation of the proprietary modified alloy zincate (M.A.Z.) solution called Bondal. This contains :

Nickel sulphate ($NiSO_4.6H_2O$)	30g/l
Zinc sulphate ($ZnSO_4.7H_2O$)	40g/l
Sodium hydroxide	106g/l
Potassium cyanide	10g/l
Potassium hydrogen tartrate ($KHCH_4H_4O_6$)	40g/l
Copper sulphate ($CuSO_4.5H_2O$)	5g/l
Ferric chloride ($FeCl_3.6H_2O$)	2g/l

This dilute complexed zincate based solution yields a superior zinc alloy film comprising approximately 86% zinc, 8% copper and 6% nickel (Such and Wyszynski 1965, 1967). However, the nickel content of the film increases with time.The growing surface of the deposit is believed to be gradually poisoned with nickel and this eventually arrests film growth. Further grain refinement is achieved by adding a small amount of ferric chloride which inhibits growth of acicular crystals from the uniform fine grained crystal matrix.

The aluminium content of the modified alloy zincate (M.A.Z.) solution increases with time. According to Wyszynski (1980), an increase to the level of 15g/l aluminium does not affect generally the adhesion of the deposit to most alloys. However, for some alloys e.g. Al-15%Si, deposit adhesion decreases with increase in aluminium content in the bath. Since aluminium forms an insoluble cyanide it can be precipitated out of solution by the addition of potassium cyanide without interference with the composition of the modified alloy zincate solution (Wyszynski, 1980).

4.4 Effect of pretreatment

Good cleaning and suitable conditioning of the aluminium is essential in order to obtain satisfactory zincating. However, specific pretreatment effectiveness depends on alloy type and condition. Although the modified alloy zincate process was initially formulated for commercial purity aluminium, Wyszynski (1980) found its extension to the complete range of aluminium alloys proved that the original etch solution (50% v/v nitric acid) was not satisfactory in every case. Golby and Dennis (1981) found that the immersion film morphology and its adhesion were influenced significantly by aluminium alloy response to the pretreatment sequence. For optimum adhesion a particular process sequence is likely to be necessary for each alloy.

4.5 Double zinc immersion technique

This double zinc immersion technique has been found useful in plating many alloys which are difficult to plate satisfactorily by the single immersion method. In this process the first zinc coating is stripped in nitric acid and a new zinc deposit is applied and this was suggested by Korpiun (1939). Golby, Dennis and Wyszynski (1981) have shown using electron microscopy that the second coating is more compact and consists of a larger number of fine grains. The application and removal of the first zinc deposit results in the production of surface with more uniform potential (Fig.13).

Monteiro and Ross (1984) compared the composition of single dip and double dip deposits from modified alloy zincate solutions using Auger electron spectroscopy and argon ion milling to measure the change in composition through the film from the substrate to the outer surface. The double film was only 120 nm thick, compared with 280 nm for the single dip film. The double dip film was found to contain a higher proportion of aluminium and copper with a corresponding lower proportion of zinc, compared with the single dip film.

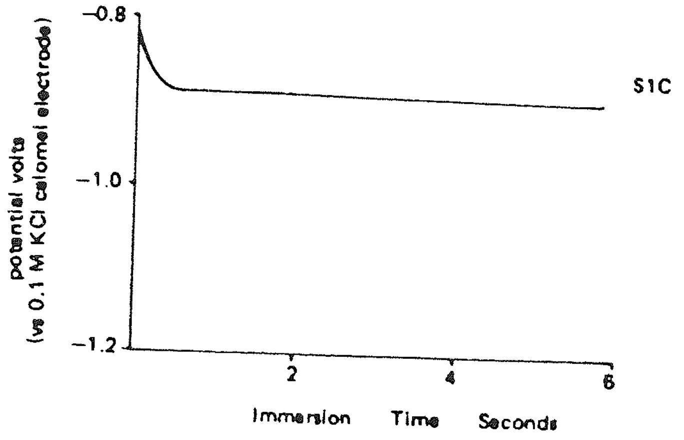


Fig.13. Change in potential of aluminium on immersion in modified alloy zincate solution at room temperature using a double dip sequence (Golby et al, 1981).

4.6 The effect of temperature on the zincate solution

Keller and Zelley (1950) found a relationship between the solution temperature and thickness of the deposit obtained from the concentrated simple zincate solution (Fig.14). The graph shows at higher temperatures the initial rate of deposition is increased appreciably. Bailey (1951) showed that in 100g/l ZnO and 500g/l NaOH, good adhesion was achieved with 1 to 3 minutes immersion at room temperature. However, at 85°C good adhesion was achieved after 1 minute immersion but was poor after 3 minutes. Longer immersion time was required at temperatures below room temperature to obtain good adhesion. At - 6°C the reaction rate slowed down considerably and required 20 minutes immersion in order to obtain good adhesion.

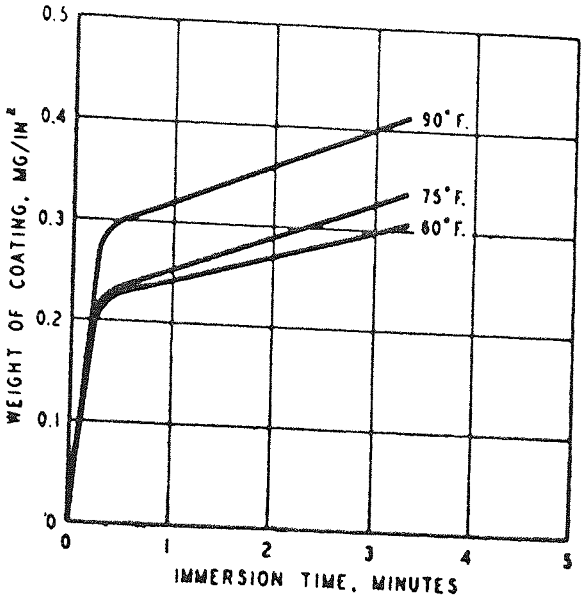


Fig.14. Effect of temperature of the concentrated simple zincate solution (100 g/l ZnO + 525 g/l NaOH).

Wyszynski (1980) studied the influence of temperature on the composition of the film formed using the modified zincate solution. He found the increase in temperature is beneficial in the case of some alloys, since it enables the optimum film thickness of 0.2-0.3 µm to be reached more quickly but it cannot be allowed in the case of high copper and high magnesium alloys. Also as the rate of film build-up increased, its composition altered and became progressively richer in copper with the subsequent reduction of adhesion of the deposit.

Therefore it is essential that the zincate solution be operated within the recommended temperature range. The effect of temperature on process characteristics has a considerable practical significance since dissolution of aluminium is an exothermic reaction. The temperature of the solution can rise fast during use with a progressive reduction of bond strength unless the volume of the process solution is substantial or artificial cooling is introduced. However, a proprietary solution such as bondal is formulated for room temperature operation where close control over film weight is possible.

In this project Bondal solution (W.Canning Materials Ltd) was used at room temperature in order to produce zincate immersion films on aluminium alloys, the solution was stirred during immersion. Single and double dip sequences were used to vary the adhesion level. The Bondal solution was also diluted in order to vary the level of adhesion.

CHAPTER 5

NON - DESTRUCTIVE ADHESION TESTS

5.1 DEVELOPMENT OF A NON-DESTRUCTIVE ADHESION TEST

Expertise has been established in the Department of Mechanical and Production Engineering at Aston in the use of "Modal Testing" for other purposes. Since this involves the striking with a hammer of a freely supported sample, it is possible that ultimately this method may be easier to convert into a readily usable test procedure. Also software is available for analysis of the vibrational data. Consequently it was decided to commence this project by attempting to evaluate this method for use with coated samples.

5.2 Introduction to Modal Testing

Since the very early days of awareness of vibrations, experimental observations have been made for the two major objectives of : (a) determining the nature and extent of vibration response levels and (b) verifying theoretical models and predictions. The two vibration measurement objectives represent two corresponding types of test. The first is one where vibration forces or, more usually responses are measured during "operation" of the machine or structure under study. The second one is a test where the structure or component is vibrated with a known excitation.

The second type of test is generally made under much more closely-controlled conditions than the former and consequently yields more accurate and detailed information. This type of test - including both the data acquisition and its subsequent analysis - is called "Modal Testing".

5.3 Philosophy of Modal Testing

One of the major requirements of the subject of modal testing is a thorough integration of three components :

(i) the theoretical basis of vibration

(ii) accurate measurement of vibration and

(iii) realistic and detailed data analysis.

In the 'Analysis ' stage the measured data (invariably, frequency response functions or mobilities) are subjected to a range of curve-fitting procedures in an attempt to find a mathematical model which provides the closest description of the actually - observed behaviour. There are many approaches, or algorithms, for this phase and as is usually the case, no single one is ideal for all problems.

There is a clear distinction between the free vibration and forced vibration analyses, these usually being two successive stages in a full vibrational analysis.

For the single degree of freedom(SDOF), a free vibration yields its natural frequency (f_0) and damping factor while a particular type of forced response analysis, assuming a harmonic excitation, leads to the definition of the frequency response function - such as the mobility or the ratio of velocity response to force output. These two types of results are referred to as "modal properties" and "frequency response characteristics" respectively. The three alternative ways of plotting the plots of the mobility or other types of frequency response are shown in Fig.15.

The most widely used modal analysis method is known as "Single Degree of Freedom Curve Fit", or often ,"the Circle Fit" procedure. This method uses the fact that at frequencies close to a natural frequency, the mobility can often be approximated to that of a single degree of freedom system plus a constant offset term (which approximately accounts for the other modes). This assumption allows the use of the circular nature of a modulus /phase polar plot (the Nyquist plot) of the frequency response function of a SDOF system (Fig15) by curve - fitting a circle to just a few measured data points as illustrated in Fig.16. This process can be repeated for each resonance individually until the whole curve has been analysed.

The overall objective of the test is to determine a set of modal properties for a structure . These consist of natural frequencies, damping factors and mode shapes. The procedure consists of three steps :

(i) measure an appropriate set of mobilities;

(ii) analyse these using appropriate curve-fitting procedures; and

(iii) combine the results of the curve fits to construct the required model.

Using the knowledge of the theoretical relationship between mobility functions and modal properties, it is possible to show that an "appropriate" set of mobilities to measure consists of just one column in the mobility matrix. In practice, this either means exciting the structure at one point and measuring responses at all points or measuring the response at one point while excitation is applied separately at each point in turn. This last method is most conveniently achieved using a hammer or other non-contacting excitation device.

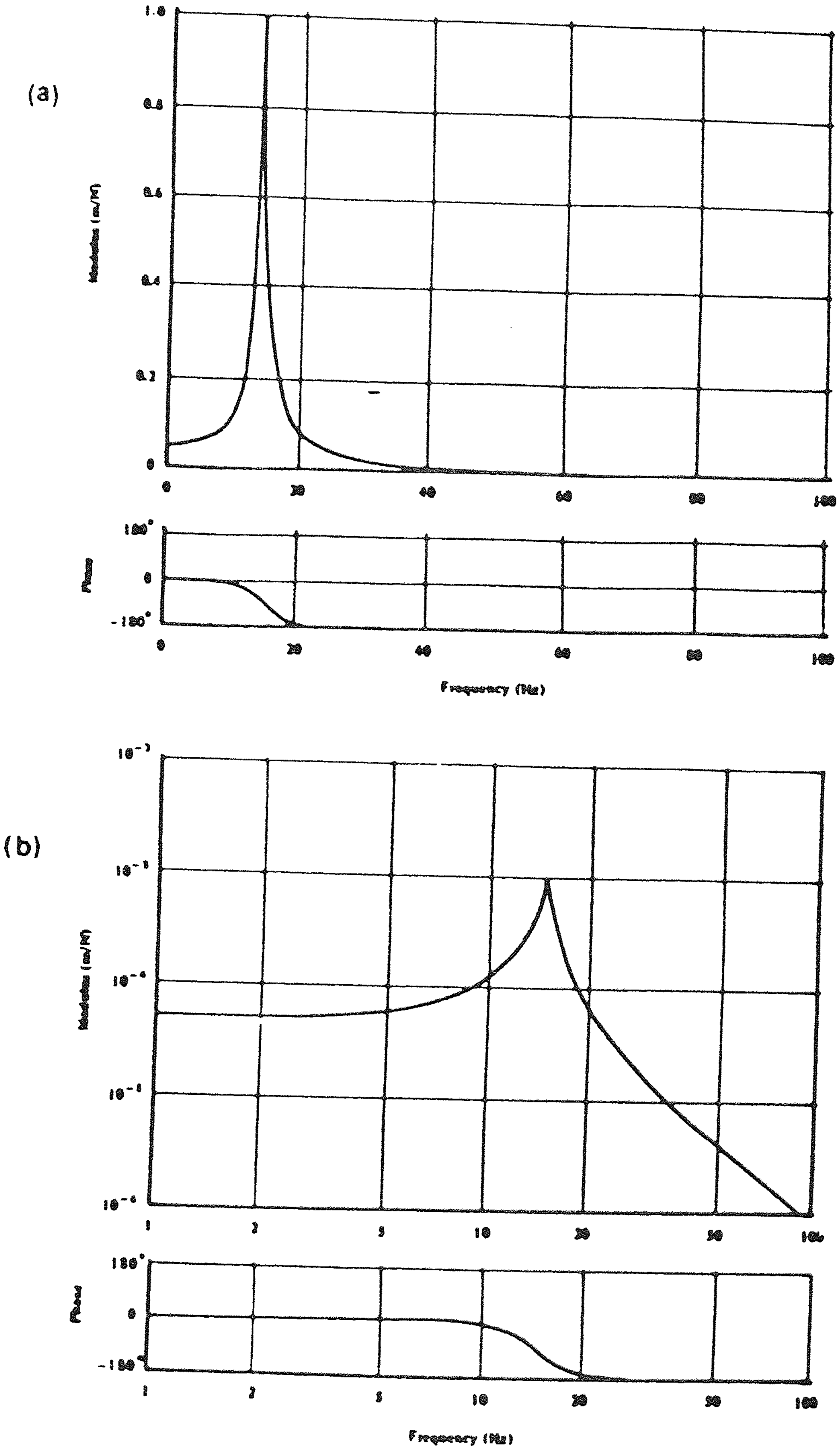


Fig.15. Alternative Formats for display of frequency response function of a single degree of freedom.

a) Linear

b) Logarithmic

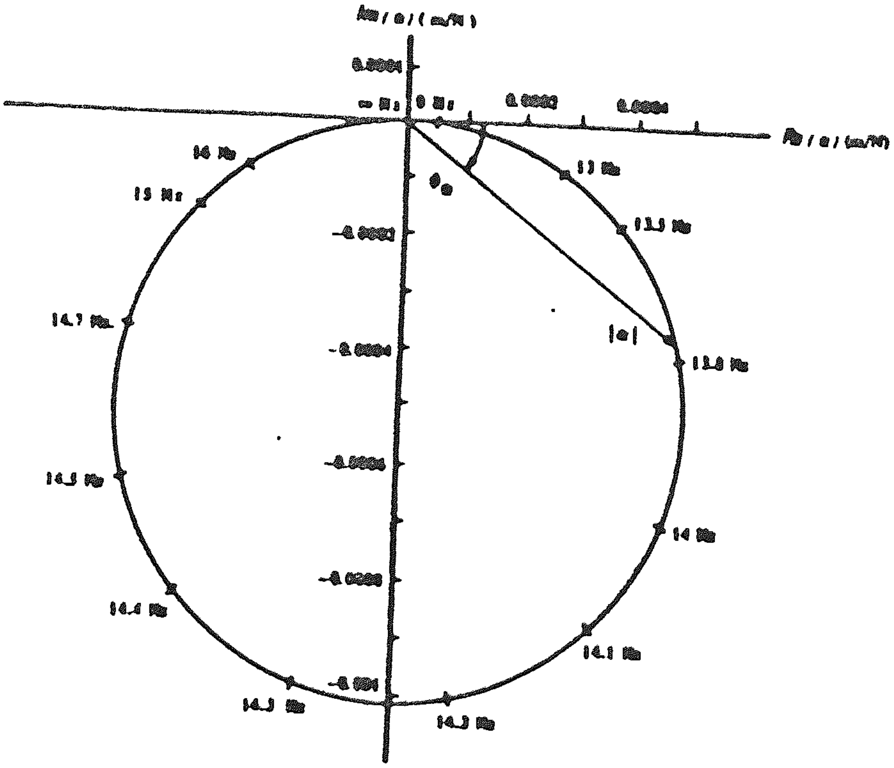
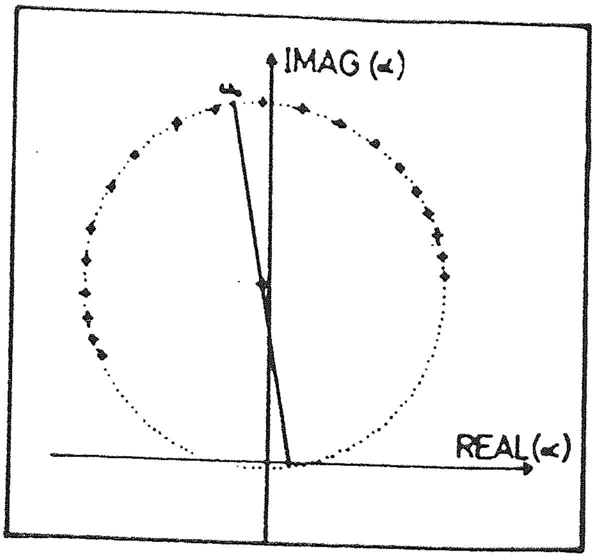


Fig.15.c. Nyquist Plot.



Circle-Fit to Resonant Data

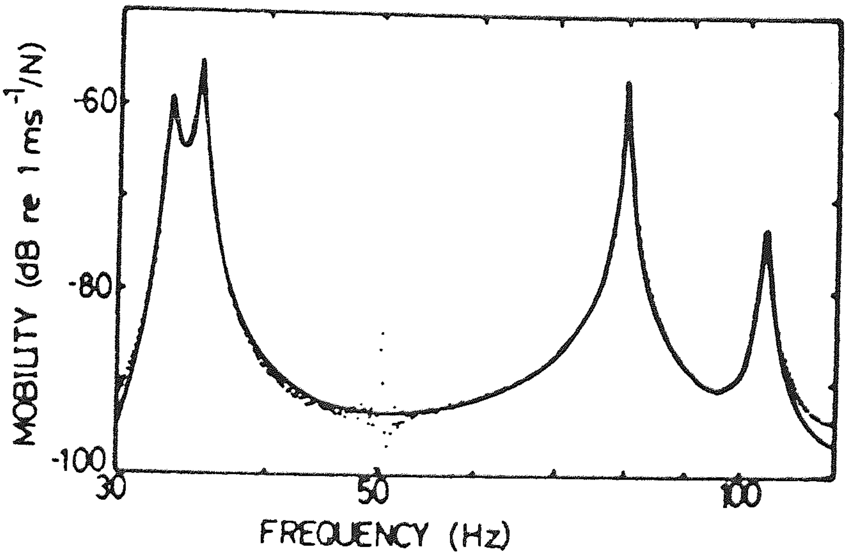


Fig.16. Regenaration of Mobility Curve from Circle-Fit Data.

5.4 Dual Channel Signal Analyser

The Dual Channel Analyser Type 2032 (B & K) is a flexible, fully self contained two channel FFT analyser system having 801 lines resolution with a frequency span from 156 Hz to 256 kHz,selectable in a binary sequence. The selected frequency span can then be placed anywhere in the 0 to 256 kHz baseband frequency range. The real-time frequency of the analyser is 800 Hz in dual channel operation, rising to 16 kHz for single channel operation.

The analyser is used to measure input-output and statistical relationships associated with mechanical, acoustical and electrical systems. Its 801 lines resolution are of special importance with respect to measurements on mechanical systems, since more modes of vibrations can be identified and characterised in a single analysis.

The analyser has a fully instrumented input. This means that it can accept signals from most Bruel & Kjaer microphone preamplifiers and via the Line Drive Amplifier Type 2644, most B & K accelerometers, in either of its channels, and without the need for amplifiers or preamplifiers. It can store and display data.

5.5 "Q" Measurements

The measurement of the decay of oscillations or the internal friction (Q^{-1}) has been widely used in the study of the mechanical properties of materials. Essentially, it is a measure of energy dissipated internally within a vibrating specimen when mechanical energy is applied externally. The various methods which can be used in the measurement of internal friction (Q^{-1}) in solids are as follows :

(i) Measurement of the energy input required to maintain an object under test in vibration of constant amplitude.

(ii) Determination of the resonance curve during forced vibration (Bandwidth). In this method the two frequencies are found at two half power points. The lower the internal friction (Q^{-1}) the sharper the resonance peak. The accuracy of this method decreases as the Q increases.

$$Q = f_r / f_2 - f_1 \qquad (7)$$

where

f_r is the resonant frequency

f_2 is the frequency higher than resonant frequency which has amplitude 0.707 that of resonant frequency (half power points)

f_1 is the corresponding frequency on the other side.

(iii) Semi - static determination of the hysteresis loop in the stress curve during forced vibration. This method is suitable for evaluating the damping effects due to plastic deformations in the material.

(iv) Measurement of the decay rate of vibration. In this technique the number of oscillations between two predetermined voltage levels (amplitudes) is counted by an electronic instrument when the excitation source is removed and the vibrations are decaying freely at the natural frequency of the specimen.

A variety of instruments has been described in the literature for measuring Q^{-1} using the decay technique. Fusfield (1950) and Pattison (1954) described devices in which the decaying signal was rectified and smoothed, the resulting envelope was used to trigger further circuitry, producing time markers for preselected amplitudes of oscillation. Q was calculated by measuring the resonant frequency of the sample and the time interval between these markers by means of a counter. This technique loses precision at low frequencies due to difficulty in smoothing the rectified signal. Also the filter components should really be changed for each value of decrement and frequency. From the Fusfeld instrument about 20 readings could be taken per minute by two operators.

These limitations were circumvented by Swartz (1964) by eliminating the rectification procedure and using the decay oscillation directly to trigger the threshold level devices. Q is measured by counting the number of oscillations between two preset amplitudes of frequency below 80 Hz for Q values below 100.

Mason (1969) and Eder (1973) developed devices which work in a similar way by counting the decrement oscillations. In the Mason device the frequency range is 5 Hz to 25 kHz for Q values between 6 and 200, while Eder's device has a frequency range of 10 Hz to 40 kHz for Q values between some tens and some millions.

5.6 Decrement "Q" meter

An electronic instrument based on the decrement technique was constructed using Muaddi's (1982) design which has been claimed to have given a numerical method of evaluating the integrity of solids, the testing of adhesive bonds and similar component assemblies. Obviously the availability of much improved I.C. electronic components have been a major factor in achieving an instrument of high accuracy.

The principle of the equation of the instrument is the exponential equation of damped amplitude.

$$A_n = A_o \exp(-\pi n/Q) \qquad (8)$$

where

Ao is the initial amplitude

An is the amplitude after number of oscillations

n is the number of oscillations

Q is the "Q" factor.

The instrument counts the number of oscillations of the freely decaying vibration between two defined levels of amplitude. Noting that A_o/A_n has been chosen to be 23.14 and that ln23.14 is equal to π then the above equation establishes that n is equal to Q i.e. the number of pulses counted is equal to Q value of the test sample.

Considering the solid body to be isolated so that energy dissipation due to support conditions and radiation of sound into the surrounding can be neglected, the dissipation mechanisms inherent to the solid material collectively produce what is referred to as internal friction (which is the inverse of quality factor Q). The Q may be understood by an idealised mechanical vibrator with a single degree of freedom. Such a system as shown in Fig.17, consists of a spring of stiffness K, viscous damping $R_m X$ and a mass, M, represents the material. In case of a bar the components are distributed but can nevertheless be represented by this lumped component model.

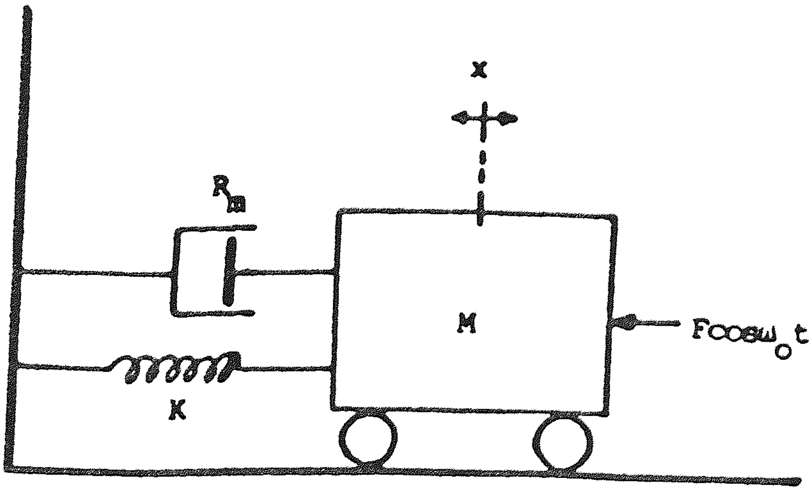


Fig.17. An idealised mechanical system with mass, spring and damping.

The equation of motion for the system is given by :

$$MX + R_m X + KX = F\cos\omega_o t \qquad (9)$$

In the absence of the driving force $F\cos\omega_o t$ the motion is governed by :

$$MX + R_m X + KX = 0 \qquad (10)$$

When decrement is low, the condition applicable throughout this work, the system vibrates at its natural frequency $\omega_o = (K/M)^{1/2}$ and the general solution is given by the equation

$$X = A_o \exp(-R_m t / 2M) \operatorname{Sin}(\omega_o t + \phi) \qquad (11)$$

A is the amplitude of vibration (A_o at time $t = 0$) and it will decay by a term exp ($- R_m t / 2M$) as shown in Fig.18.

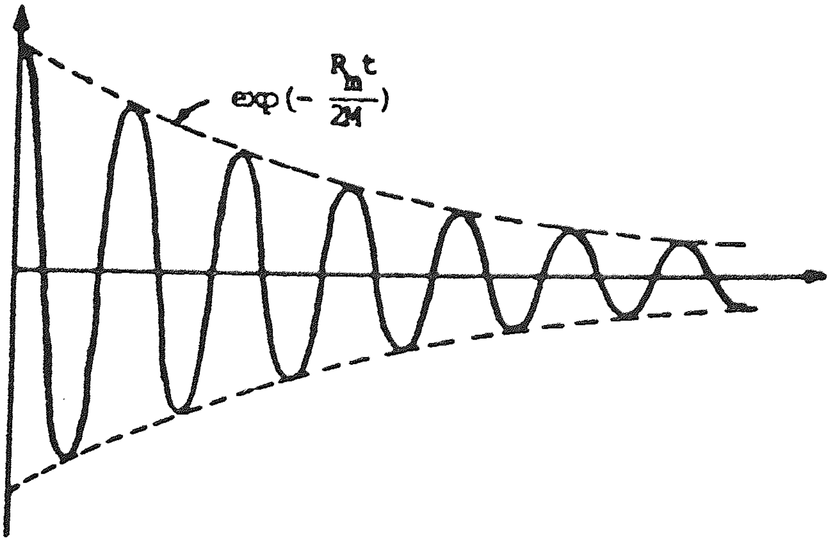


Fig. 18. Damped oscillatory motion. The amplitude decays with exp ($- R_m t / 2M$).

After n vibrations the amplitude at time $t = t_n$ is given by

$$A_n = A_o \exp(-R_m t_n / 2M) \qquad (12)$$

and the decay of energy is given by

$$E_n = E_o \exp(-R_m t / M) \qquad (13)$$

The Q factor which can be defined in both mechanical and electrical terms as

$Q = 2\pi$ (energy stored / energy lost per cycle).

$$Q = 2\pi \; E_n / -dE_n = 2\pi E_n / R_m E_n T/M = \omega M / R_m \qquad (14)$$

where $-dE_n = R_m E_n T/M$ is the energy lost per cycle of period T.

Equation (14) relates Rm of equation (10) to Q.

It follows that

$$E_n = E_o \exp(-\omega t/Q) = E_o \exp(-2\pi n / Q) \qquad (15)$$

Where n is the number of oscillations.

In equation (14) the time and frequency terms have been eliminated, and Q is expressed in terms of amplitude and the number of oscillations as

$$A_n = A_o \exp(-\pi n / Q) \qquad (16)$$

This equation is the basis of the instrument developed by Muaddi. This method has been

This equation is the basis of the instrument developed by Muaddi. This method has been used in order to evaluate the Q meter and has been discussed in chapter 6 .

CHAPTER 6

EXPERIMENTAL TECHNIQUES

6.1 SELECTION OF METAL TO PLATE

The object of this experimental work was to produce a range of adhesion levels between a substrate and electrodeposited metal and to study whether the Q meter developed could detect the variation at the interface. As has been indicated in the literature review, the adhesion of the plated metal on aluminium is very much dependent on the alloy type and the pretreatment given prior to plating. Therefore by altering the pretreatment sequence prior to plating it is possible to obtain varying degrees of adhesion level on aluminium. The aluminium alloys therefore chosen were S1C and HE9. S1C alloy is the commercially pure aluminium alloy and is expected to produce good or higher level of adhesion when plated with electrodeposited nickel. The other alloy chosen was HE9 a commercial aluminium alloy containing a higher silicon content. This is a more difficult to plate alloy and would result in lower levels of adhesion on plating. Information on alloys involved in the test programme is given below in Table6.

All specimens were cut and machined as required to dimensions of 12.8cm x 2.5cm x 0.625cm except where otherwise stated.

Table 6 Composition,Condition and Mechanical Properties Of The Aluminium Alloys Used

Alloy	Material designation %								Min. U.T.S	Min.elong N.mm^{-2}
Type	Condition	I.S.O.	Main alloying additions %							
			Al	Si	Fe	Mn	Mg	Zn		
S1C Non-heat treatable wrought.	M	Al(99%) remainder impurities mainly Fe,Si.	Rem.	0.5	0.7	0.1	-	0.1	70	11
HE9	TF	AlZnSi	Rem	0.3	0.4	0.1	0.4	0.2	150	6

M = As manufactured, as cast, as extruded and rolled etc.
TF = Solution and precipitation heat-treated.

6.2 SELECTION OF PLATING BATH

Since it was intended to carry out destructive tests on the test samples after taking Q readings in order to establish the degree of adhesion between the substrate and the electrodeposited metal, such as peel adhesion and bending tests, it was necessary to produce an adherent, ductile electrodeposit which would be suitable for destructive tests.

Therefore it was decided to use Watt's nickel. The solution produces a dull deposit which is soft, has a moderate internal stress, low tensile strength and high ductility. The solution was operated at 55^{o}C, at pH 4.5, and current density between 3.5 - 4.0 A/dm^2. The solution was made up as below :

Nickel Sulphate	300g/l
Sodium Chloride	28 g/l
Boric Acid	40 g/l.

The weight/thickness of the deposited nickel was monitored using an ampere minute meter. The rate of deposition of the electroplated nickel was approximately 30 µm per hour.

6.3 Pretreatment

The pretreatment process sequences employed in this work are shown in Table 7; these are based on the work carried out by Golby and Dennis (1981). However, the process sequence had to be modified due to chemical attack on the base metal and apparently resulted in poor adhesion. A much milder precleaning sequence was also used as shown in sequence V in Table 7 below.

Table 7 Pretreatment Process Sequences

Sequence I

(1) Acetone degrease as required

(2) Cathodic alkali clean (load live) at 60°C for 2 min, water rinse

(3) Cathodic alkaline clean (load live) at room temperature for 2 min, water rinse

(4) Dip in 50% HNO_3 (acid etch no. 1), running water rinse

(5) Dip in modified alloy zincate solution (W.Canning's Bondal solution) at room temperature, running water rinse

(6) Electroplate

Sequence II

As sequence I except that the 1 min 50% HNO_3 dip (acid etch no.1) used in stage 4 is replaced by a 1 min 5% HF, 50% HNO_3 acid dip (acid etch no. 2)

Sequence III

The double dip equivalent of sequence I : as sequence I except that stages (4) and (5) are repeated prior to plating

Sequence IV

The double dip equivalent of sequence II : as sequence II except that stages (4) and (5) are repeated prior to nickel plating

Sequence V

(1) Acetone degrease as required

(2) Soak clean in 12 g/l NaOH + 12 g/l Na_2CO_3 at 70°C for 30 seconds, water rinse

(3) Dip in 50% HNO_3 for 1 min, water rinse

(4) Double dip sequence as in sequence I.

6.4 Peel Adhesion Test

As a standard or comparison some of the plated samples were peel tested after non-destructive testing. An Instron tensile testing machine in conjunction with a peel test attachment was used. The test consists of recording the load required to peel off a strip of the deposit from the substrate.

The samples were first slit with two parallel lines along the length of the specimen 1cm apart. It was then necessary to lift a tab of the deposit to start peeling. Normally in nickel plating on aluminium one end is left without immersion in the zincate treatment to prevent adhesion and to allow a tab to be lifted. In this work the full length of the bars were coated with immersion zinc and plated all over in order to minimise the effect of an unplated patch on the Q value of the full length of the aluminium bars.

The peel test rig consists of a flat plate free to move on ball races horizontally across the crosshead. The specimen is attached to the plate with the cut grooves running parallel to the direction of movement of the plate. The tab at the end of the strip is then attached to a clamp and an extension to the top load cell. To maintain the point at which the peel occurs directly underneath the load cell, ie. peeling at 90°, a cord is attached to the plate and via a pulley to the side column. Downward movement of the crosshead then causes the plate to move horizontally across the crosshead and thus maintains a constant angle of peeling. Two marks were placed 1.0 cm apart along the strip a constant distance from the tab end. The chart recorder was then used to record the load at all points between the marks, thus ensuring that the same area was tested for all samples. Peeling was carried out at a speed of 2 cm.min.

It was possible to produce varying degrees of adhesion on the aluminium samples using the above pretreatment sequences, and by using the peel adhesion test it was possible to physically observe good and poor levels of adhesion on the samples.

6.5 Non-Destructive Adhesion Tests Developed

The three types of non-destructive adhesion tests methods studied in this work were :

i. Modal Analysis

ii. Decrement Q meter as developed by Muaddi and its subsequent modification involving continuous wave drive. An electromagnetic transducer was used to excite the samples.

iii. The new Q meter developed based on an impulse technique using a miniature hammer to excite the samples.

6.5.1 Modal Analysis

Expertise has been established in the Department of Mechanical and Production Engineering at Aston in the use of "Modal Testing" for other purposes. Since this involves the striking with a hammer of a freely supported sample, it is possible that ultimately this method may be easier to convert into a readily usable test procedure. Also software is available for analysis of the vibrational data. Consequently it was decided to commence this project by attempting to evaluate this method for use with coated samples.

6.5.2 Description and Operation of the Instruments

A schematic diagram of the apparatus is given in Fig.19. An impact hammer Type 8202, manufactured by B&K, (Trade name for Bruel and Kjaer) has been used for impact testing for determining frequency response. The test material used was in the form of a beam. The impact hammer is an instrumented hammer for testing structural behaviour when used in conjunction with a dual or multi - channel Spectrum Analyser.

An impact from such a hammer imparts to the test structure a smooth excitation spectrum over a broad frequency range. The force is measured by the built-in Force Transducer Type 8202 (B&K) while the structural response is measured with a separate accelerometer fitted to the test object. The B & K Dual Channel Analyser Type 2032 has a number of features which make it ideally suitable for impact testing using the Impact Hammer Type 8202. These features include :

(1) Autoranging of the input attenuators for impulse measurements. This facility optimises signal to noise ratio.

(2) Automatic rejection of "Overloaded " signals

(3) Advanced triggering facility

(4) Line drive facility enables the force and the response transducers to be connected directly to the Analyser via the Line-Drive Amplifier Type 2614

(5) The Dual Channel Analyser contains a preprogrammed set up for impact testing.

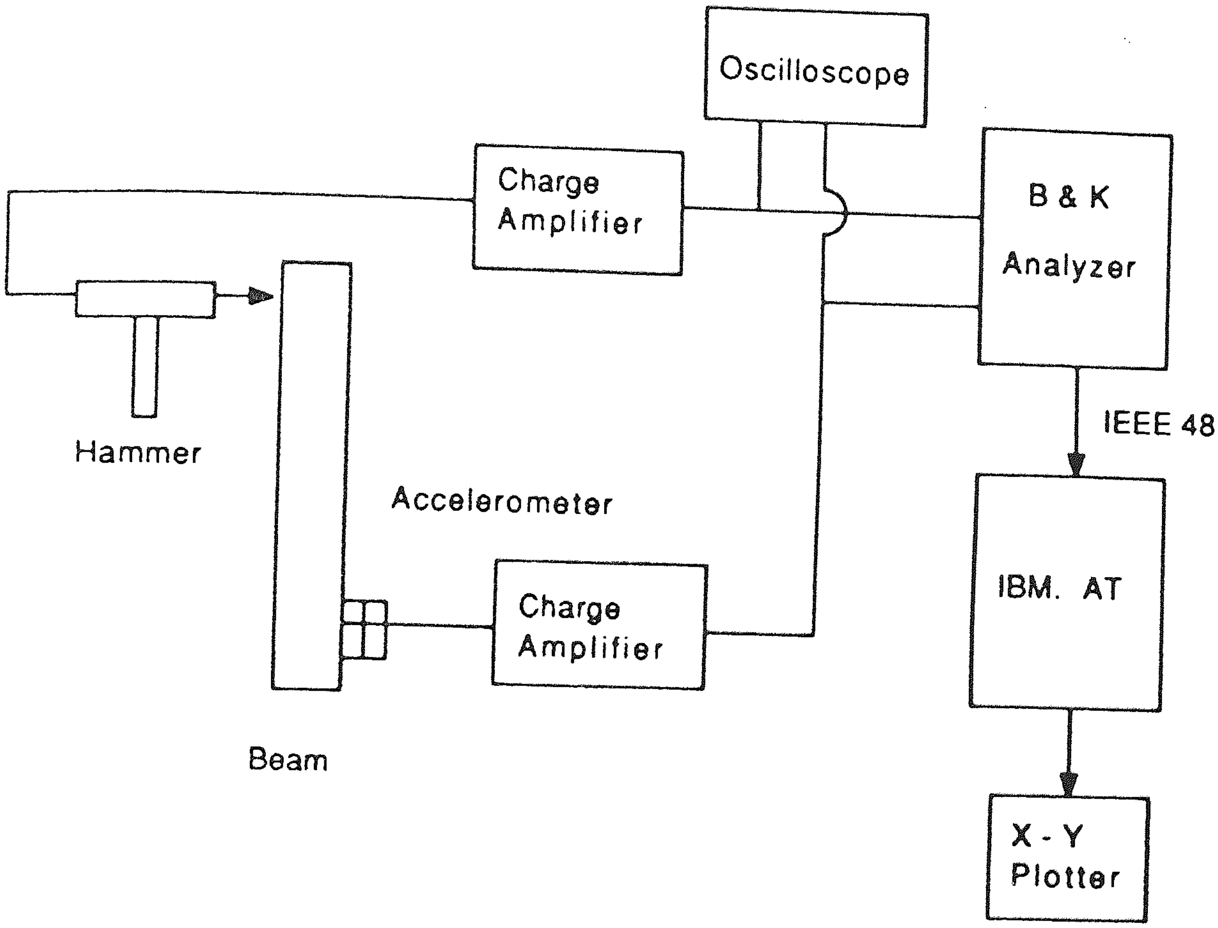


Fig. 19. Schematic diagram of the instrumentation set up used in Modal Analysis.

6.5.3 Structural Analysis

The capabilities of of the impact hammer and dual channel analyser combination for modal analysis is greatly enhanced by the addition of a desk-top computer with a dedicated software package. The software package is used to extract modal parameters i.e. natural frequency, modal constant and damping.

The desk computer used in this work is an IBM.AT with IEEE48 interface. The specially developed software used for extracting the modal parameter is called "SPIDERS". The computer can also be connected to a plotter. Figure 19 shows the experimental set up used in this experiment for measuring damping of sample beams. The beam were suspended with two elastic bands.

Elastic bands were used for suspension as these would have very high damping compared to that of steel or aluminium beams, hence would not interfere with the natural frequencies of the beam. The accelerometer was attached to the beam with wax at the lower end of the beam. Force was applied to the beam with an Impact Hammer Type 8202.

Mild steel and aluminium beams and plates of various thicknesses were used for modal testing without any coating. It has been observed that narrow metal beams (e.g. 2.5 cm wide) give better frequency response than wider ones (6 cm wide). It was also found difficult to obtain frequency response from thin, light-weight beams.

Before obtaining the frequency response plots/damping results, the specimen was struck

10 times, therefore, each plot is an average of 10 strikes. After obtaining the mean of 10 strikes, data were retrieved from the B&K Analyser to the computer.

The computer software was then used to obtain the Nyquist plot of the frequency response function by curve-fitting a circle to a few measured data points as illustrated in Fig.16 - called Circle Fit. Modal parameters were then extracted by the computer and displayed on the screen (natural frequency, modal constant and damping).

The "SPIDERS" software package was also used to study the feasibility of the package in detecting the difference between good and poor plating in terms of adhesion of the coating by vibration measuring techniques for electroplated nickel coatings (Watts Ni) on HE9 aluminium alloys.

A sample of results obtained is shown in Tables 8- 12. The results indicate quite clearly that surface coating increases damping very significantly. Lacquering induces more damping than the electroplated nickel. However, the difference in damping figures between samples given good pretreatment prior to plating and samples given relatively poor pretreatment was not very consistent. An attempt was also made to determine the optimum position of the sensor, by positioning the sensor at different locations on the specimen. The position of the sensor did not seem to have any significant effect on damping.

As the technique did not prove satisfactory to distinguish between samples given good and poor pretreatment prior to plating no further work was continued using the modal analysis experimental procedure.

6.5.4 Development of the decrement Q meter

This section describes the electronic design developed by Muaddi to measure the Q factor. The function of the electronic system is to count the number of oscillations of decaying amplitude which will be equal to the Q factor of the material. The principle of the instrument is contained in equation (16)

$$An = Ao \exp(-\pi n/Q)$$

where

A_o is the initial amplitude

A_n is the amplitude after number of oscillations

n is the number of oscillations

Q is the "Q" factor

It is to be noted that both Q and Q^{-1} are both dimensionless. Numerically if A_o/A_n is equal to ln 23.14 then the Q factor will be equal to the number of oscillations between these two level of amplitude. The design is based on this parameter.

The instrument counts the number of oscillations of the freely decaying vibration between two defined levels of amplitude. An essential component used in the design is the integrated circuit comparator. It has two inputs, the analogue signal being applied to one and a reference voltage to the other. The output is (TTL) digital logic 1 or 0 depending on which input is the greater. The resolution is about 1mV thus if the reference voltage is zero, a sinusoidal signal is converted to an equal mark space ratio TTL square wave. With a reference bias there is only an output when the signal exceeds the bias.

In this design the decrement signal drives three comparators. The first comparator acts as a zero crossing detector, while the second and the third comparators have high and low bias voltage respectively. These two comparators produce an output when the amplitude of the input voltage exceeds predetermined reference levels. However, Muaddi's design failed to function as several important parameters as required by the circuit were not highlighted. These were discovered to be very important parameters relating to the timing of the overall circuit to function as a Q- meter.

6.5.4.(a) Zero Crossing Comparator

An integrated circuit voltage comparator is used to detect the zero crossing of the (analogue) decrement very accurately. The decrement signal drives the comparator which is unbiased and therefore is acting as a zero crossing detector.

6.5.4.(b) Decrement Comparator

This is also an integrated circuit voltage comparator. The decrement signal drives the comparator and the bias voltage was adjusted to identify the level of amplitude where the comparator ceased working. Two types of comparators were used in the design. The first one has a high bias voltage, while the second one has a low bias voltage The ratio of the two bias voltages was adjusted to have a value 23.14.

The output of these comparators interface to TTL digital devices. The three comparator outputs were applied to three monostables to produce a well defined short duration trigger pulse starting at a positive going edge.

6.5.4.(c) Modification and Evaluation of the Design of the Q-meter

The circuit diagram given in Muaddi's thesis is shown in Fig.20. After constructing the circuit as per Muaddi's thesis, it was discovered that the circuit did not operate as has been described in the thesis, hence the circuit had to be modified in order to obtain a working instrument which would provide consistent and repeatable results. As a result of some experience gathered from operating Muaddi's circuit, it was possible to construct a modified version of the Q-meter as shown in Fig.21.

An electromagnetic transducer was used to vibrate the specimen, the driving force was removed once the specimen started to resonate at its natural frequency . During this time when the specimen was being forced to vibrate to its natural frequency , the Q-meter did not respond ie. there was no count. The Q-meter responds or counts only when the specimen is at its natural frequency and the driving force had been removed.

Fig.22 shows the physical arrangement of the test sample supported by two polystyrene blocks at the two nodal points. In this set up the drive voltage was varied to observe the pick up signal as a function of amplitude. When a small drive voltage was applied to excite the test sample at its first mode there was a clear audible sinusoidal signal. The vibrations were picked up by a miniature microphone positioned as close as possible to the vibrating surface. Moving the microphone over the surface enabled the nodes to be identified. The signal was a maximum at the anti-node and reached a null at the nodes. By comparing the signal phase with that of the drive the nodal positions were obtained, on crossing any nodal line the signal phase reversed, this was clearly observed using an oscilloscope. In order to obtain meaningful values for internal damping of a material, the supports must be located as near as possible to the nodes.

However, the signal received by the microphone had to be magnified in order to drive the Q-meter (Figs.22, 23). The amplified input signal was then fed as a damping signal to the digital Q-meter (Fig.21). The digital Q-meter then monitors the free oscillations as produced by the sample under test producing output pulses until ratio terms A_o/A_n = ln23.14 is no longer satisfied. The output signal from the digital Q-meter is accumulated and displayed by the LCD display as Q.

The output signal from the modified circuit enters the LCD decoder and is displayed as Q (Fig.24). Figure 25, shows photographs of the physical arrangements of the experimental set up.

With the modified circuit it was possible to vibrate magnetic materials ie. nickel plated aluminium samples at the fundamental modes and obtain Q values, but at times it was found difficult to resonate the as-received non-magnetic aluminium sample bars. Therefore a reasonable comparison could not be made between samples given good and poor pretreatments before plating.

In this technique the number of oscillations were counted by the electronic instrument when the excitation source was removed and vibrations were decaying freely at natural frequency of the specimen. The function of the electronic system was to count the number of oscillations of decaying amplitude which will be equal to the Q factor of the material.

In order to test the design, experiments were carried out on aluminium bars before and after plating and samples given various pretreatments. However, using this technique it was not possible to obtain consistent and repeatable results from any sample, although there was a significant difference between plated and unplated samples. Problems were also encountered in resonating the non-magnetic aluminium sample bars before plating. From time to time it was observed when using the same specimen on the test rig that by removing the test sample from the test rig and replacing to its original position on the rig the Q-meter produced inconsistent results both before and after plating. There were significant differences in the Q-values and these could not be accepted as being reproducible on the same specimen. Therefore, this instrument failed to give the desired Q-values ie. consistent and repeatable results.

It then became imperative to improve the design of the Q-meter so that consistent and repeatable results could be obtained over a period of time on any given sample and also to obtain significant differences between plated and unplated samples, particularly the level of adhesion. This resulted in the development of a new Q-meter discussed in the following section.

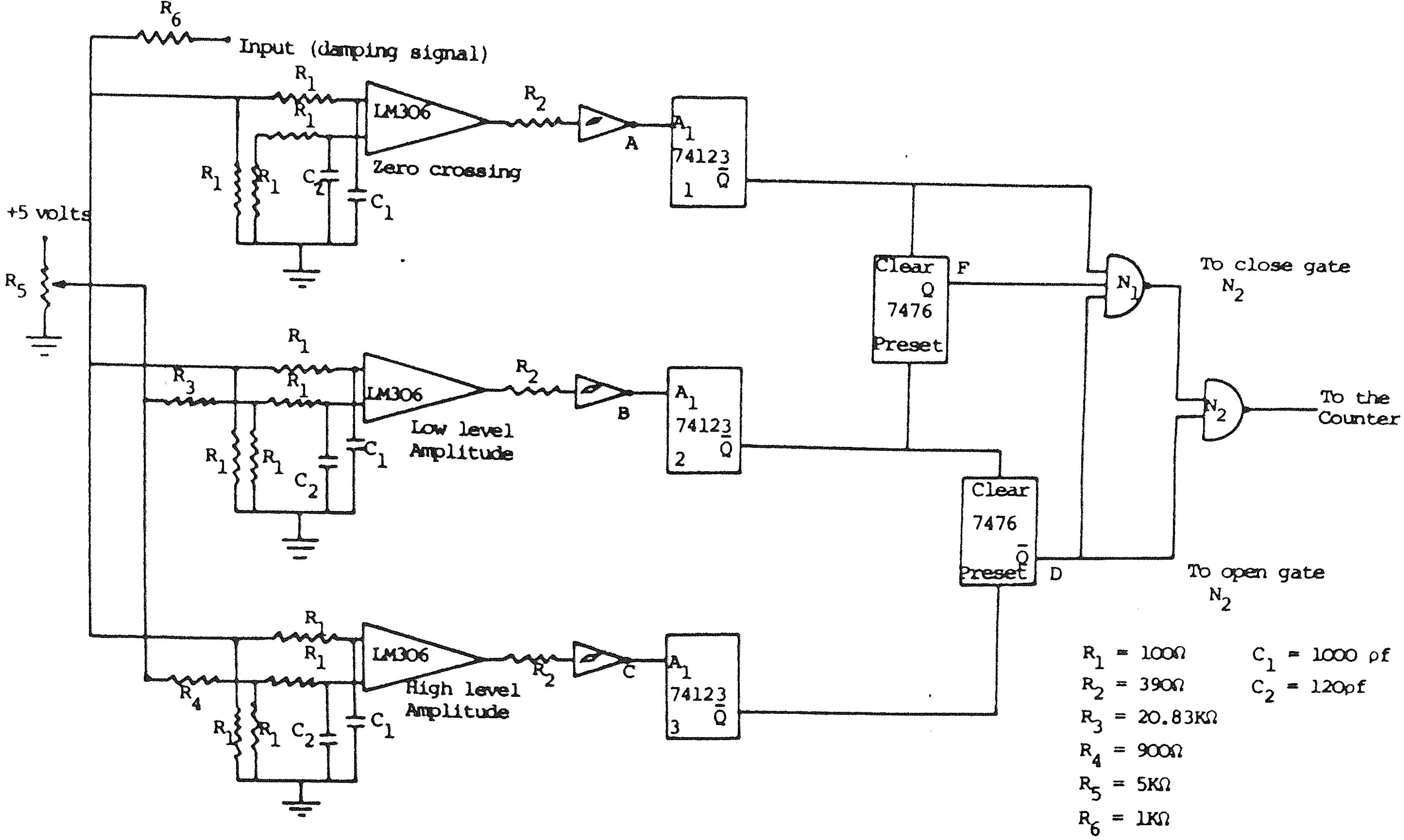


Fig.20. Muaddi's circuit diagram as shown in the thesis (1982).

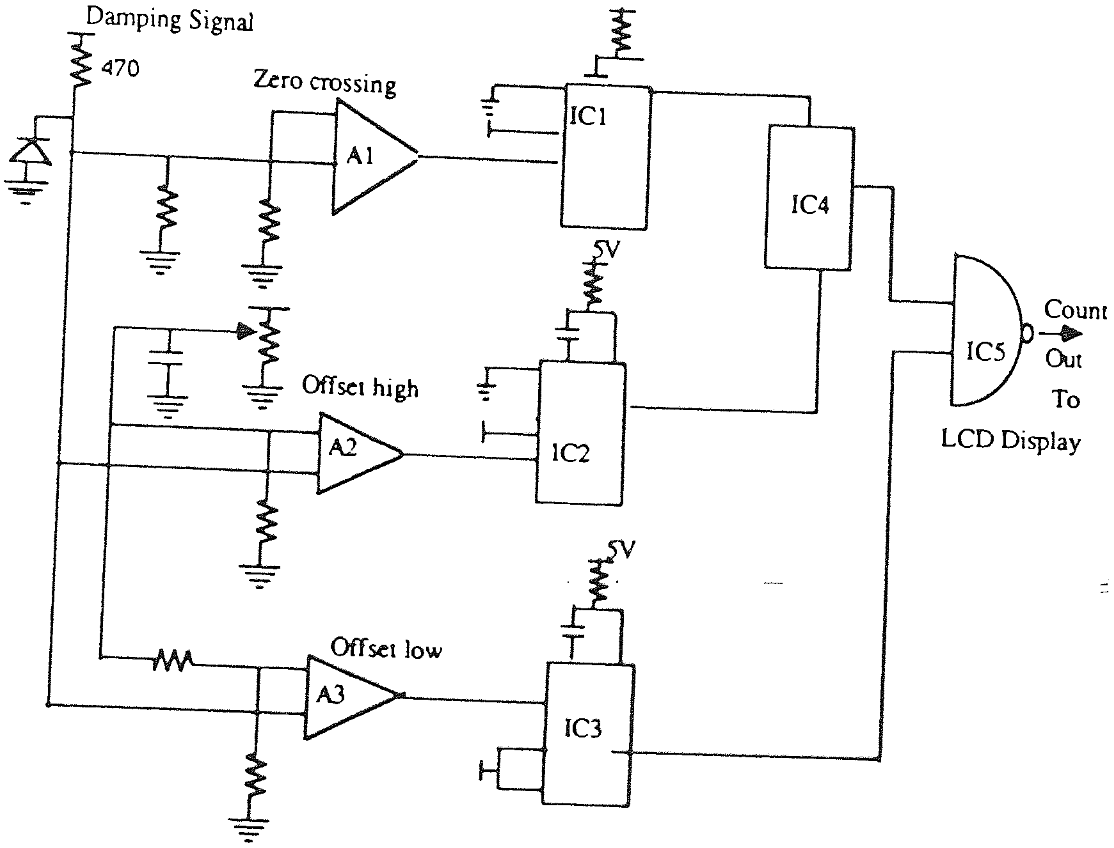


Fig.21 Modified Circuit Diagram

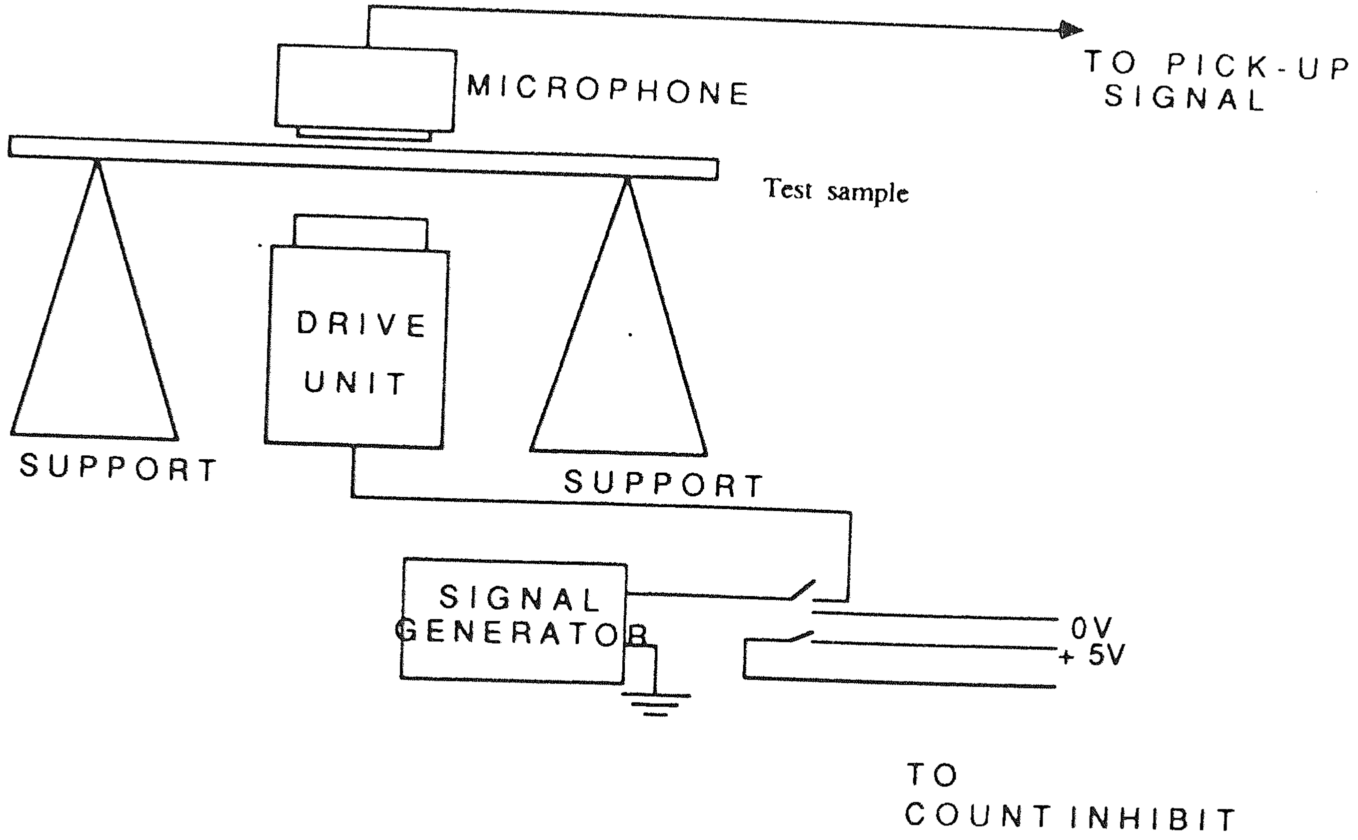


Fig.22. Schemetic diagram shows the physical arrangement of the test sample for vibration analysis.

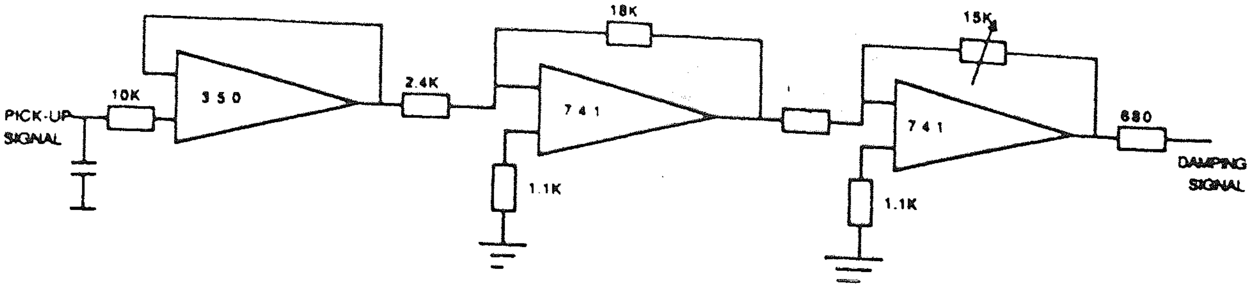


Fig. 23. Amplification of the pick up signal received by the microphone.

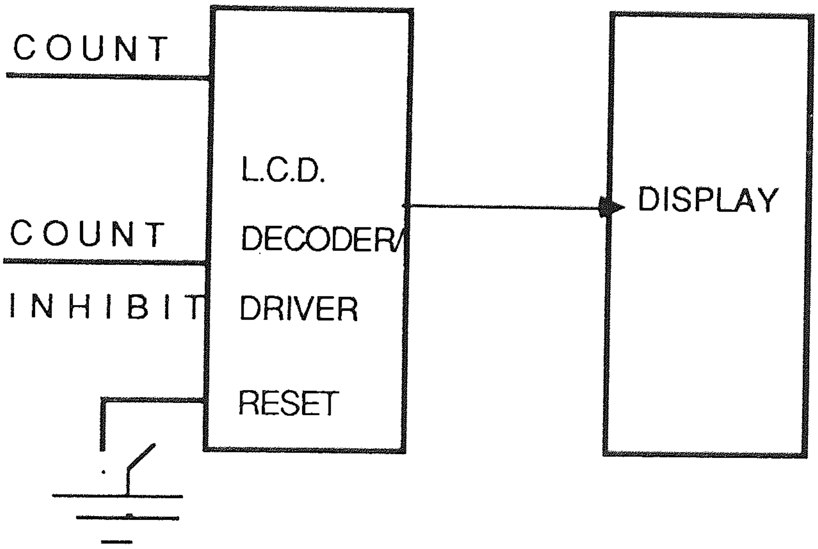


Fig.24 LCD Decoder and Display Counter

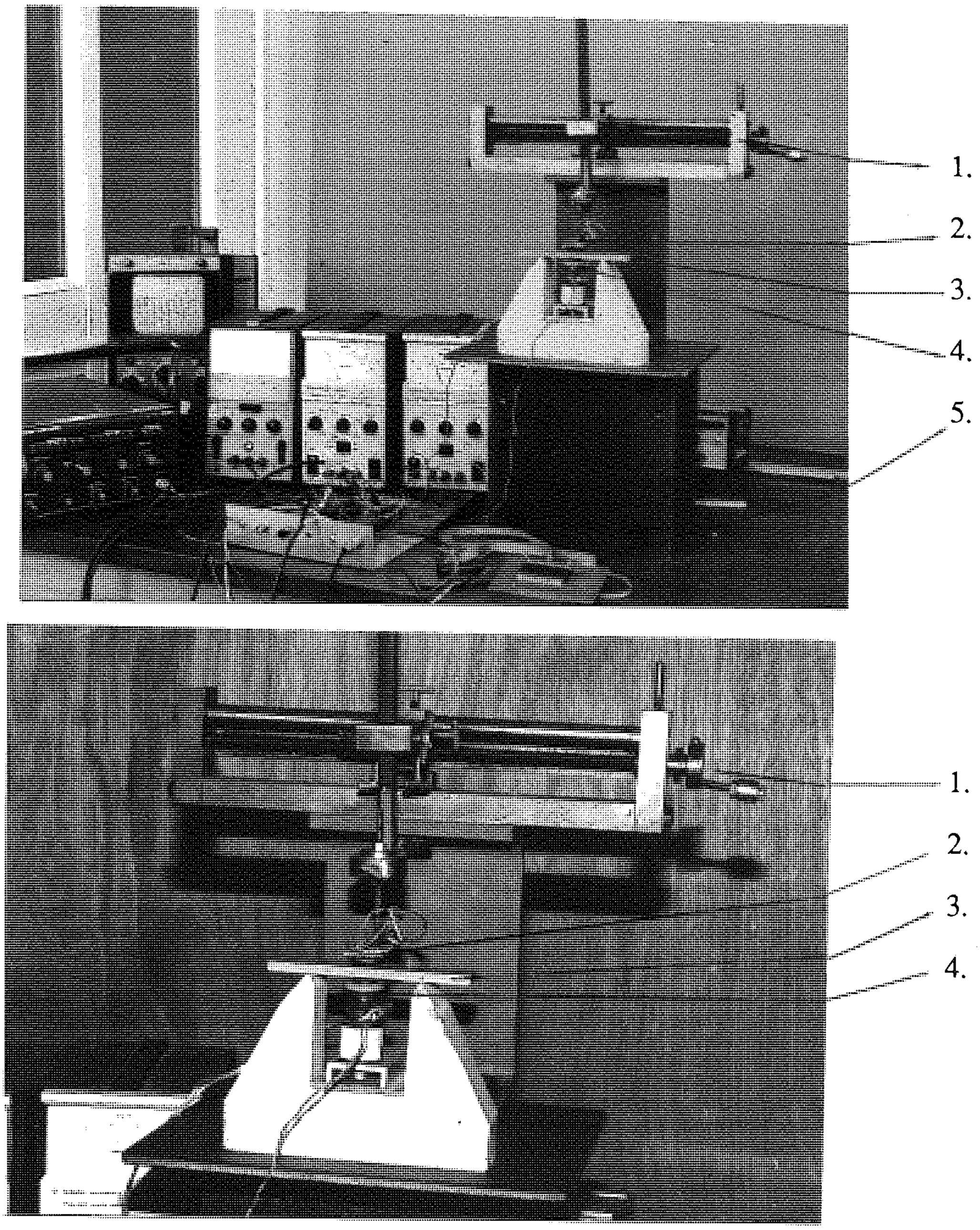


Fig.25. Experimental set up used in the modified Q-meter.

1. Mechanical device for sideways, upward and downward movements of the microphone.
2. Microphone.
3. Test sample.
4. Electronic hammer.
5. Digital counter.

6.5.6 The development of a new Q meter based on Impulse Technique

In order to meet the requirements stated earlier a new Q-meter was developed based on impulse technique which does not require tuning and was therefore easy to operate. The electronic set-up was still the same i.e. measuring decrement as in the earlier Q-meters. The method of suspension was, however, improved by using nylon threads. A regulated miniature hammer was used to excite the test specimen at the fundamental mode. The circuit operation is shown schematically in Fig.26. Figure 27 shows the photograph of the instrument set up. The vibrations were picked up by a microphone positioned as far away as practical from the vibrating test piece so that the signals could be picked up without excessive amplication. The two nodal positions of the rectangular test pieces were pre-calculated and marked on the specimen. The test pieces were supported / suspended at the two pre-determined nodal points using nylon threads. The dimensions of the test pieces were kept constant throughout the experimental work, as far as practical.

In this technique the number of oscillations between two pre-determined voltage levels is counted by an electronic instrument when the excitation source is removed and the vibrations are decaying freely at the natural frequency of the specimen. As in the decrement Q-meter in this circuit the signal from the vibrating surface is picked by the microphone and also amplified. Since the amplifier magnifies all the signals received a band filter pass was therefore used to attenuate all the frequencies except required range which was around 2000Hz in this case (Fig.28). One end of the graph passes high frequencies and attenuates low frequencies whilst the other end passes high frequencies and attenuates low frequencies. Fig.26 shows two comparitors, comparitor 1 and comparitor 2 and they were connected to reference 1 and reference 2 respectively. Reference 1 is maintained at a constant voltage supply. When the input signal exceeds the reference voltage an output is produced, comparitor 1 clears the counter on receiving this signal. Reference 2 is maintained at a slightly lower voltage, comparitor 2 counts the number of impulses received within the set amplitude level and produces a count in the Q-counter (Fig.29).

Since it is difficult to measure frequencies to a great accuracy a high frequency oscillator was employed which produces an accurate and stable frequency counts and displayed on the frequency counter.

The output from this instrument was found to be more consistent and repeatable then any other instruments mentioned earlier. A detailed statistical analysis has been carried out on the results obtained from this instrument in order to establish the accuracy, reliability and repeatability of the instrument. Therefore, a chapter has been devoted to statistical analysis and main bulk of the Q-readings were taken using this instrument.

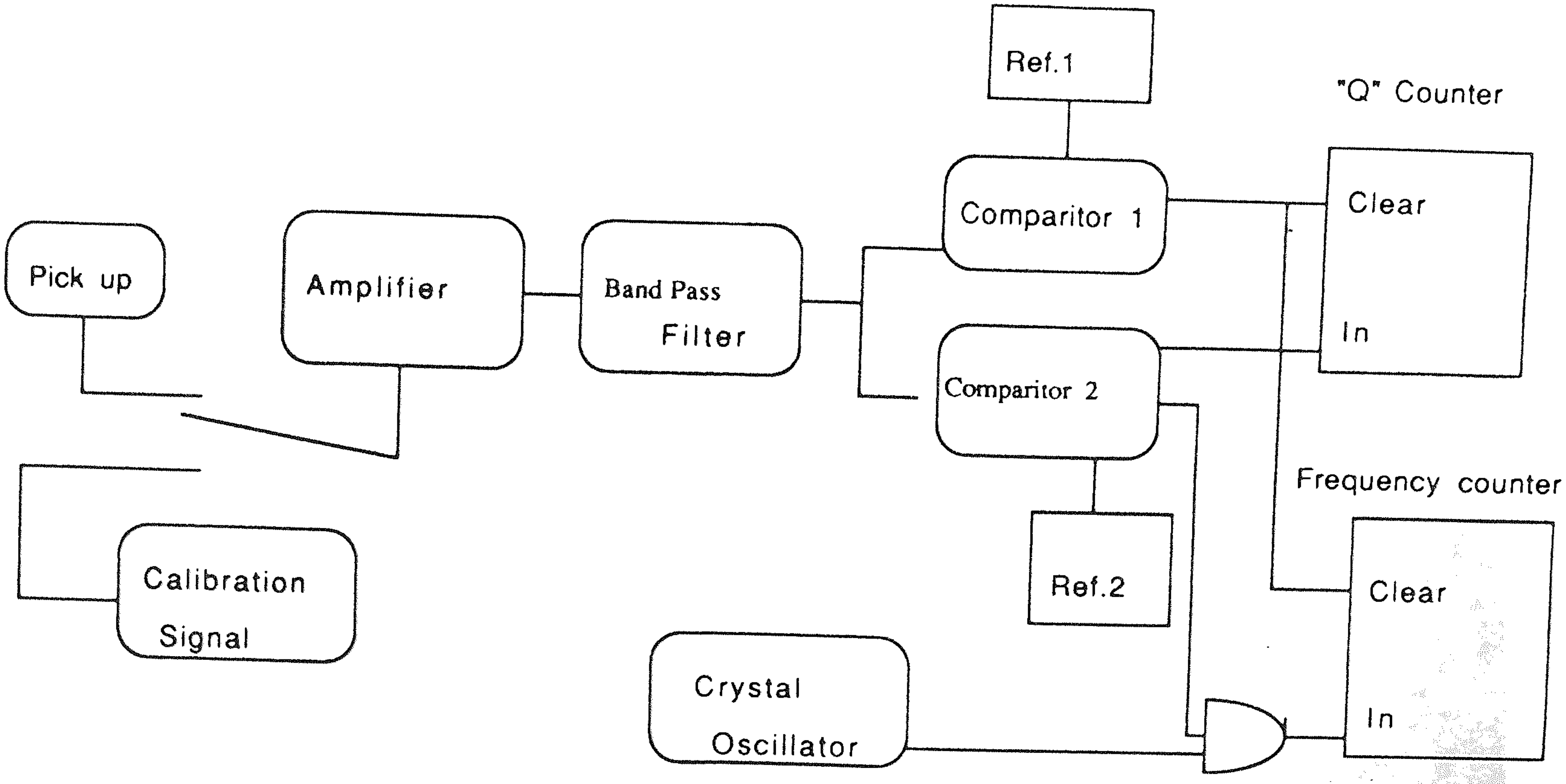


Fig.26 Schemetic diagram of the new Q-meter based on ImpulseTechnique..

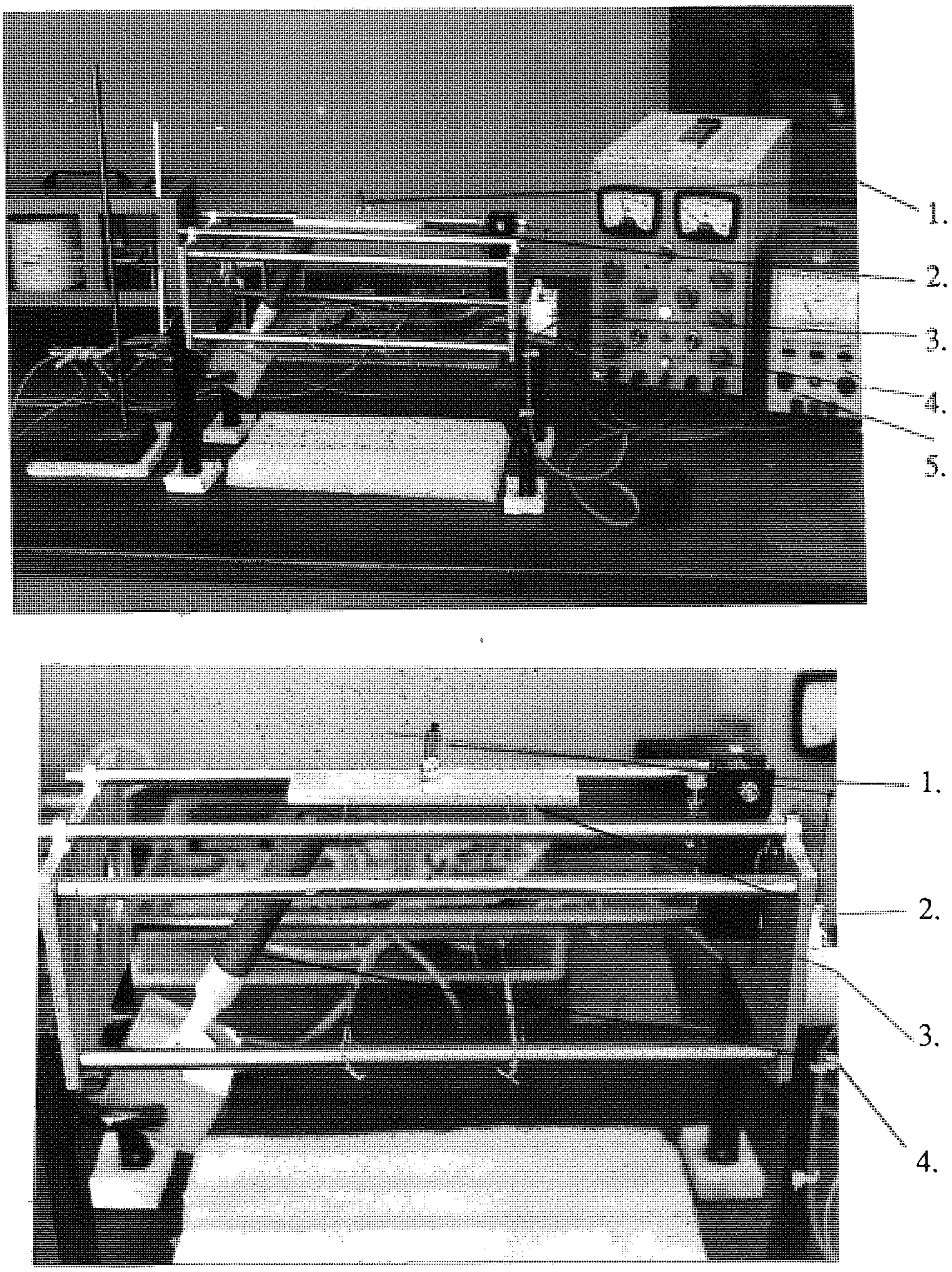


Fig. 27. Instrument set up used in the new Q-meter developed based on an Impulse Technique.

1. Miniature hammer.
2. Test sample
3. Test rig.
4. Microphone.
5. Power supply.

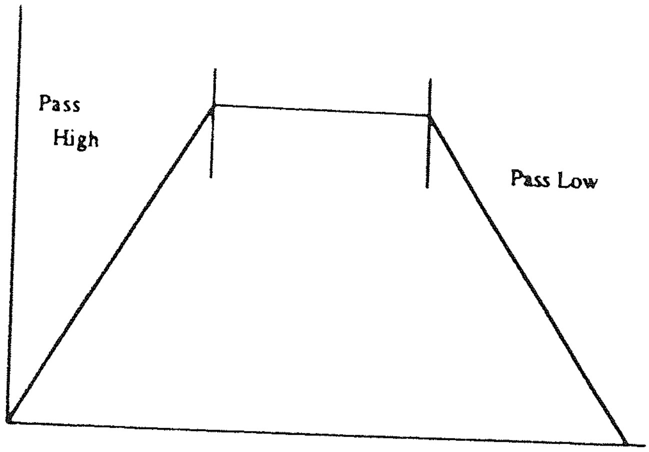


Fig. 28 Operation of Band pass filter

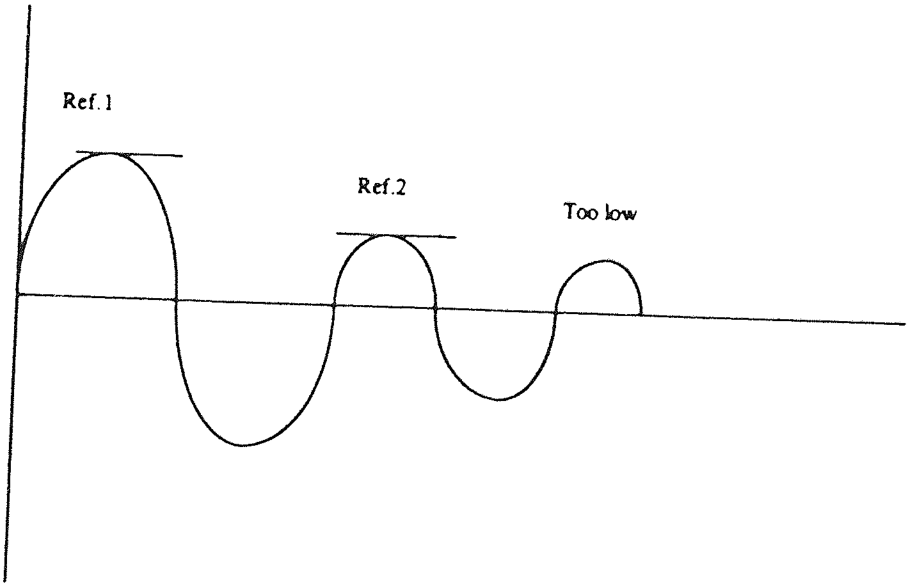


Fig.29 Shows the setting of the amplitude levels for Q-measurements.

CHAPTER 7

EXPERIMENTAL RESULTS

7.1 MODAL ANALYSIS

Tables 8 to 12 show the damping values (Q^{-1}) of the samples measured before and after coating ie. plating and lacquering with relative positions of the sensors (transducer). The tables show quite clearly that the beams as received (without any coating) have the lowest damping figure. The mean damping figures of the two coatings indicate that lacquer has caused a slight increase in damping compared with that of electroplated nickel.. However, the results are not significantly different from each other but plating and lacquering have both increased damping of the samples.

Table 8. Damping Results (Q^{-1}) Before and After Plating Using Modal Analysis with different positions of the sensor (transducer).

Before	After	Position of Sensor
0.01175	0.02112	A
0.01148	0.02157	A
0.01174	0.02064	A
0.01048	0.02010	B
0.01109	0.02147	B
0.01037	0.01978	B
0.01086	0.02083	C
0.01107	0.01921	C
0.01224	0.01837	C

Sample given good pretreatment (Al 11).

Table 9. Damping Results (Q^{-1}) Before and After Plating Using Modal Analysis

Before	After	Position of Sensor
0.00930	0.02072	A
0.00952	0.02046	A
0.0110	0.01968	A
0.01148	0.01855	B
0.01390	0.02131	B
0.01015	0.01901	B
0.01422	0.02189	C
0.01156	0.02293	C
0.01022	0.02233	C

Sample given good pretreatment (Al 2).

Table 10. Damping Results Before and After Plating Using Modal Analysis

Before	After	Position of Sensor
0.00978	0.01946	A
0.00945	0.01897	A
0.00969	0.01898	A
0.00979	0.01970	B
0.01011	0.01779	B
0.01045	0.01870	B
0.00993	0.0721	C

Sample given good pretreatment (Al 4)

Table 11. Damping Results Before and After Plating Using Modal Analysis

Before (Q^{-1})	After (Q^{-1})	Position of Sensor
0.01178	0.01806	A
0.01170	0.01915	A
0.01189	0.01893	A
0.01182	0.01839	B
0.01288	0.01872	B
0.01414	0.02007	B
0.01175	0.02209	C
0.01478	0.02194	C
0.01244	0.02133	C

Sample given poor pretreatment (Al 3).

Table 12. Damping Results (Q^{-1}) Before and After Lacquering Using Modal Analysis.

Before	After	Position of Sensor
0.01048	0.02513	A
0.01072	0.02160	A
0.01171	0.02246	B
0.01176	0.02508	B
0.01055	0.02254	B
0.01145	0.02254	C
0.01191	0.02263	C

Notes

Electroplated Nickel thickness was approximately 80 μm.

Good plating sequence is as below:-

1. Degrease in hot non-alkaline cleaner (60°C)
2. Caustic etch for 30 seconds at 60°C
3. Desmut in nitric/hydrofluoric acid mixture(70% and 5% respectively)

For relatively poor pretreatment steps 2 and 3 were replaced by a 50% nitric acid dip.

Position A

Accelerometer attached on the lower end of sample and hammer was struck on the opposite side of accelerometer.

Position B

Accelerometer positioned as in (A) and hammer struck at top end opposite side of accelerometer.

Position C

Accelerometer attached at lower end and hammer was struck on top end but same side as accelerometer.

7.2 The Modified Q Meter

A sample of results obtained using the modified Q-meter is shown in Chapter 8 [Statistical Analysis]. Using this instrument it was difficult to resonate the unplated aluminium samples and obtain consistent Q-values, although resonating the plated samples was no problem as nickel is magnetic. Therefore no comparison could be made between samples before and after plating, hence this instrument was not used for further analysis.

7.3 The New "Q" Meter based on Impulse Technique

This section shows the experimental results obtained using the new Q-meter that was developed using Impulse Technique. In this work all the frequencies measured were in hertz (Hz). Table 13 shows frequencies and Q values before and after various pre-treatments. In these samples the weight changes due to various pre-treatments have also been shown. It can be observed that electrocleaning decreased the weight of the samples in all the cases. The effect of nitric acid etch was not very consistent, however, Bondal dip has increased the weight of all the samples but the weights were less than their original values in the as received condition. An observation of the Q (mean) values before and after various pretreatments shows that the Q values decreased slightly after electrolytic cleaning, the nitric acid dip increased the Q values and the Bondal dip caused a reduction of the Q values. Although the changes in the Q values were very small due to pretreatments, they were consistent in all the samples.

Table 13. Changes in weight and Q values due to various pretreatments (*without* plating).

SAMPLE 1

	As received	After Pretreatment		
		Electroclean	Nitric acid dip	Bondal dip
Weight (g)	51.85519	51.69226	51.69190	51.69784
Frequency (Hz)	1005	1006	1005	1005
Q 1	5756	5741	5813	5807
2	5703	5742	5863	5800
3	5720	5688	5802	5802
4	5788	5715	5842	5768
5	5838	5731	5872	5729
6	5841	5695	5833	5744
7	5873	5732	5877	5708
8	5814	5759	5860	5795
9	5844	5703	5879	5804
10	5809	5784	5847	5775
Mean	5799	5729	5849	5773

SAMPLE 2

	As received	After Pretreatment		
		Electroclean	Nitric acid dip	Bondal dip
Weight (g)	52.02933	51.92153	51.92124	51.92679
Frequency	1004	1005	1005	1005
Q 1	5765	5742	5790	5716
2	5820	5757	5770	5736
3	5779	5780	5734	5716
4	5808	5704	5734	5710
5	5830	5757	5679	5681
6	5845	5729	5784	5730
7	5844	5751	5774	5708
8	5864	5762	5816	5734
9	5859	5789	5780	5747
10	5833	5775	5791	5746
Mean	5825	5755	5765	5722

SAMPLE 3

		As received	After-Pretreatment		
			Electroclean	Nitric acid dip	Bondal dip
Weight (g)		51.87391	51.71777	51.71681	51.7223
Frequency		1004	1007	1007	1008
Q	1	5919	5853	5840	5881
	2	5896	5857	5984	5895
	3	5871	5847	5964	5852
	4	5897	5891	5983	5891
	5	5895	5833	5988	5844
	6	5907	5906	5953	5863
	7	5898	5905	5947	5901
	8	5861	5906	5977	5903
	9	5885	5881	5912	5840
	10	5892	5945	5998	5914
	Mean	5892	5882	5955	5878

As received	Samples were cleaned with detergent and acetone to remove oil and grease from the surface.
Electroclean	Electrolytically cleaned in Bondal cleaner for 2 minutes at 60°C.
Nitric acid dip	Samples dipped in 50% nitric acid for 1 minute.
Bondal dip	Samples dipped in Bondal solution for 2 minutes at room temperature (20°C).

The object of this study was to establish whether this Q-meter developed could detect changes in the Q values due to various plating and pretreatments. The above results indicate that the instrument is capable of detecting small changes due to various pretreatments. The next stage of this work was to investigate whether this instrument could detect any changes in the adhesion level due to good and poor pretreaments given before plating.

Fig.30.a. Changes in Q due to pre-treatments

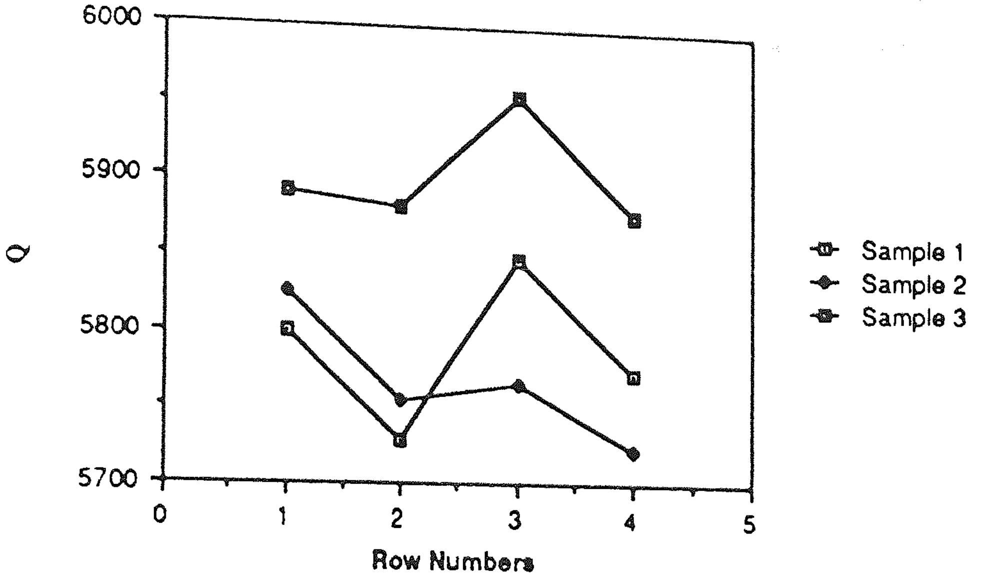


Fig. 30.b . Weight changes due to pretreatments

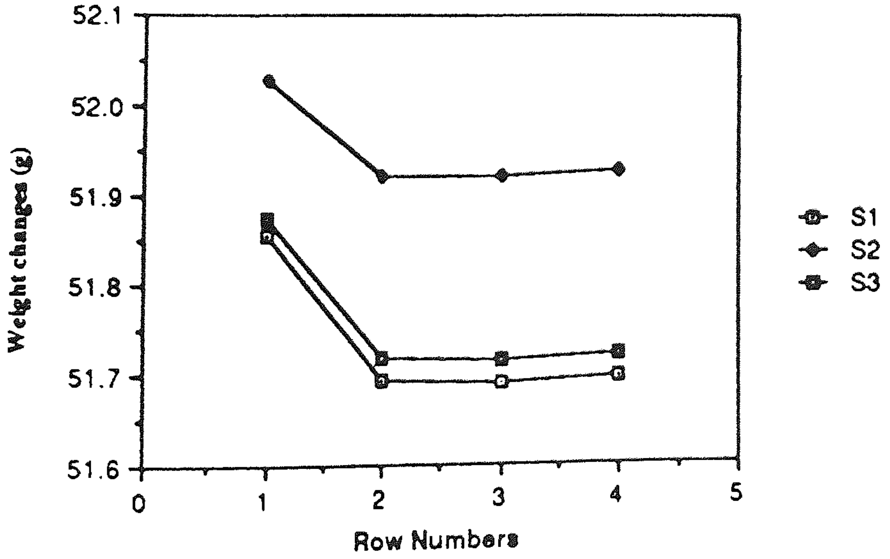


Table 14 shows the effect of plating HE9 aluminium alloy bars with and without ultrasonic cleaning. The results indicate that the instrument was not able to pick up any obvious differences between samples prepared with and without ultrasonic cleaning.

Table 14. %Change in the Q values due to plating HE9 alloys with and without ultrasonic cleaning.

Sample no.	Time of plating	% Change in Q after plating	
		With ultrasonic	Without ultrasonic
46D	5 hour	91.9%	92.7%
15D	5 hour	91.2%	91.5%
44D	5 hour	92.7%	-
45D	5 hour	93.1%	-

Samples were cleaned in a ultrasonic cleaning bath for 10 minutes before double Bondal sequence of plating using 50% nitric acid dip.

Table 15 shows the effect of plating HE9 alloys with double Bondal, single Bondal and 50% diluted Bondal in the pretreatment stage. These samples were plated for 1/2 hour. Table 15 shows double and single Bondal treatments did not show any obvious differences after plating, the percent drop in Q-values were about the same in both the cases. However, 50% diluted Bondal indicated slightly higher percent drop in the Q-values.

Table 15. Effect of double Bondal, single Bondal and 50%diluted Bondal dip on the Q values of 1/2hour plated HE9 alloy.

% Change in Q values

Double Bondal	Single Bondal	50%diluted Bondal	
60	60	64	
59	60	63	(Six Samples)

Double Bondal - 5 minutes ultrasonic clean after acetone clean and 50%HNO_3 double Bondal sequence of plating.

Single Bondal - acetone clean only; single Bondal plating sequence.

50% diluted Bondal - Bondal solution was diluted with water, single Bondal plating sequence.

Table 16 shows effect of plating S1C aluminium alloy bars with 50% nitric acid and 5%HF/50%HNO_3 acid dips in the pretreatment stage. It was expected that as 5%HF etch produces a better bond significant differences would be obtained between these two treatments. However, the results showed no consistent differences due to different acid etches.

Table 16. Effect of 50% nitric acid and 5%HF/50%nitric acid etch on 5hour plated S1C alloy (Double Bondal).

% Change in Q values

50% HNO_3	5%HF/50%HNO_3	
64	55	
59	58	(Four samples)

Figure 31 shows changes in the Q-values with time of an HE9 aluminium alloy bar which was only cleaned with detergent and acetone swabbed. The plot shows a decline in the initial stages and a substantial increase followed by another drop. The Q was constantly going up and down. The overall fluctuation was around 2.5%, although the instrument was found to be accurate within +/- 1% range.

Figure 32 shows Q plots of three HE9 sample bars which were given the following treatments :

i) ultrasonically cleaned

ii) polished on a metallurgical wheel polish

iii) buffed on a mop

both the samples ii and iii were then cleaned with acetone. The plots show that after all the three treatments Q went up very sharply initially. Both polishing and buffing had reduced the Q compared to that of ultrasonic cleaning. It is possible that after ultrasonic cleaning all the debris and solid particles loosely adhering to the surface were effectively removed. Whereas after both the polishing operations it is possible that some solid particles became attached to the metal surfaces and this had resulted in the big differences between ultrasonic cleaning and polishing in the Q plots. Also polishing would have introduced compressive stresses on the surfaces. However, the fluctuation of the Q values were present in all the three samples.

Fig.33 shows Q plot of an HE9 alloy sample bar polished on a metallurgical wheel polish. The Q had gone up after polishing. The overall fluctuation was around 3% which is slightly higher than the sample in Fig.31(as received). The sample was showing fluctuations even after 650 hours. The fluctuation pattern indicates some kind of growth and breakdown occurring continuously with time.

Figures 34 and 35 show plots of samples pretreated to nitric acid dip, all the samples show an initial increase in first 30 hours. However, Fig.34 shows Q-readings from a sample which were taken over a long period of time. This shows that after long exposure this sample had also started to show fluctuations even after 400 hours in common with all the previous samples but the fluctuations were much reduced and was around 1.8%, very close to the accuracy of the instrument. It seems that the passive film produced after nitric acid etch had somehow started to breakdown after long exposure. It has been observed in Figs. 30,34 and 35 that after the nitric acid etch Q had gone up above the as received values.

Nitric acid etch is associated with film formation in aluminium alloys, therefore it can be concluded from these results that film formations increase Q. From Table 13 it could not be deduced that weight loss is associated with an increase in Q or vice versa, however, Q went down even when there was weight loss or gain. In Fig.34 the presence of four peaks indicate that the first pre-treatment produced a peak (Q increase) which showed a decline after about 100 hours, followed by another increase and decline followed by a sharp rise possibly then the oxide layer was thickened, the fourth peak was relatively short lived compared to the first and third peaks. These fluctuations were also present in the samples shown in figures 32 and 33 which were polished.

Figures 36 and 37 show Q plots of samples pre-treated to Bondal dip. The pattern after Bondal dip is similar to that of samples treated to nitric acid dip. Q went up gradually in the first 50 to 80 hours. Fig.36 shows a sample reading which was taken over a long period of time.This sample shows a decline after about 100 hours followed by a fluctuation pattern which was also present in the samples pre-treated to nitric acid etch, the fluctuation range was around 4% and a lot more than what has been observed in any samples so far.

Figures 38 to 41 show Q plots of samples which were plated for 1/2 hour. Although these samples were treated differently ie. single Bondal, double Bondal and 50% diluted Bondal treated, plated with and without polishing. No significant differences were produced due to any of the treatments. The Q plots show that the weight of plated nickel has reduced Q values substantially, the Q then increased slightly in all the samples and started to show fluctuation with time.

Figures 42 to 44 show Q plots of samples plated for 1 hour, 2 hour and 3 hour, these samples were not polished before plating. The fluctuation pattern is similar to 1/2 hour plated samples, ie. Q increased in the initial period and then started to show fluctuations. The weight of the nickel has caused a further reduction in Q values.

Figure 45 shows the effect of plating thickness on Q. Q had decreased with plating thicknesses. It seems the instrument is capable of measuring thickness very consistently and could possibly be used as a non-destructive thickness tester.

Figures 46 shows Q plots of an 1 hour plated sample, the graph show s a sharp increase in the initial period, followed by small increases but with continuous fluctuations which continued even after 100 hours after plating.

After 5 hour plating Q drop was more dramatic, about 90% drop due to plating. The pattern is an increase immediately after plating followed by a sharp increase after about 10hours (Fig. 47) which was followed by another increase after about 40 hours, the fluctuation pattern was similar in all the three samples. Figure 47 had started to show a decline after this although this was not clear in other samples. However, in the thick nickel coatings the Q-plots with time show that fluctuation were present but Q-drop was very marked.

Fig.45 shows changes in Q with time of samples plated with progressively increased nickel thickness. It can be observed that Q drop is related to the thickness of the coating. However, the fluctuation of Q with time was a common phenomenon in all the plated samples.

As no significant differences were detected between samples given good and poor pre-treatments before plating, it was then decided to plate S1C aluminium alloy bars for five hours with good pre-treatment ie. double Bondal and compare these results with samples plated directly onto aluminium without the Bondal dip which would definitely produce different levels of adhesion. Tables 17 and 18 indicate there was no change in percentage drop in Q due to the different pre-treatments. Although the Q-meter did not pick up differences in the adhesion levels ie. in terms of changes in Q values, peel adhesion test results [7.4] showed quite convincingly that it has been possible to produce different levels of adhesion by varying the pre-treatment sequences in both the S1C and HE9 alloy sample bars.

Plating time was further reduced to 1 hour (Tables 19,20) and then to 3 minutes (Tables 21,22) hoping that the weight of the nickel would not interfere with the interface. Plating directly on to aluminium had resulted in higher percentage drop in Q in S1C(ii) samples both after 1 hour and 3 minutes of plating (Table 25). As this particular alloy was not available for further investigations, 3 minutes plating with and without the Bondal dip was carried out on S1C(i) and HE9 alloys. Tables 23 and 24 show Q of HE9 alloy bars before and after 3 minutes plating with and without the Bondal dip, although the results show slight differences due to plating with and without the Bondal dip, but Table 25 shows that there was no obvious pattern due to this treatment. However, the Q before plating of all the three alloy samples were significantly different and could not be mixed up with each other. This pattern was also repeated after plating irrespective of plating time. HE9 samples always showed higher percentage drop in Q after all the plating (5 hour, 1 hour and 3 minutes) followed by S1C(ii). S1C(i) had a low Q to start with and this was reflected on the Q after plating.

The experimental results indicate that this instrument was unable to detect changes in Q due to good and poor pre-treatments before plating. Peel adhesion tests were carried out to confirm the adhesion levels of the test samples and the results are shown in the following section.

Table 17. Q values before and after plating of an aluminium S1C alloy (5hr Plated) plated *directly* onto Al after HNO_3 dip without the Bondal dip.

		Before plating	After plating	
Frequency		762	737	
Q	1	4965	1146	
	2	4925	1175	
	3	4891	1136	
	4	4938	1152	
	5	4889	1149	
	6	4883	1140	
	7	4832	1149	
	8	4854	1164	
	9	4843	1164	
	10	4832	1144	
	Mean	4885	1152	%change in Q due to plating **76.5%**
	S.d. n-1	46	12	

Tables (18 to 24) below show mean and standard deviations of the Q values. Mean indicates an average of 10 Q-readings.

Table 18. Q mean before and after plating of an aluminium S1C alloy plated for 5 hr (pre-treatment Sequence V, Single Bondal)

		Before Plating	After plating	
Frequency		760	739	
Q	Mean	3928	917	%change in Q due to plating **76.6%**
	S.d. n-1	27	21	

Table 19. Q mean before and after plating of an aluminium S1C alloy bar (1hr Plated) plated directly onto Al after HNO3 dip without the Bondal dip.

		Before plating	After plating	
Frequency		757	749	
Q	Mean	4680	2467	%change in Q due to plating **47.3%**
S.d.n-1		30	19	

Table 20. Q mean before and after plating of an aluminium S1C alloy bar plated for 1 hr (pre-treatment Sequence V, Double *Bondal*)

		Before Plating	After plating	
Frequency		760	752	
Q	Mean	4666	2322	%change in Q due to plating **50%**
	S.d. n-1	21	28	

Table 21. Q mean before and after plating of an aluminium S1C alloy (Plated for 3 minutes) plated directly onto Al after HNO$_3$ dip *without* the Bondal dip.

		Before plating	After plating	
Frequency		704	765	
Q	Mean	5252	4799	%change due to plating **8.62%**
	S.d. n-1	24	17	

Table 22. Q mean before and after plating of an aluminium S1C alloy plated for 3 minutes (pre-teratment sequence V, double Bondal)

		Before plating	After plating	
Frequency		759	757	
Q	Mean	4841	4628	%change in Q due to plating **4.41%**
	S.d. n-1	28	17	

Table 23. Q mean before and after plating of aluminium HE9 alloy (Plated for 3 minutes) plated directly onto Al after HNO_3 dip *without* the Bondal dip.

		Before plating	After plating	
Frequency		1001	1001	
Q	Mean	5805	5271	%change in Q due to plating **9.21%**
	S.d. n-1	25	19	

Table 24. Q mean before and after plating of an aluminium HE9 alloy bar plated for 3 minutes, (pre-treatment sequenceV, double Bondal).

		Before plating	After plating	
Frequency		999	998	
Q	Mean	5983	5273	%change in Q due to plating **11.8%**
	S.d. n-1	26	21	

Table 25. %Change in the Q values due to plating aluminium alloys with and without the Bondal dip.

Al alloy type	Time of plating	With Bondal	Without Bondal
S1C(i)	5 hour	64.9%	-
S1C(i)	1 hour	31.28%	-
S1C(i)	3 minutes	1.41%	1.74%
S1C(i)	3 minutes	3.5%	3.08%
S1C(i)	3 minutes	5.23%	3.3%
S1C(ii)	5 hour	76.5%	76.6%
S1C(ii)	1 hour	47.3%	50%
S1C(ii)	3 minutes	4.41%	8.62%
HE9	5 hour	91.5%	
HE9	1 hour	47.1%	-
HE9	3 minutes	11.8%	9.21%
HE9	3 minutes	10.71%	11.49%
HE9	3 minutes	10.13%	10.89%
HE9	3 minutes	10.1%	12.04%

All the sample readings were taken 10 minutes after removing the samples from the plating bath.

Fig.31. Changes in Q with time of untreated HE9 alloy.

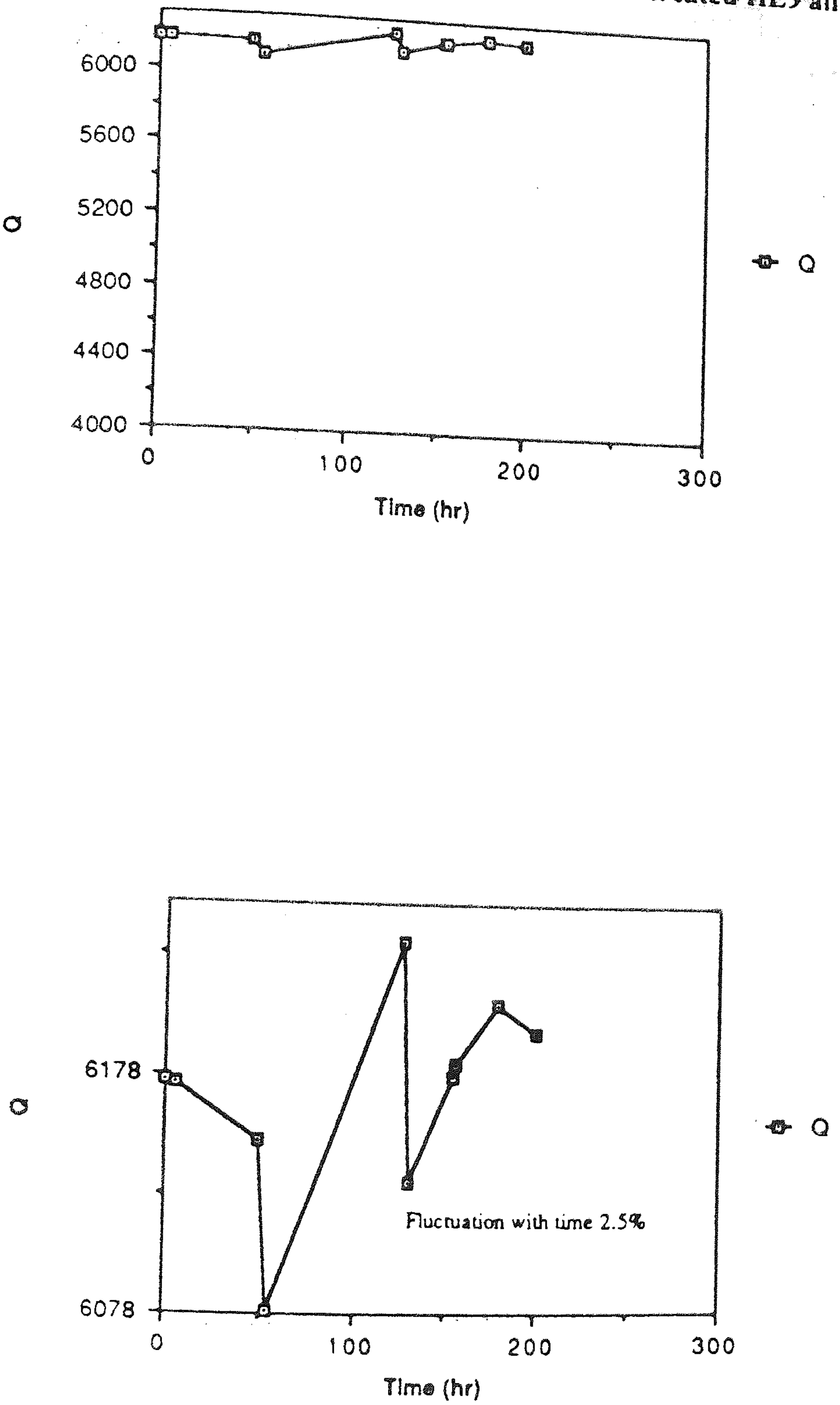


Fig.32. Effect of ultrasonic cleaning and polishing on Q.

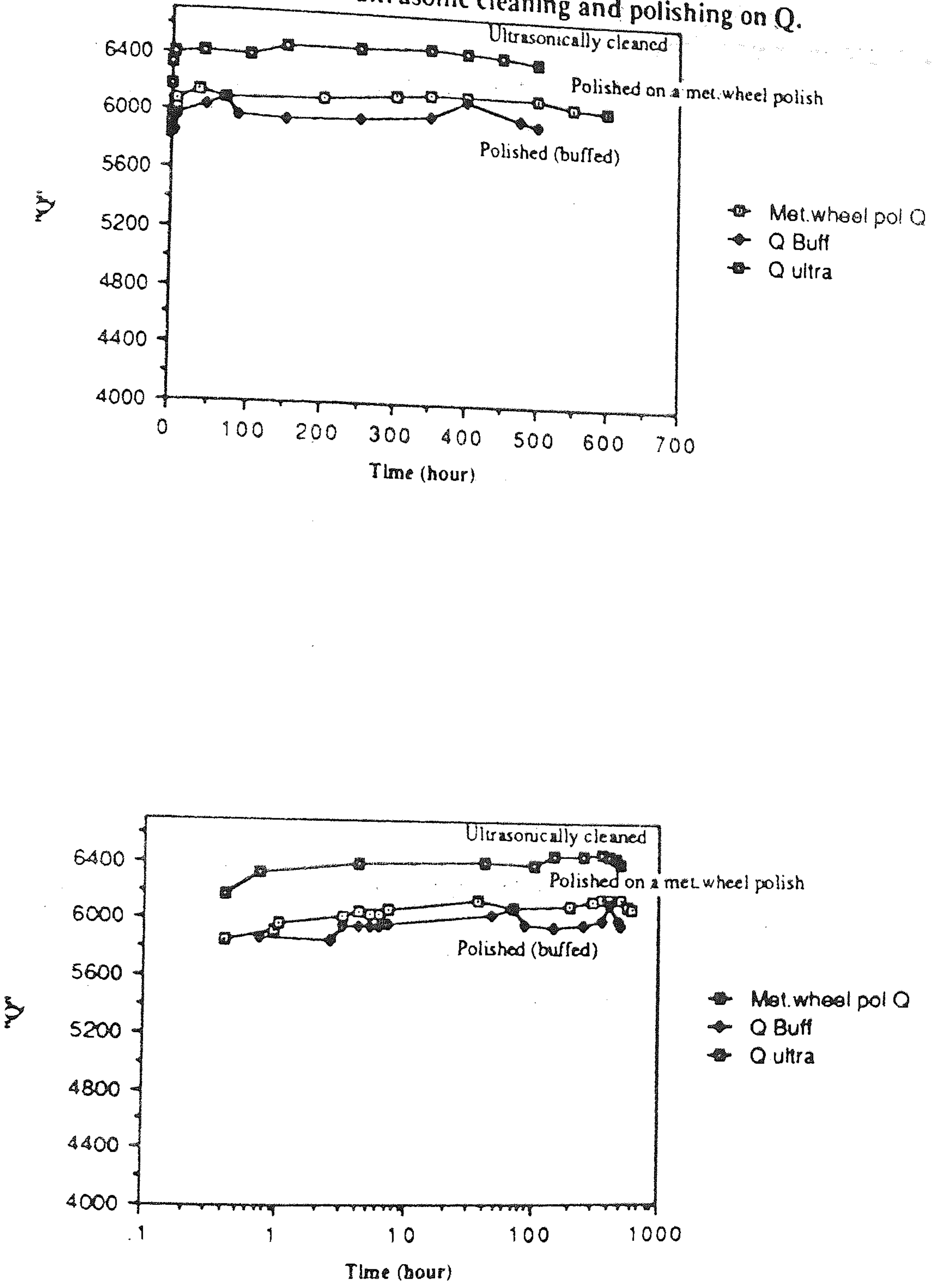


Fig.33. Changes in Q with time of a sample polished on a wheel polish

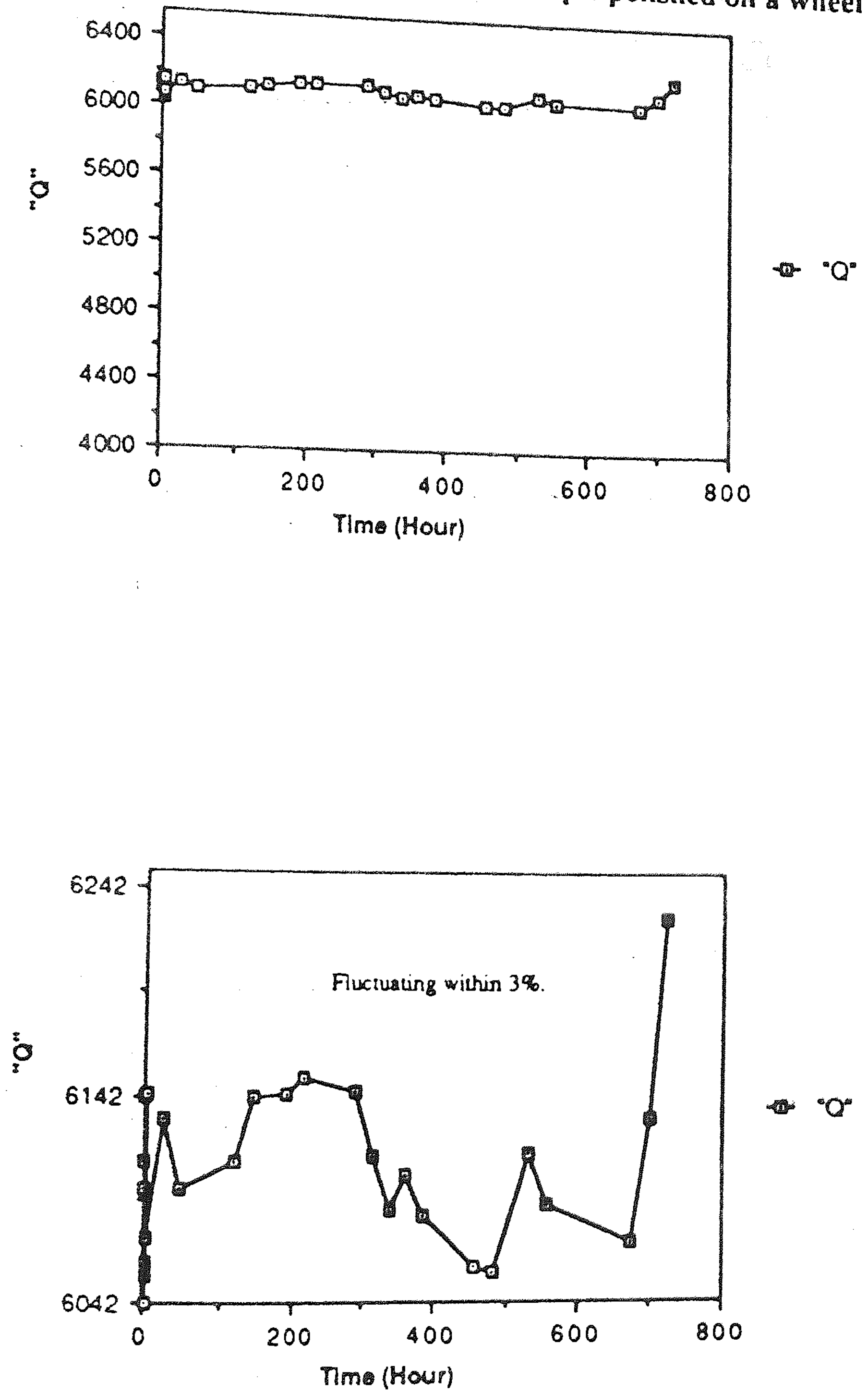


Fig.34. Changes in Q with time (hr) of an HE9 sample bar pretreated to nitric acid treatment.

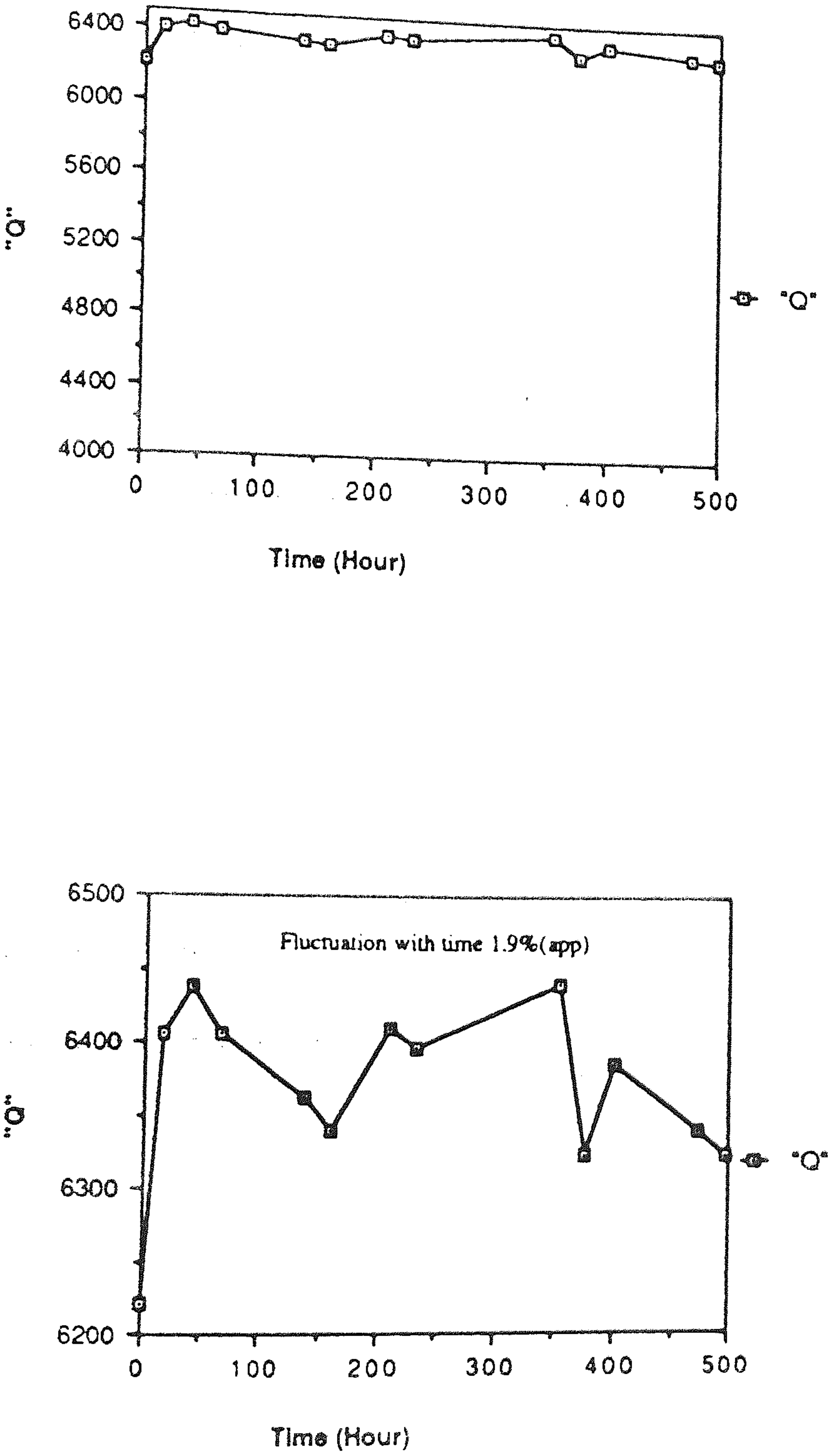


Fig.35. Changes in Q with time of an HE9 alloy bar pretreated to nitric acid dip.

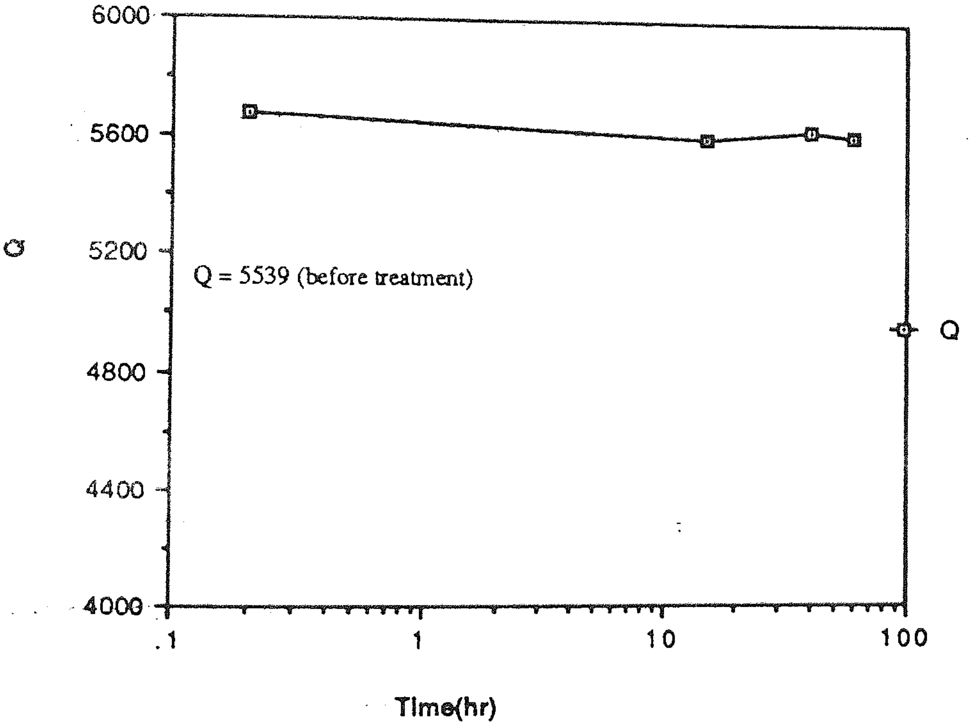
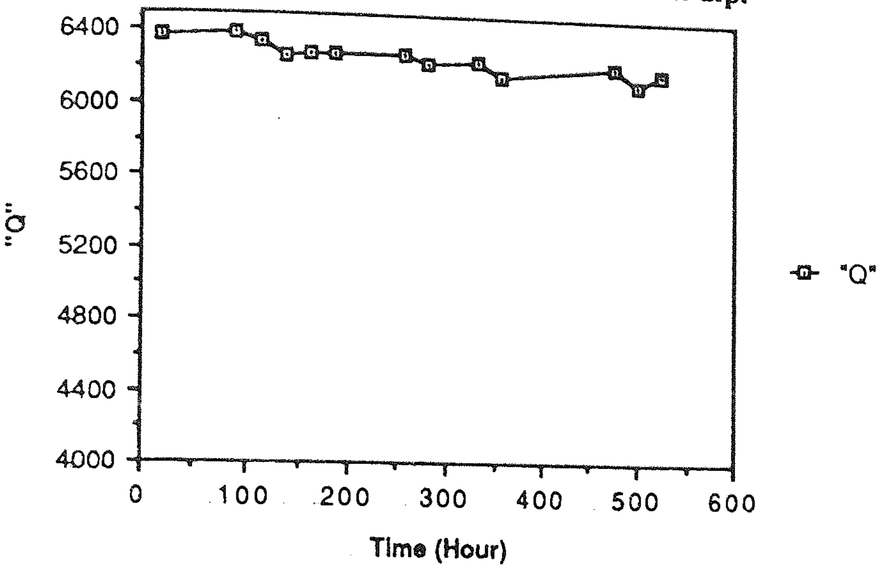


Fig.36. Sample pre-treated to Bondal dip.



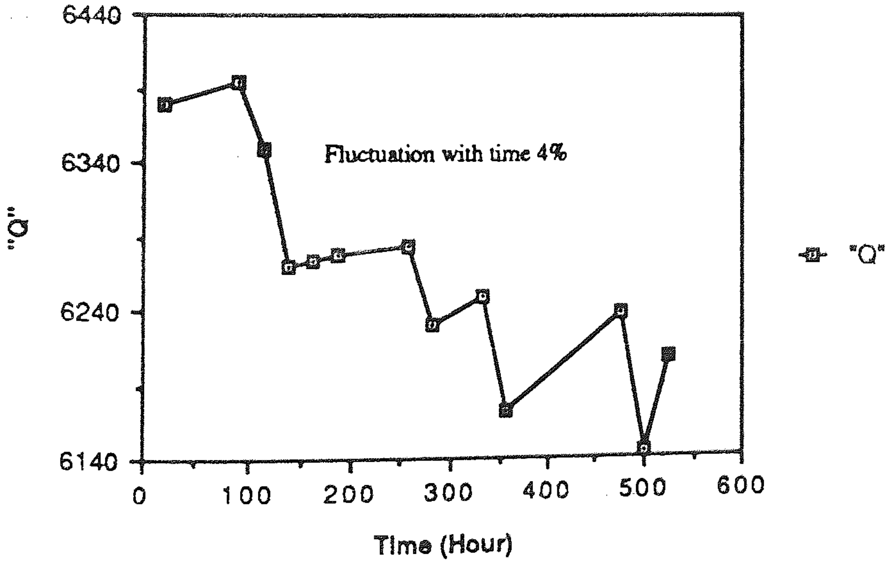


Fig.37. Changes in Q with time of an HE9 sample pretreated to Bondal dip.

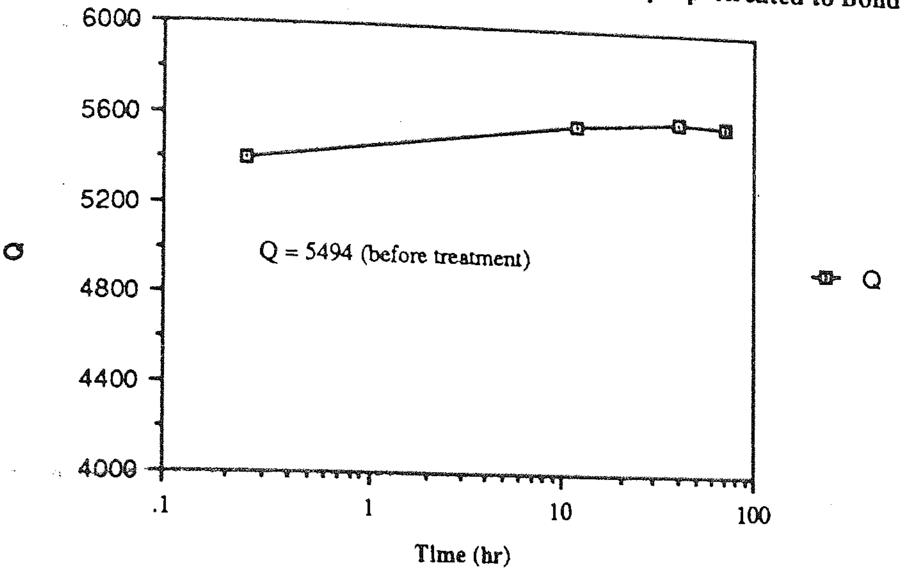


Fig.38. Changes in Q of a 1/2hr plated sample (single Bondal treated).

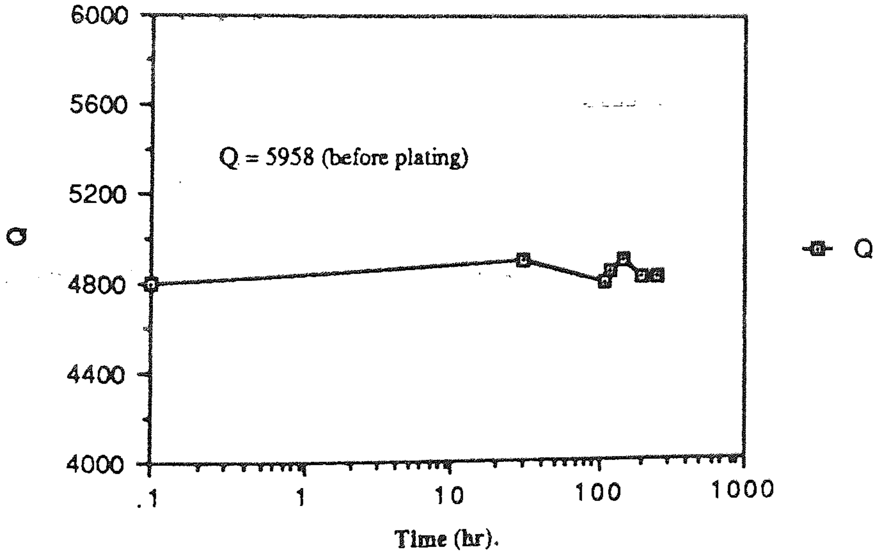


Fig.39. Variation in Q with time of a 1/2 hr nickel plated HE9 polished sample bar (plated with double Bondal treatment).

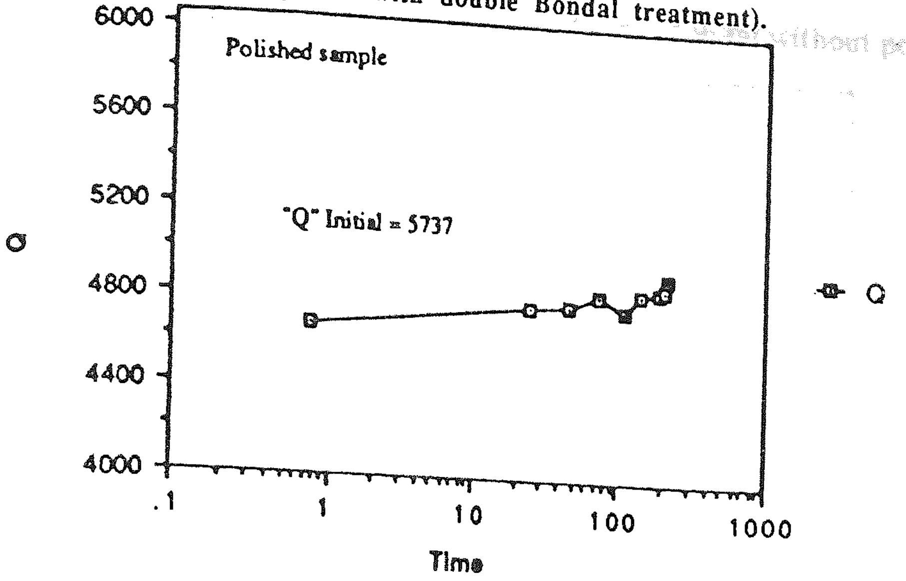


Fig.40. Variation in Q with time of a 1/2 hr nickel plated HE9 sample bar (plated with double Bondal treatment, without polish).

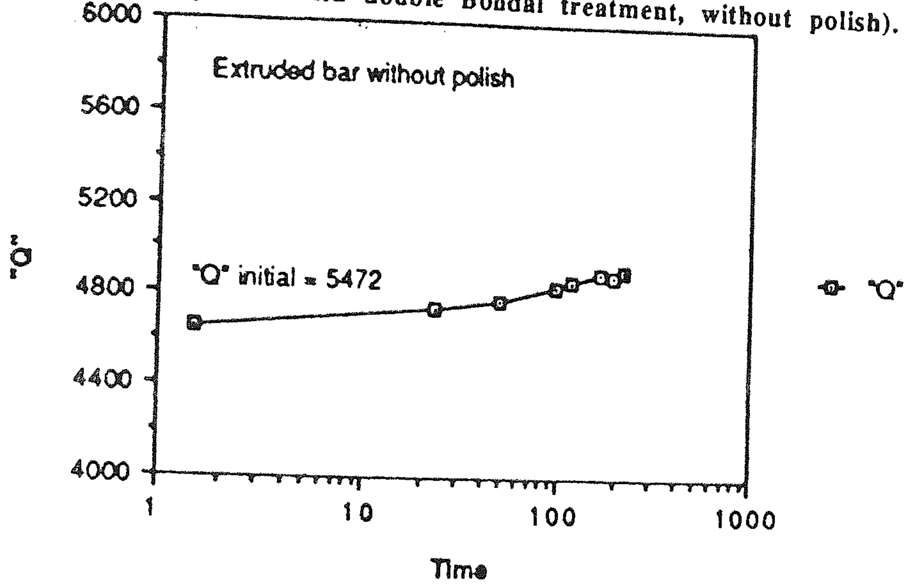


Fig.41. Variation in Q with time of a 1/2 hr nickel plated HE9 sample bar (plated with 50% diluted Bondal treatment, without polish).

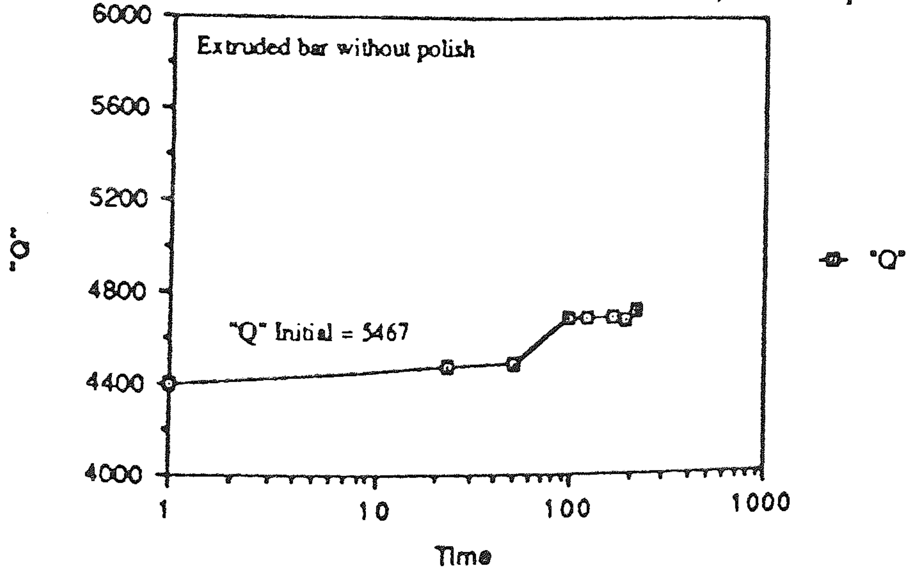


Fig.42. 1Hr. Plated Sample, double Bondal without polish.

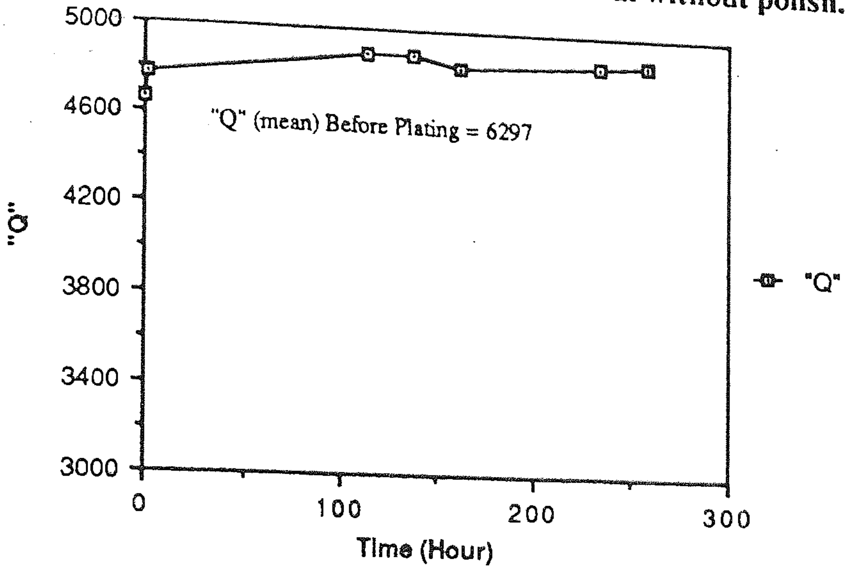

"Q" (mean) Before Plating = 6297

Fig.43. 2Hr. Plated Sample Plot, double Bondal without polish.

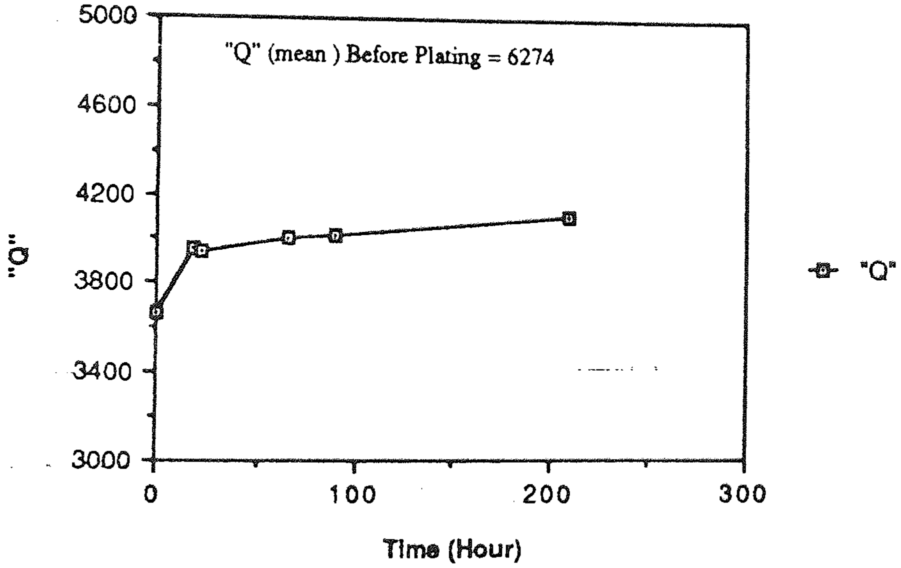

"Q" (mean) Before Plating = 6274

Fig.44. 3Hr Plated Sample Plot, double Bondal without polish.

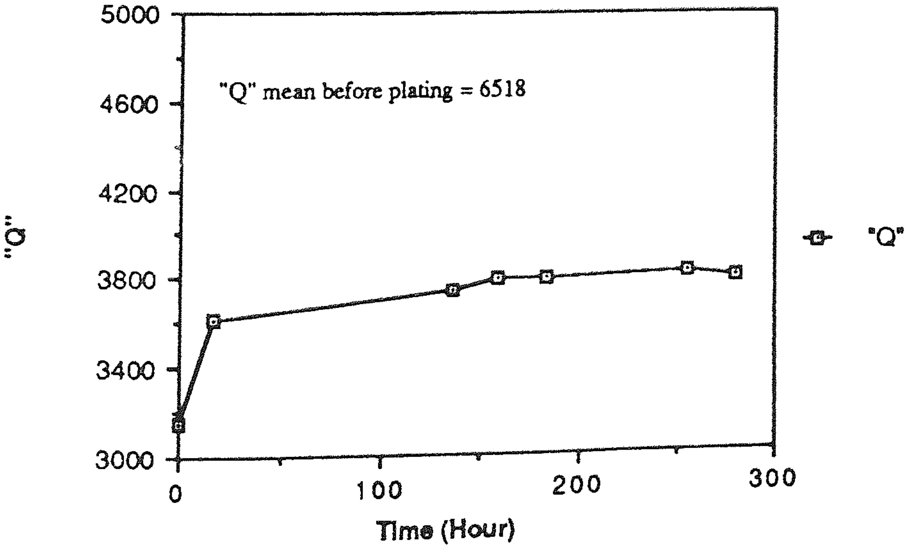

"Q" mean before plating = 6518

Fig.45. Effect of plating thickness on Q measurements..

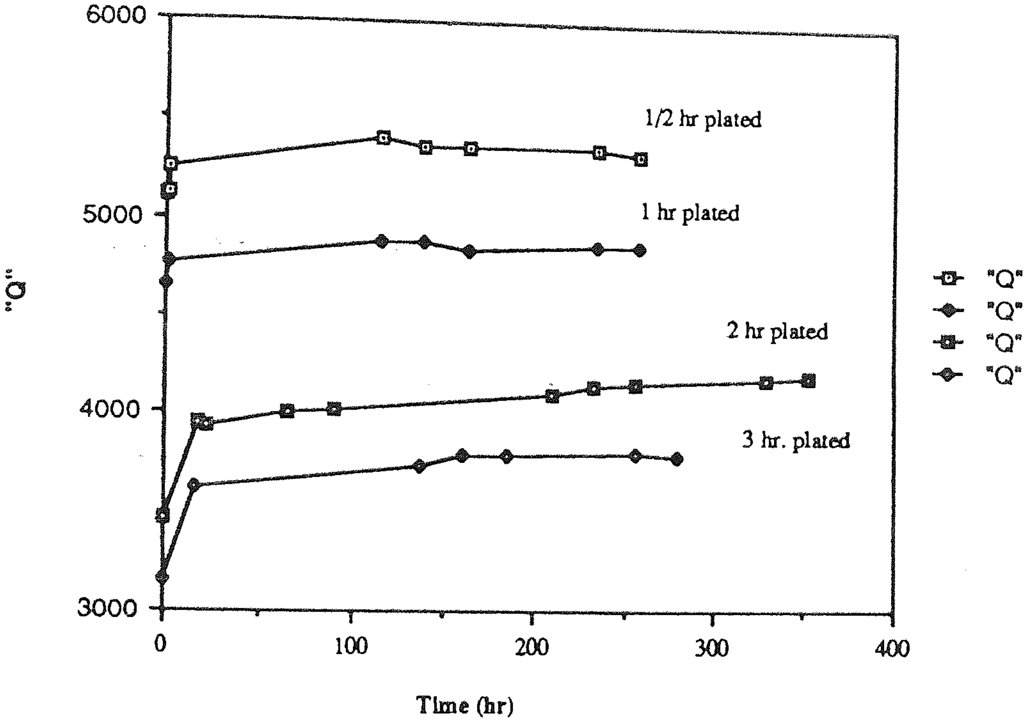


Fig.46. Changes in Q with time of an HE9 unpolished bar (1 hr plated).

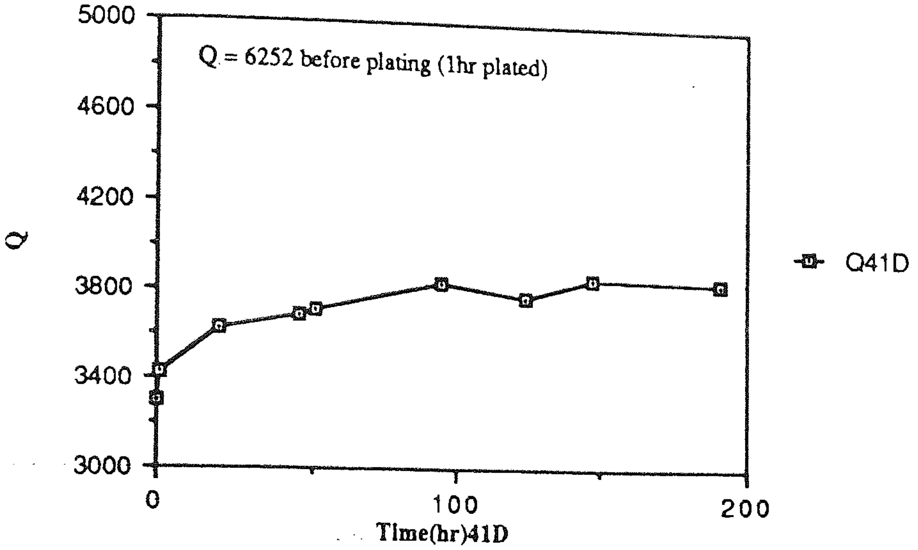
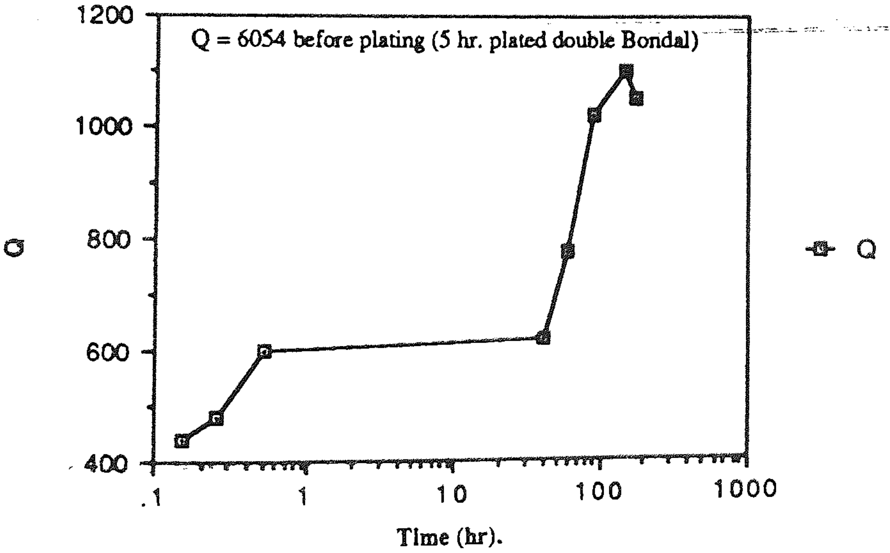


Fig.47. Changes in Q of a 5 hr. Ni plated sample (plated without polish).



7.4 Peel Adhesion Test

In order to carry out peel adhesion tests a number of aluminium samples, both S1C and HE9, were plated with thick nickel deposits, approximately 150 μm thick. Q readings were taken before starting the pretreatment sequence and 10 minutes after plating. After plating, the samples were rinsed in running water and wiped dry with tissue paper and not touched with hands. An attempt was made to produce good and poor adhesion levels in both the aluminium types. The samples were given the following three types of treatments:

i) Ultrasonically cleaned for 5 minutes, then given sequence III [6.3] i.e. double Bondal treatments with 50% HNO_3 dip.

ii) Samples plated with single Bondal dip, sequence I [6.3], but without electrolytic cleaning.

iii) Samples plated directly with nickel after 50% HNO_3 dip without Bondal dip.

Normally one end of the aluminium samples plated with nickel for peel adhesion tests, is left without immersion in the zincate treatment to prevent adhesion and to allow a tab to be lifted. However, in this work the samples were plated all over in order to minimise the effect of the patch without the Bondal on the overall mode of vibration of the samples. Before starting the peel test one end of the sample had to be filed and an end of the nickel lifted up. As had been expected the samples plated directly with nickel without the Bondal dip did not need any significant force to lift up a tab and no apparent bond was visible between the base metal and nickel deposit.

It was observed that samples given pretreatment (i), produced relatively good adhesion levels in both the S1C and HE9 samples, compared to process (ii), mentioned above. With samples given relatively poor pretreatment, it was possible to pull the nickel tab by hand without much difficulty. To pull the samples given double Bondal treatment, pliers were needed, which indicated a fair bond between the aluminium base and the deposited nickel. S1C samples were found to produce a better bond than the HE9 samples given similar treatments ie. more force was required to peel the nickel.

The Q readings showed a large percentage drop compared with samples plated with thicker nickel coatings. However, it was not possible to differentiate a good bond from a poor bond by reading the Q values. The weight of plated nickel was more dominant than the surface irregularities and also the modulus of aluminium is different from that of nickel.

The peeled surfaces of S1C samples were significantly different from those of HE9 given similar plating pretreatments. Peeled S1C surfaces showed a large proportion of white areas, indicating failure at the aluminium base level and less dark/grey areas. The peeled HE9 surface showed an opposite sequence ie. more dark/grey areas than the white areas indicating failure at the zincate layer rather than at the bulk aluminium base.

Samples which showed more white areas on the peeled surfaces also showed better bond strength when pulled and the presence of a higher proportion of grey/dark areas was related to poor bond strength when peeled. Peeling test results indicated that it was possible to vary the adhesion level in the aluminium alloy bars by altering the pretreatment sequences.

7.5 SEM /XPS Analyses of the peeled surfaces.

After peel adhesion tests, samples of failed surfaces on the alloy substrate and the back of the peeled foils were cut from the test panels. Samples were vacuum coated with gold-palladium alloy. Four peeled samples were studied using scanning electron microscopy. Further studies were carried out using XPS analytical technique on the peeled surfaces. Two of these samples were S1C and the other two were HE9. In each case one sample was given good and the other poor pretreatment in order to produce good and poor adhesion levels. These four samples showed four different levels of adhesion.

Sample 12S (HE9) was given no electrolytic cleaning and plated with single Bondal dip. This sample exhibited minimal adhesion, the plated layer came off just by pulling by hand once the tab was lifted up, the other side when peeled with the Instron machine, virtually came off without any force. On visual examination, the peeled surfaces were found to be very smooth and dark/grey in appearance. The electron micrographs (Figs. 48-49) of foil and the base showed no evidence of any ductile failure, the two surfaces simply came apart without any plastic deformation.

Sample S1C7 was an S1C sample given poor treatment as in sample 12S above. This sample did not come off on pulling, but needed a bit of force when pulled by hand. Some resistance to peeling was evident. Peel test using the Instron machine did not show much difference in the force required to peel than sample 12S. Visual examinations of the peeled surfaces showed some surface roughness and some evidence of tearing was apparent. The grey surface appearance as observed in sample 12S was much reduced and showed white areas indicating some failure at the aluminium base. Electron micrographs (Figs. 50-51) show some evidence of tearing on both base and the foil but not all over, there were some patches which did not show much ductile features. The peeled surfaces indicate rupture occurring partially within the substrate.

Figure 52 shows an electron micrograph of the peeled foil of an HE9 alloy sample given good pretreatment before plating. Fig.53 shows the base of the same sample. The failure exhibited was ductile in nature, the base showed no signs of materials being pulled away from the surface. Failure was almost within the substrate, a fair amount of which was detached on the peeled electrodeposit. The tab did not come off easily on pulling by hand

and a pair of plier was needed to peel it. This sample had exhibited improved adhesion level, the chart recorder showed some readings but they were very low.

Figures 54 and 55 show electron micrographs of foil and base of a failed S1C sample given a good pretreatment before plating. This sample showed maximum resistance to peeling. Rupture occurred almost entirely within the substrate giving a high adhesion value. The foil shows particulate attachments which were pulled away from the base. This sample showed maximum force required in the peel test (54 N/cm) but not as high as had been expected. The peeled surfaces were rough and almost white showing presence of aluminium on both foil and the base.

It was found difficult to carry out a quantitative analysis on the peeled surfaces using EDAX, therefore a quantitative elemental analysis was carried out using XPS surface analytical technique on the peeled surfaces in order to establish the presence of different metals on the surface after peeling. The results obtained are shown in Table 26. The XPS analysis carried out on sample 12S, which showed poor adhesion, indicated a large amount of zinc on the base of the metal ie. the bulk, and also there was some present on the foil. As the Bondal layer is very thin and would also contain small amount of nickel, the elemental analysis showed the presence of nickel on both the base and the foil. The XPS analysis would be confined to about 30 atomic layers therefore no aluminium was present on either surfaces of the failed 12S sample, apparently the failure was at the zincate layer in this weakly bonded plated sample.

Sample 46S shows about 8% zinc on the base which is a lot more than what was observed on sample S1C10 (about 5%). The amount of zinc was dramatically reduced in the S1C10 foil compared to sample 46S. The aluminium content on both the bulk surfaces was about the same. However, the foil of sample S1C10 shows the presence of a large amount of aluminium, compared to that of sample 46S. As the level of adhesion was increased more aluminium was observed (sample S1C 10) on the peeled surfaces indicating the failure was not totally but was partially occurring at the aluminium base.

These results indicate that with S1C samples it was possible to produce a maximum level of adhesion given good pretreatment before plating. The adhesion level was very poor with HE9 samples when plated with poor pretreatment sequence.

Table 26. XPS Analysis of the Peeled Surfaces.

Sample no.	Elements present	Bulk %	Foil %
12S	Zn	80.44	37.67
	Ni	19.56	62.33
	Al	0	0
46S	Zn	7.85	43.4
	Ni	0.59	4.57
	Al	91.55	52
S1C10	Zn	4.68	10
	Ni	4.08	13.96
	Al	91.23	76

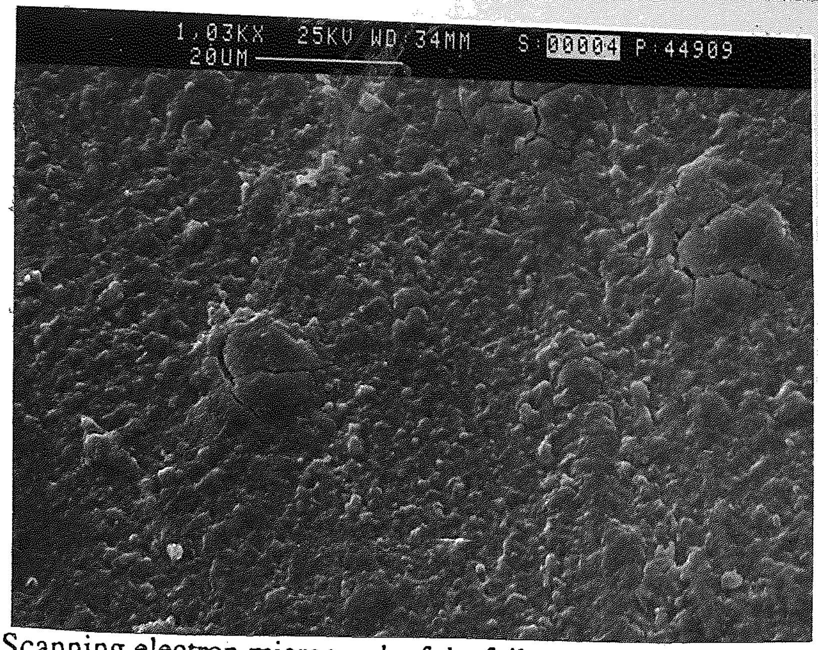


Fig.48. Scanning electron micrograph of the failure surface after peel adhesion testing of HE9 alloy (5 hr. plated), plated with single Bondal process sequence but without any hot soak or electrolytic cleaning, showing the back of the peeled nickel foil.

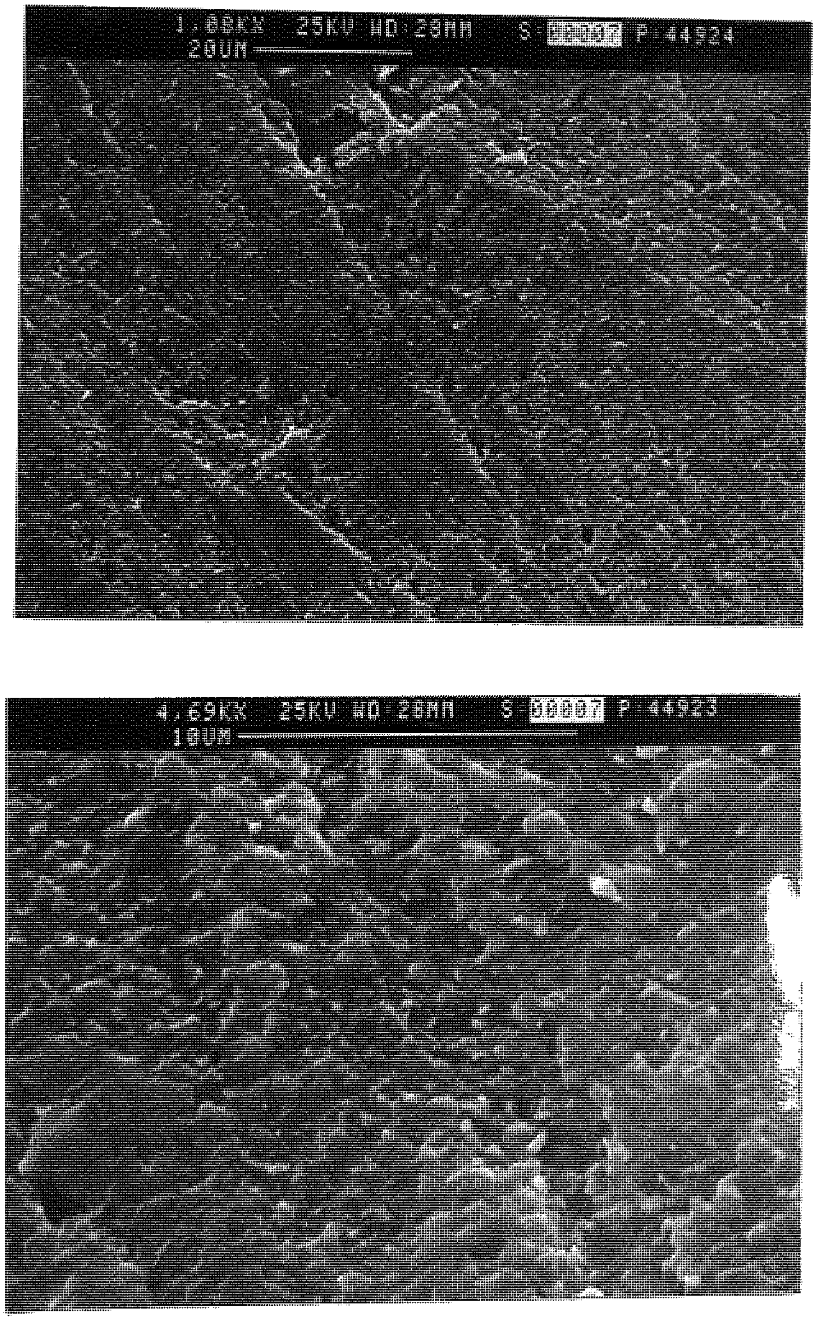


Fig.49. Scanning electron micrographs of the failure surface after peel adhesion testing of HE9 alloy (5 hr. plated), plated with single Bondal process sequence but without any hot soak or electrolytic cleaning, shows the alloy surface after peeling off the nickel foil.

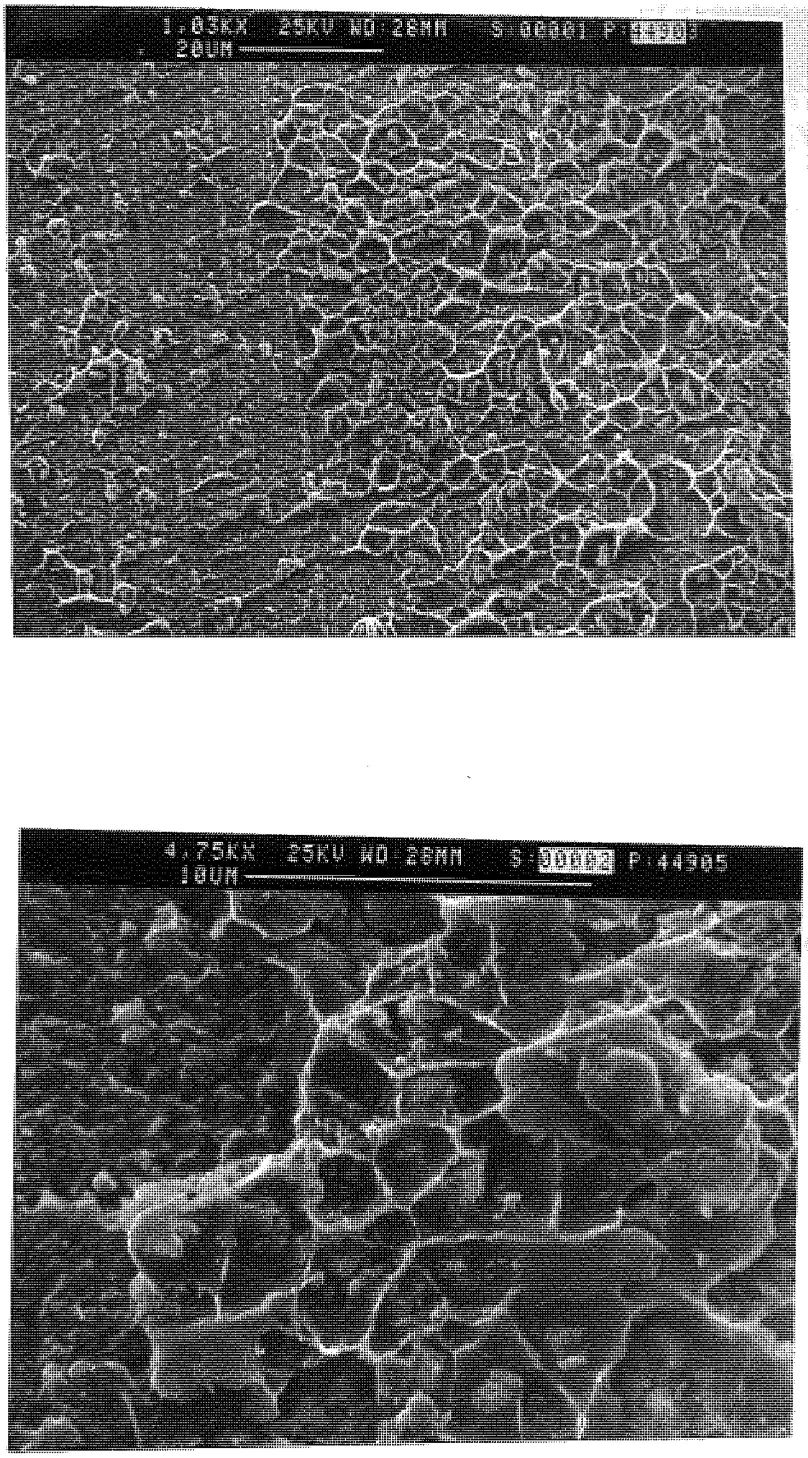


Fig.50. Scanning electron micrographs of the failure surface after peel adhesion testing of S1C alloy (5 hr. plated), plated with single Bondal process sequence but without any hot soak or electrolytic cleaning, showing the back of the peeled nickel foil.

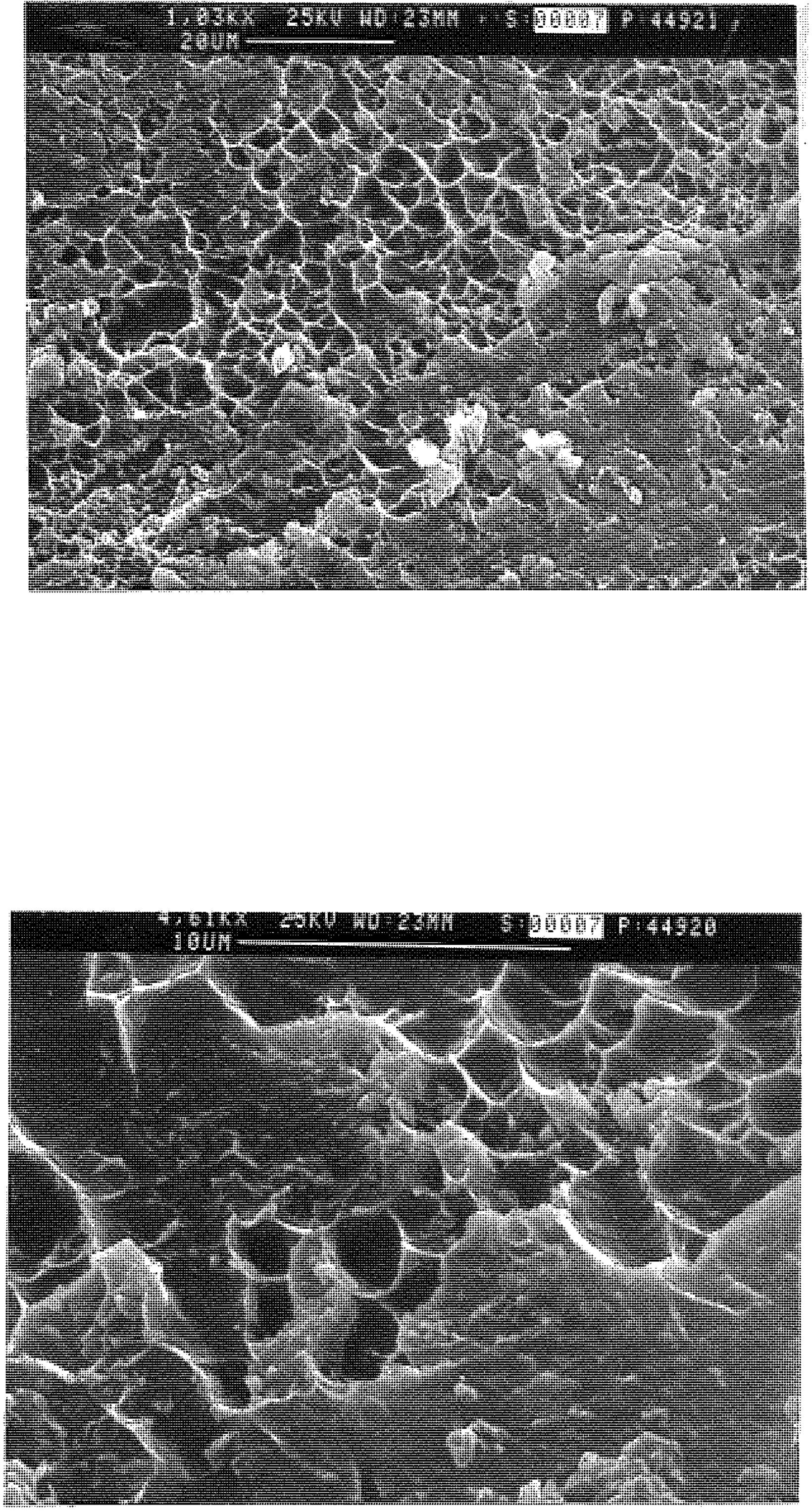


Fig.51. Scanning electron micrographs of the failure surface after peel adhesion testing of S1C alloy (5 hr. plated), plated with single Bondal process sequence but without any hot soak or electrolytic cleaning, shows the alloy surface after peeling off the nickel foil.

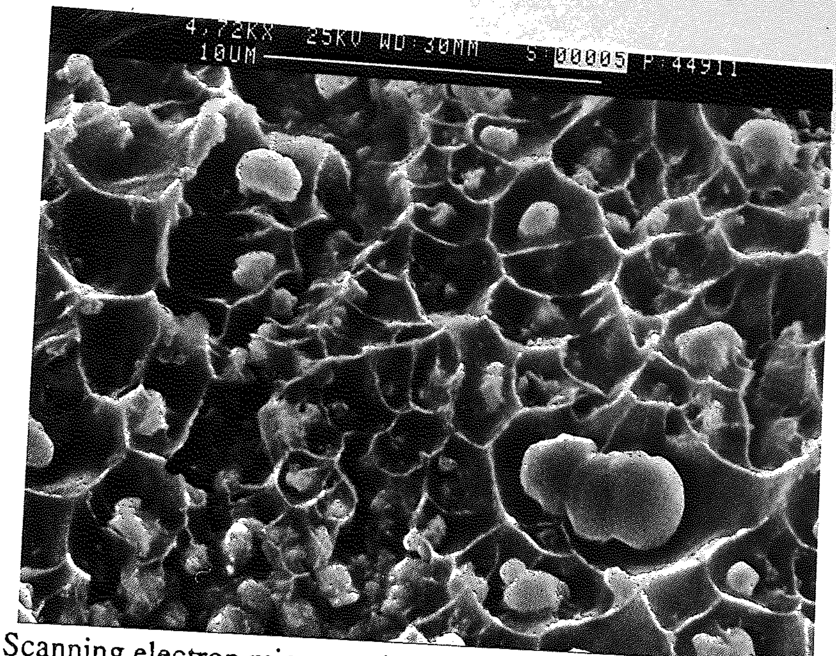


Fig.52. Scanning electron micrograph of the failure surface after peel adhesion testing of HE9 alloy (5 hr. plated), plated with double Bondal process sequence (iii), showing the back of the peeled nickel foil.

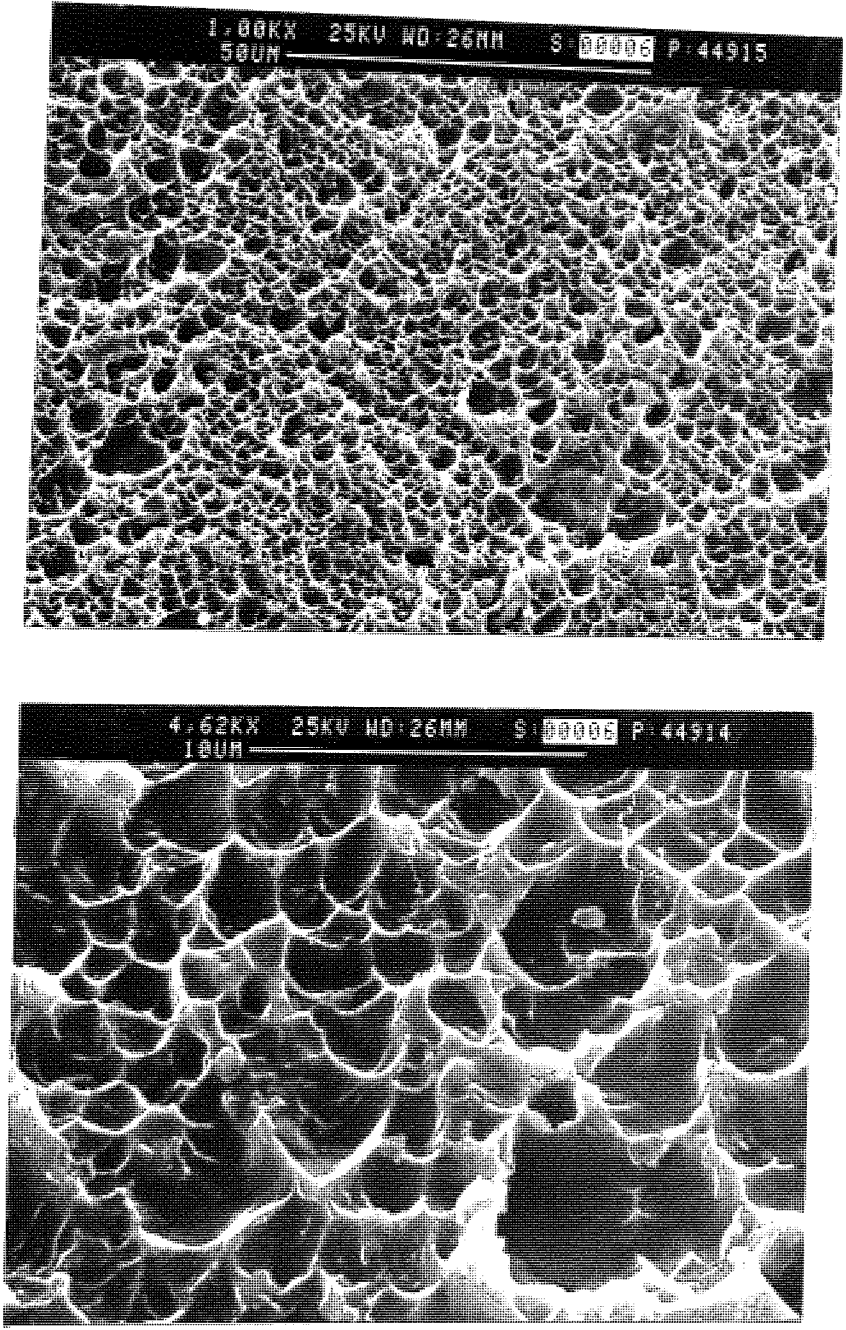


Fig.53. Scanning electron micrographs of the failure surface after peel adhesion testing of HE9 alloy (5 hr. plated), plated with double Bondal process sequence (iii), shows the alloy surface after peeling off the nickel foil.

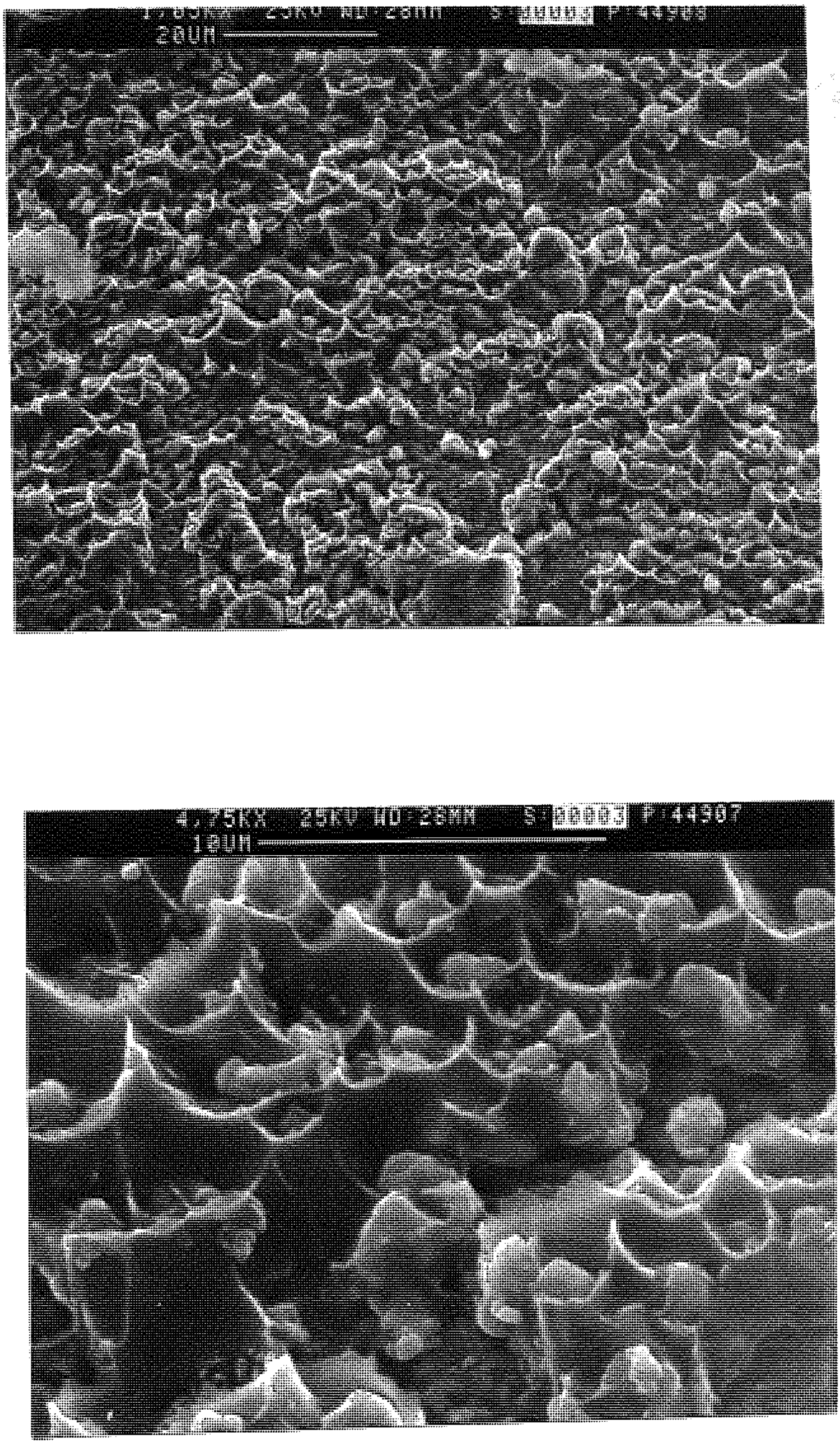


Fig.54. Scanning electron micrographs of the failure surface after peel adhesion testing of S1C alloy (5 hr. plated), plated with double Bondal process sequence (iii), showing the back of the peeled nickel foil.

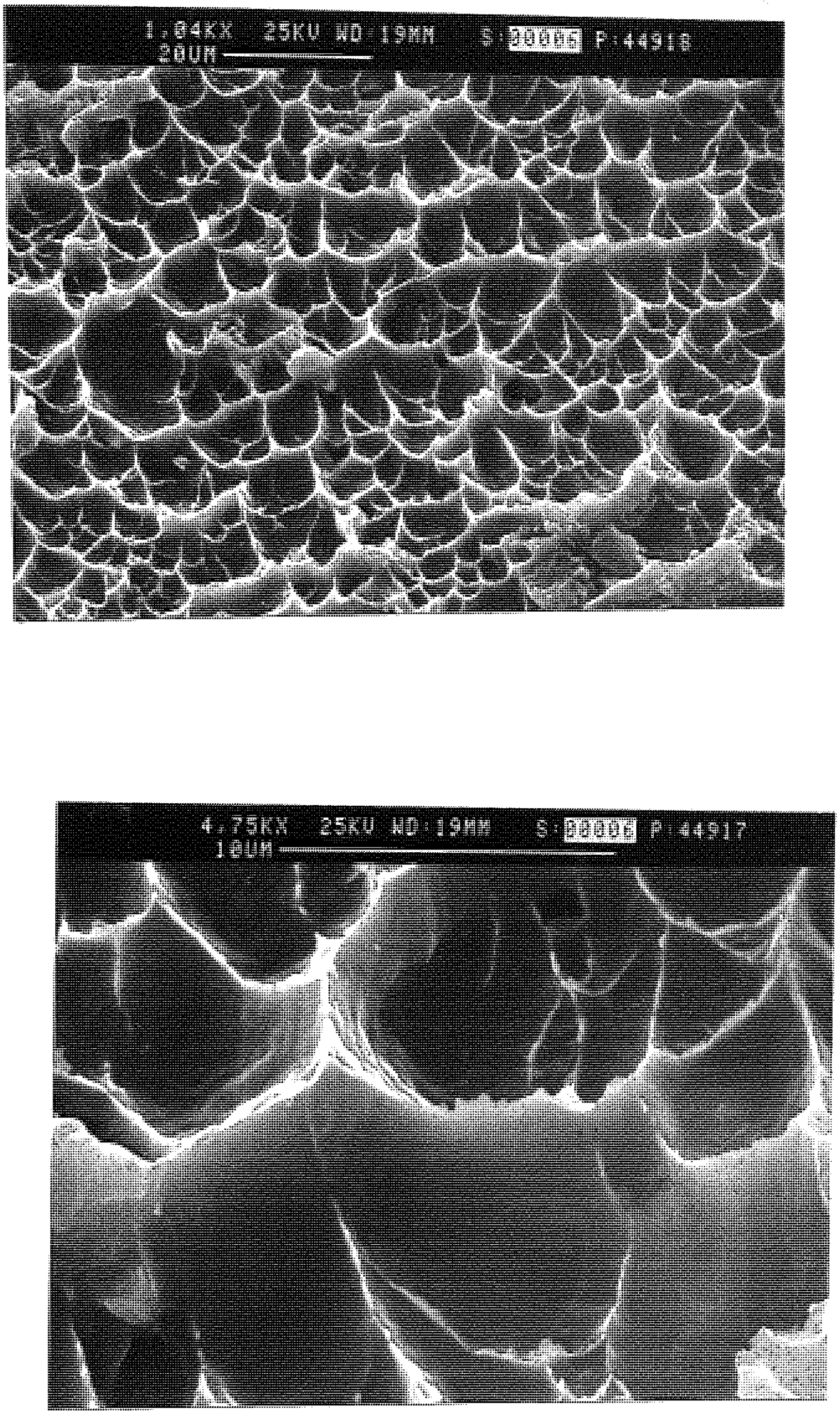


Fig.55. Scanning electron micrographs of the failure surface after peel adhesion testing of S1C alloy (5 hr. plated), plated with double Bondal process sequence (iii), showing the alloy surface after peeling off the nickel foil.

7.6 Heat-treatment of aluminium samples.

The instrument was unable to show any significant differences between samples given good and poor pretreatments, although the peel adhesion test quite clearly showed that different levels of adhesion were achieved with the plated samples given good and poor pretreatments.

An attempt was then made to study whether the instrument could detect any differences due to different heat treatments given to the aluminium samples. It was decided to anneal a number of aluminium samples at 400 °C for three hours and solution treat at 530 °C for half an hour and quench in water at room temperature. Q readings were taken before and after heat treatment over a period of time. Some success was achieved as can be observed in the results shown below. All the samples were heat-treated in a thermostatically controlled air circulatory furnace.

Materials are heat-treated in order to make them suitable for further working or to impart properties which enable the materials to perform satisfactorily in service. During heat-treatment changes takes place in the solid state, and these result in the desired microstructure and properties being achieved. When the term 'heat-treatment' is applied to aluminium alloys, its use is frequently restricted to the specific operations employed to increase strength and hardness of the precipitation-hardenable wrought and cast alloys. These are usually referred to as the 'heat-treatable' alloys, to distinguish them from those alloys in which no significant strengthening can be achieved by heating and cooling. The latter are generally termed 'non heat-treatable' alloys; in wrought form they depend primarily on cold work to increase strength. Heating to decrease strength and increase ductility (annealing) is used with alloys of both types and metallurgical reactions will vary with type of alloy and with degree of softening desired.

It was expected that after annealing Q would go up due to stress relieving and microstructural changes and the situation would be reversed after solution treatment. Tables 27-30 show the results obtained by annealing HE9 samples bars at 400 °C for 3 hours. Q and hardness readings were taken before and after annealing. Table 27 also shows readings taken after 30 hours of annealing. Figure 56 shows Q and hardness plots of the above samples before and after annealing.

Tables 31-35 show Q and hardness values obtained from HE9 alloy bars solution treated at 530 °C for 1/2 hour. The results indicate that Q went up after solution treatment and hardness dropped but was not as low as after annealing. These samples show an increase in Q after ageing at room temperature for 24 hours, hardness also went up after this room temperature exposure. Figure 57 shows the Q and hardness plots of the above samples before and after solution treatment.

Table 27. Q and hardness values of an aluminium HE9 alloy bar before and after annealing at 400 ^{o}C for 3hours.

Sample 1 (HE 65)		Before Annealing	16hrs after Annealing	30hr after Annealing
Frequency		1004	1002	1003
Q	1	5855	5219	5082
	2	5892	5231	5096
	3	5911	5255	5074
	4	5890	5282	5068
	5	5881	5262	5064
	6	5891	5240	5090
	7	5922	5208	5105
	8	5849	5261	5057
	9	5894	5239	5074
	10	5893	5217	5097
	Mean	5888	5241	5081
	S.d.n-1	22	24	16
Hardness		(81 HV)	(27 HV)	(27 HV)

Tables 28-35 show Q values with standard deviation and hardness values. In the tables below Q mean indicates that the results are an average of 10 Q readings. Hardness values (HV) are an average of 3 hardness readings.

Table 28. Q and hardness values of an aluminium HE9 alloy bar before and after annealing at 400°C for 3 hours.

Sample (HE 1)		Before Annealing	After Annealing
Frequency		1005	1003
Q	Mean	5736	5147
	S.d.n-1	28	26
Hardness		(81 HV)	(28 HV)

Table 29. Q and hardness values of an aluminium HE9 alloy before and after annealing at 400 °C for 3 hours.

Sample (HE 2)		Before Annealing	After Annealing
Frequency		1005	1003
Q	Mean	5746	5183
	S.d.n-1	24	15
Hardness		(79 HV)	(28 HV)

Table 30. Q and hardness values of an aluminium HE9 alloy bar before and after annealing at 400 ^{0}C for 3 hours.

Sample		Before	After
(HE 3)		Annealing	Annealing
Frequency		1004	1003
Q	Mean	5822	5257
	S.d.n-1	17	22
Hardness		(86 HV)	(28 HV)

Table 31. Q and hardness values before and after heat treatment of an aluminium HE9 alloy (solution treated at 530 ^{0}C for 1/2 hr, water quenched).

Sample		Before	20 mins after	24hr,after
(HE 61)		Treatment	Treatment	Treatment
Frequency		1001	990	990
Q	1	5783	6631	6417
	2	5731	6633	6440
	3	5745	6625	6393
	4	5774	6575	6430
	5	5735	6675	6445
	6	5779	6522	6395
	7	5765	6575	6459
	8	5802	6603	6384
	9	5737	6645	6404
	10	5725	6569	6465
	Mean	5758	6605	6423
Hardness		(77 HV)	(44 HV)	(48 HV)

Tables 32-36 show Q (mean), standard deviation and hardness. Q (mean) indicates that the results are an average of 10 Q readings. Hardness values (HV) are an average of 3 hardness readings.

Table 32. Q and hardness values before and after heat treatment of an aluminium HE9 alloy (solution treated at 530^{o}C for 1/2 hr, water quenched).

Sample (HE 4)		Before Treatment	20 mins after Treatment
Frequency		1000	988
Q	Mean	5959	6543
	S.d.n-1	24	22
Hardness		80 HV	37 HV

Table 33. Q and hardness values before and after heat treatment of an aluminium HE9 alloy (solution treated at 530 ^{o}C for 1/2hr, water quenched).

Sample (HE 5)		Before Treatment	20 min after Treatment	24 hr after Treatment
Frequency		1000	987	987
Q	Mean	5868	6434	6991
	S.d.n-1	27	23	36
Hardness		(83 HV)	(37 HV)	(44 HV)

Table 34. Q and hardness values before and after heat treatment of an aluminium HE9 alloy (solution treated at 530 °C for 1/2 hr, water quenched).

Sample (HE 6)		Before Treatment	20 min. after Treatment	24 hr. after Treatment
Frequency		1005	993	993
Q	Mean	5845	6354	6966
	S.d.n-1	26	25	39
Hardness		(80 HV)	(37 HV)	(45 HV)

Table 35. Q and hardness values before and after heat treatment of an aluminium HE9 alloy (solution treated at 530 °C for 1/2 hr, water quenched).

Sample (HE 7)		Before Treatment	20min after Treatment	24 hr after Treatment
Frequency		1006	995	994
Q	Mean	5849	6527	6993
	S.d.n-1	23	32	35
Hardness		(77 HV)	(38 HV)	(45 HV)

Table 36 shows results obtained from HE9 sample bars which were solution treated at 530 °C for 1/2 hour and quenched in water (as in samples shown in Tables 31-35). These sample were then precipitation treated at 175 °C in blocks of 4 hour. Samples were taken out from the furnace after every four hours and Q and hardness were then measured. Q went down immediately after the first 4 hour treatment at 175 °C, hardness went up to almost a maximum value after a 12 hour treatment. Hardness started to show a decline after 16hour precipitation treatment. Q also started to show a decline after a 16 hour treatment but the changes were not very marked. Figure 58 shows the Q and hardness plots of the above samples before and after solution and precipitation treatments.

Table 36. Q and hardness values before and after solution and precipitation treatment of an HE9 alloy (solution treated at 530°C, water quenched at room temperature and precipitation treated at 175°C).

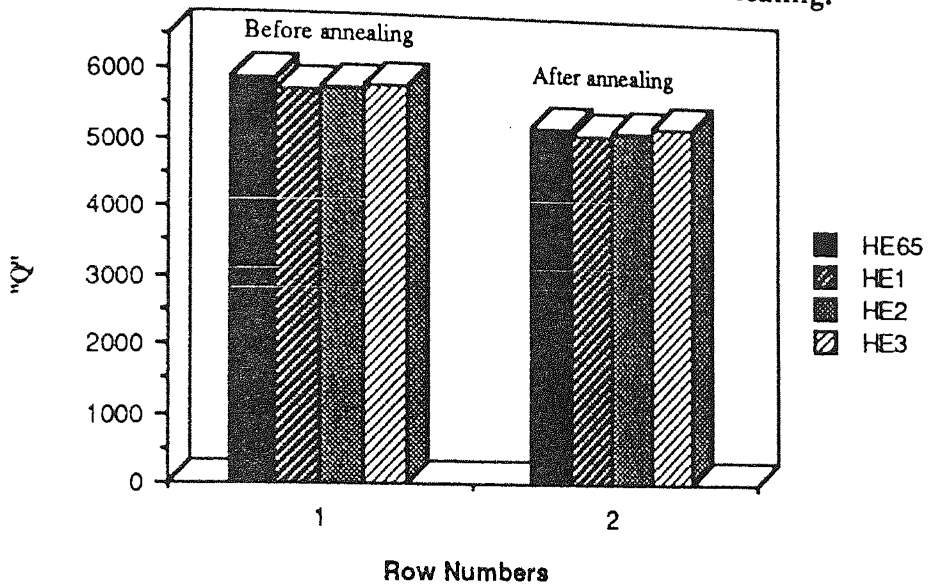
Sample HE5		As received	20 min. after Soln.Tr	24 hr. after Soln. Tr.	After 4 hr Ppt. tr.	After 8 hr Ppt.tr.	After 12 hr Ppt.tr.	After 16 hr Ppt. tr.
Frequency		1000	987	987	987	986	985	986
Q	1	5823	6407	6980	6837	7021	7046	6929
	2	5852	6418	7015	6895	6931	7035	6926
	3	5819	6419	6996	6869	7025	054	6908
	4	5892	6468	6967	6918	7036	7051	6934
	5	5890	6454	7065	6826	6990	038	6913
	6	5885	6938	6955	6916	7017	6999	6916
	7	5881	6448	6984	6881	6994	7051	6873
	8	5883	6443	7030	6900	7001	7032	6843
	9	5869	6450	6971	6880	7020	7051	6877
	10	5884	6437	6951	6850	7030	7021	6938
Mean		5868	6434	6991	6877	7007	7038	6906
Hardness		83 HV	37 HV	44 HV	77 HV	78 HV	81 HV	82 HV

Sample HE6		As received	20 min. after Soln.Tr	24 hr. after Soln. Tr.	After 4 hr Ppt. tr.	After 8 hr Ppt.tr.	After 12 hr Ppt.tr.	After 16 hr Ppt. tr.
Frequency		1005	993	993	993	992	992	992
Q	Mean	5845	6343	6967	6853	6945	6998	6781
	S.d.n-1	26	25	41	22	25	25	32
Hardness		80 HV	37 HV	45 HV	77 HV	78 HV	86 HV	85 HV

Sample HE7	As received	20 min. after Soln.Tr	24 hr. after Soln. Tr.	After 4 hr Ppt. tr.	After 8 hr Ppt.tr.	After 12 hr Ppt.tr.	After 16 hr Ppt. tr.
Frequency	1006	995	994	994	993	993	993
Q Mean	5849	6527	6993	6878	6940	6864	6899
Sdn-1	23	32	35	21	33	34	25
Hardness	77 HV	38 HV	44 HV	77 HV	78 HV	85 HV	83 HV

Tables 37 and 38 show Q and hardness values of S1C alloys before and after annealing at 400 ^{o}C for 3 hours (furnace cooled for 24 hours). In these S1C samples Q went up very significantly nearly more than twice the original Q (in as received condition) although after annealing HE9 samples showed a consistent decrease in Q by about 10% its original value. Figure 59 shows Q and hardness plots of two S1C aluminium alloys before and after annealing.

Fig.56. HE9 sample Q plots before and after annealing.



Hardness changes of HE9 samples due to annealing

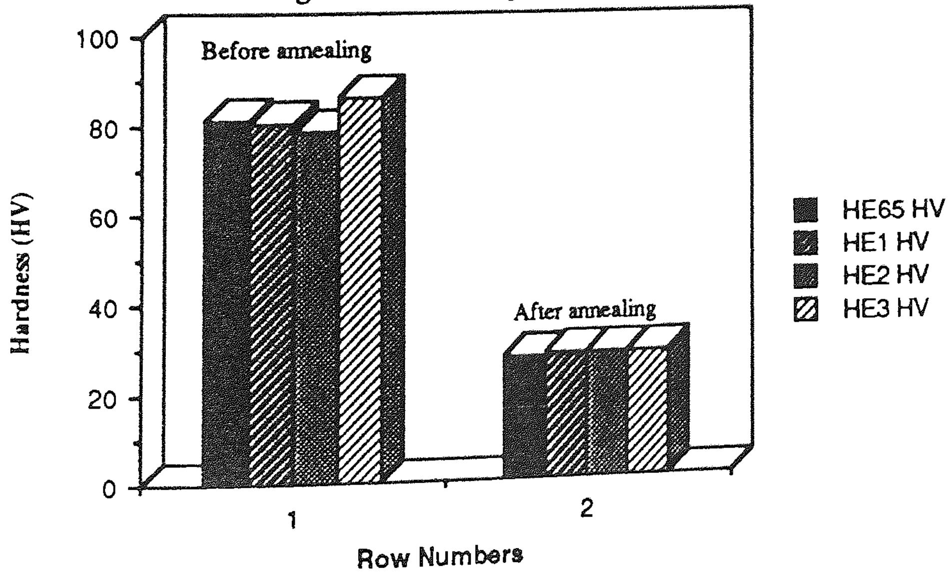
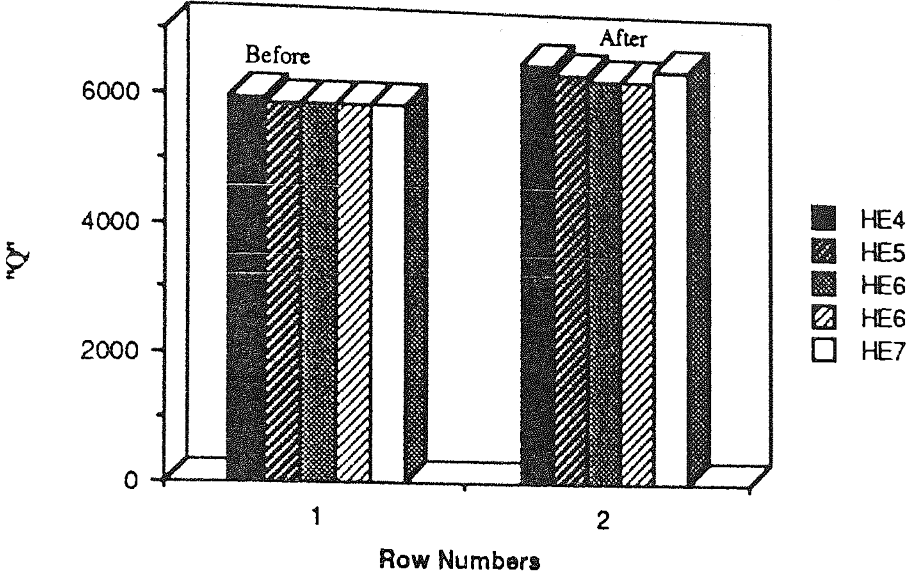


Fig.57. HE9 Q plots before and after soln. treatment



Hardness changes of HE9 samples due to soln.tr.

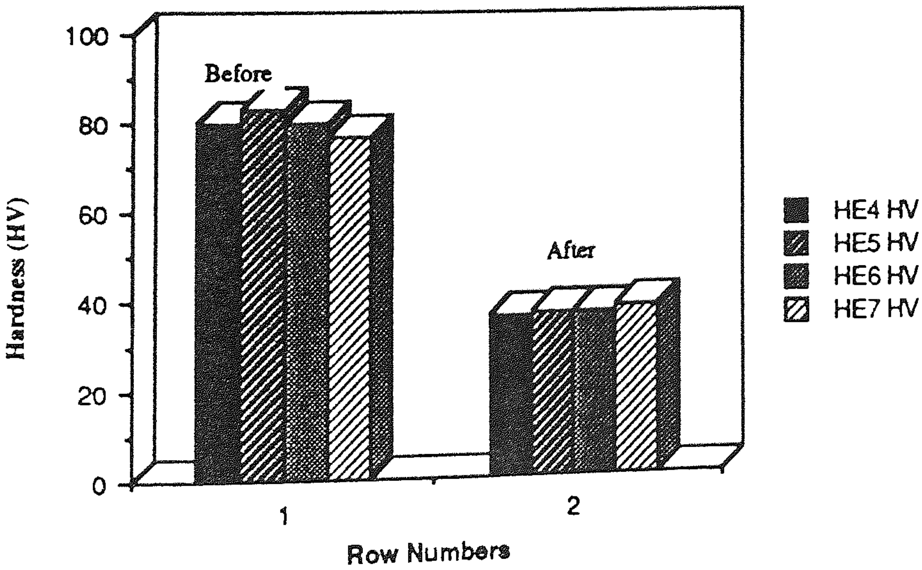
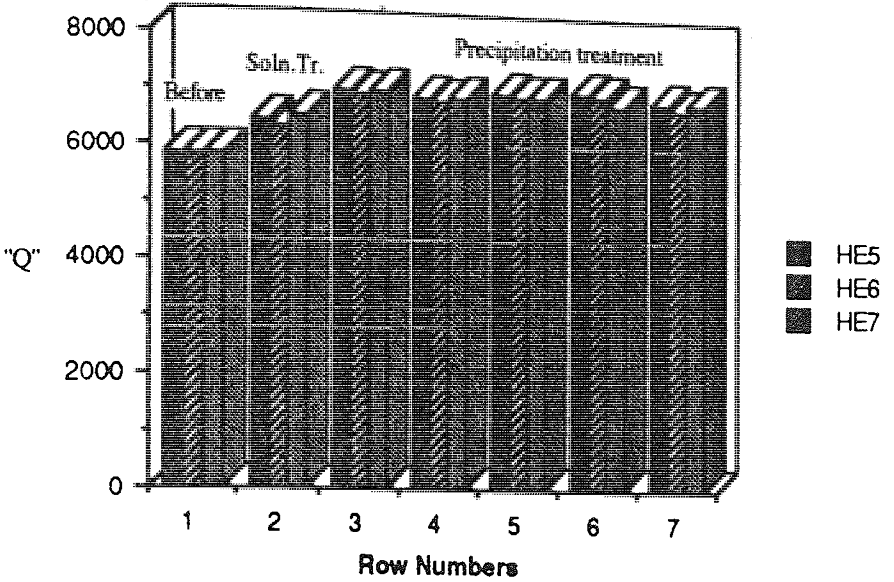


Fig.58. Q plots of 3 (HE9) samples before and after solution and precipitation treatments.



Hardness plots of 3 (HE9) samples before and after soln and ppt.tr.

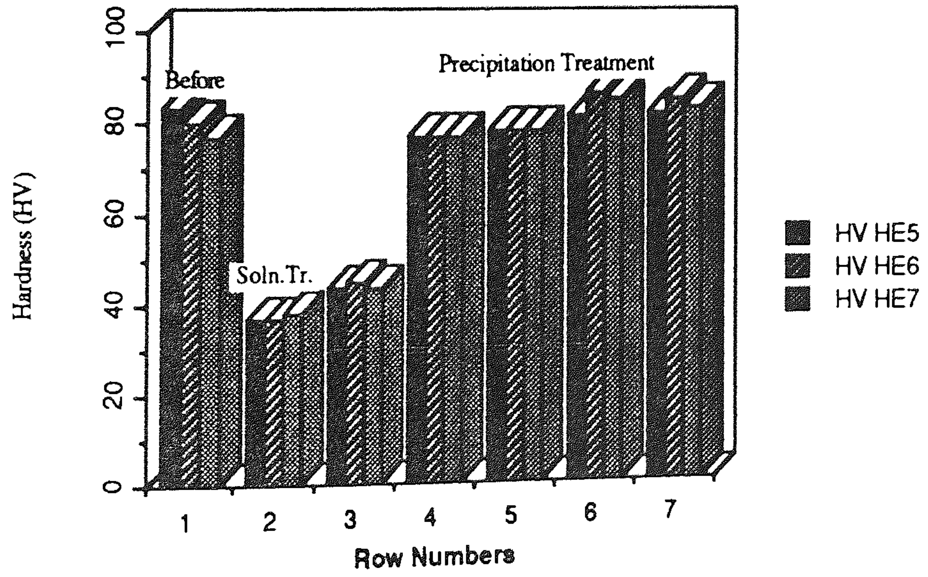


Table 37. Q and hardness values of an aluminium S1C alloy before and after annealing at 400 ^{o}C for 3hrs.

Sample		Before	16 hr after	30hr,after
(S1C 28)		Annealing	Annealing	Annealing
Frequency		909	919	918
Q	1	1677	3583	3800
	2	1635	3561	3794
	3	1663	3551	3757
	4	1677	3565	3786
	5	1671	3603	3721
	6	1665	3572	3767
	7	1689	3613	3735
	8	1654	3609	3753
	9	1658	3571	3759
	10	1634	3570	3762
	Mean	1662	3580	3763
		Hardness (41 HV)	Hardness (19 HV)	Hardness (20 HV)

Table 38. Q and hardness values of an aluminium S1C alloy before and after heat treatment (annealed at 400 ^{o}C for 3hrs).

Sample		Before	After
(S1C 20)		Annealing	Annealing
Frequency		922	931
Q	Mean	1462	3548
	S.d.n-1	23	23
	Hardness	(41 HV)	(28,HV)

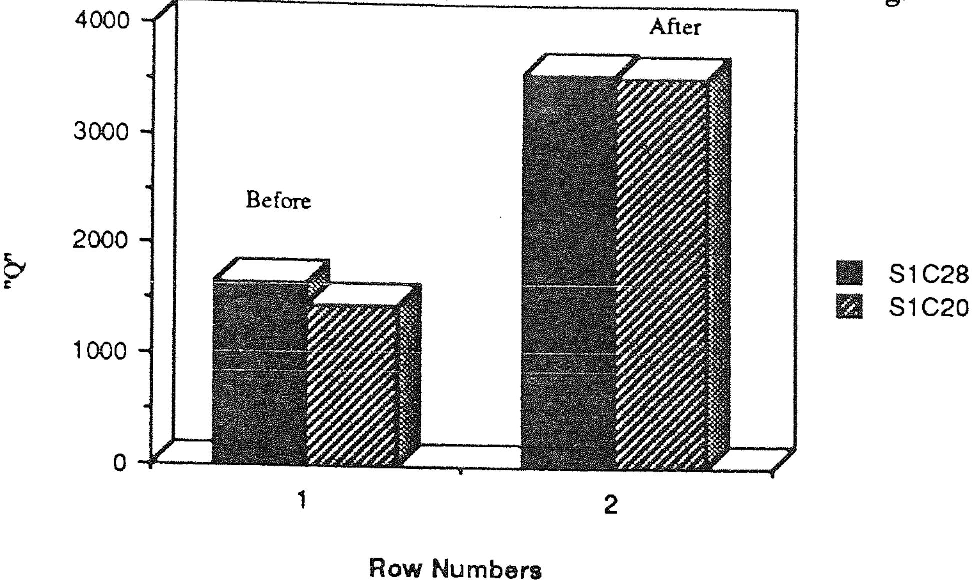
Table 39 shows Q and hardness values of S1C alloy solution treated at 530 ^{o}C for 1/2 hour and water quenched at room temperature. After solution treatment Q have gone up even higher than after annealing (Tables 37, 38) although the changes in hardness was not very consistent. Figure 60 shows Q and hardness plots of the sample bars before and after solution treatment. In this alloy system Q had gone up after both the treatments but was a lot higher after solution treatment than after annealing.

Table 39. Q and hardness values before and after heat treatment of an aluminium S1C alloy (solution treated at 530 ^{0}C for 1/2 hour, water quenched).

Sample (S1C 29)	Before Treatment	After Treatment
Frequency	908	919
Q 1	1748	4536
2	1738	4591
3	1750	4574
4	1742	4506
5	1755	4509
6	1763	4527
7	1754	4595
8	1736	4543
9	1719	4509
10	1719	4512
Mean	1742	4540
S.d.n-1	15	34
Hardness	(39 HV)	(30 HV)

Sample (S1C 27)	Before Treatment	After Treatment
Frequency	907	921
Q Mean	1582	4562
Hardness	(41 HV)	(21 HV)

Fig.59. S1C sample Q plots before and after annealing.



Hardness changes due to annealing.

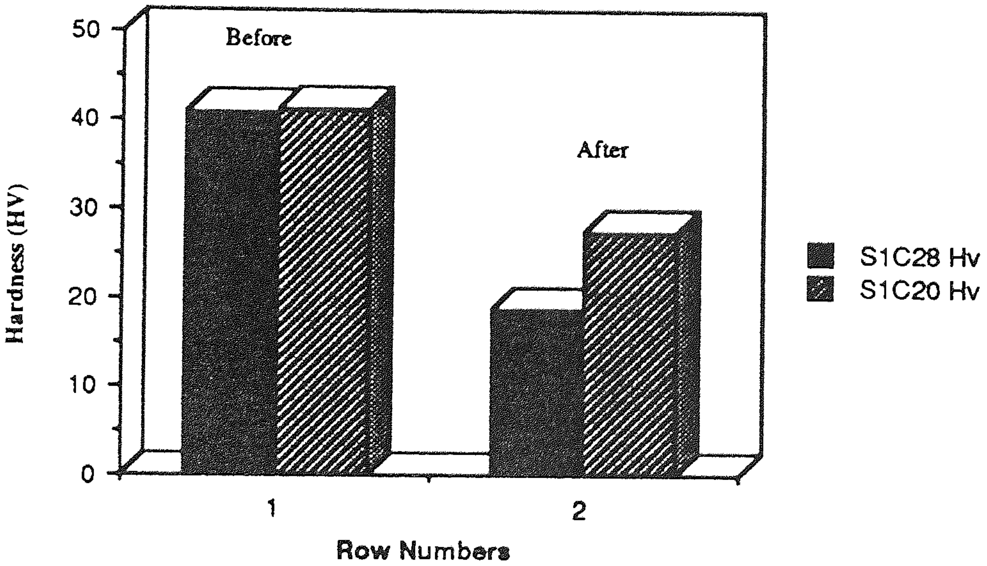
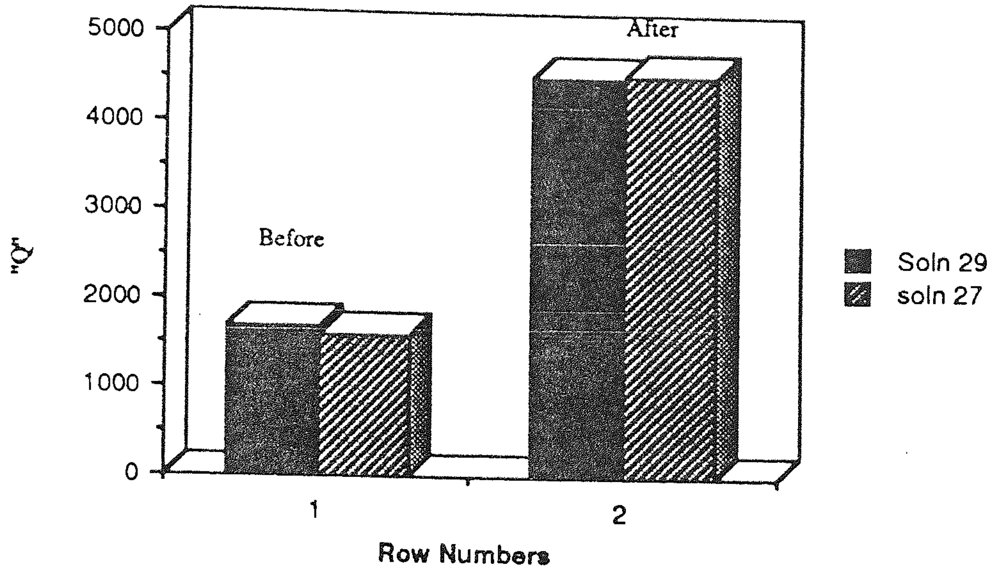
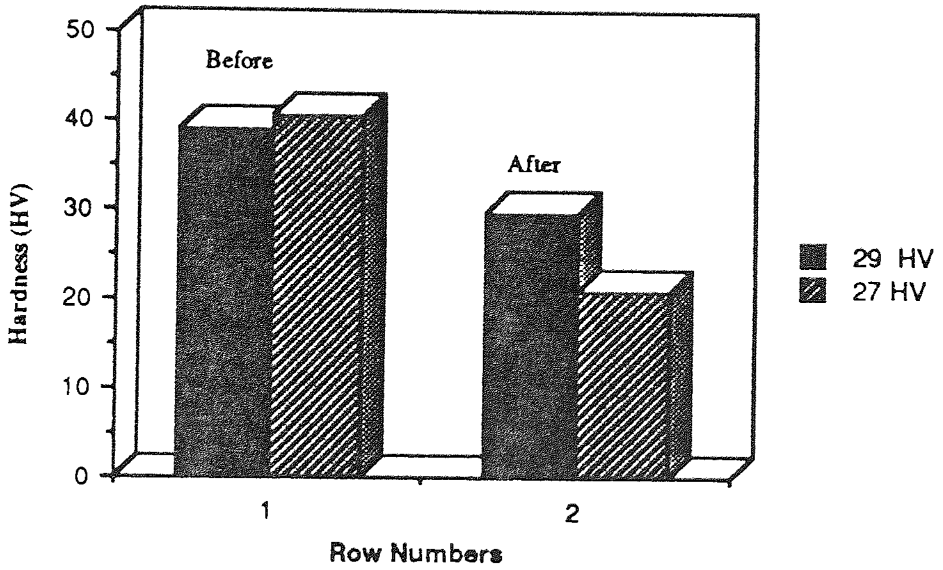


Fig. 60. S1C sample Q changes due to solution treatment.



S1C hardness changes due to solution treatment.



HE9 alloy samples showed a significant drop in both Q and hardness values after annealing but the solution treatment of this alloy system in effect decreased the Q-values although the hardness dropped quite significantly after both the treatments.

The S1C samples which are non-heat-treatable alloy and are not supposed to respond to heat-treatment showed an increase in Q-values after annealing and solution treatment.

In both, the heat-treatable (HE9) and non-heat treatable alloys (S1C alloys) annealing removes the the effects of cold work within the temperature range from about 300 to 450 ^{o}C. For the heat-treatable alloys, the phases formed by combination of solute atoms with aluminium are sufficiently thoroughly precipitated by full annealing to stabilise them and prevent further age hardening. In this work the full annealing treatment was carried out at 400 ^{o}C for three hours and had resulted in the softening of both the alloys and this would have taken the alloy into the single phase field and dissolved all the foreign atoms in the aluminium to give a random substitutional solid solution.

The HE9 samples probably had a more uniform structure and were much more stress free. After annealing the precipitates had overaged and lost the strains and consequently reached a more stress free condition. After solution treatment all the precipitates would be in solid solution. As can be expected with solution treatment due to the severity of the quench some residual stresses would be developed within the alloy matrix. The Q-meter was measuring Q which is related to stress and not hardness. After annealing, the HE9 alloy showed a significant drop in the Q values but after solution treatment the Q went up.

A s received S1C alloy can be expected to have a large amount of dislocations and strain hardened due to cold rolling, the severity would of course depend upon the sheet reduction during rolling, higher percent reduction would increase dislocation concentration. Although this alloy is not supposed to respond to any heat-treatment as there are very little alloying elements present, also showed an increase in the Q-values after both treatments but solution treatment had resulted in higher Q-values than annealing.

The precipitation hardening results show a range of Q-values which altered after the various treatments that were applied. The plots show a gradual rise after solution treatment and 24 hour ageing, there is a slight drop in the Q after 4 hour precipitation treatment and an increase up to 12 hour treatment; after a 16 hour treatment the Q values have started to show a decline. It can be expected that after 4 hour precipitation treatment the alloy will be less stressed but will contain a large number of precipitates which would grow in size and also in number with increased time of precipitation treatment. After 12 hour precipitation treatment the size and distribution of the precipitates would be expected to have reached an optimum for effectively preventing dislocation movement. After 16 hours the precipitates would be growing too large and will have lower strain levels therefore become less effective in locking dislocations. The hardness values showed as expected a rise with time of precipitation treatment and started to decline after 16 hour treatment.

It appears the Q-meter is also sensitive to strain associated with the formation of surface oxides which would have increased substantially with high temperature exposures and this was interfering with the expected Q which was not observed. The meter was monitoring changes in the oxide layers rather than the changes within the material.

7.7 Effect of Lacquering and Anodising HE9 Aluminium Alloys.

It was thought that the continuous fluctuation of Q with time was related to the formation and breakdown of surface oxide films at room temperature. One way of determining this was by lacquering the alloy surface so the bulk of the aluminium surface would be prevented from direct contact with free oxygen. Some oxygen would be expected to reach the aluminium surface but at a considerably reduced rate.

Q readings were taken of an aluminium HE9 sample before lacquering. The lacquer used was printed circuit lacquer. It can be observed that lacquering had resulted in considerable drop in Q. Table 40 shows Q and standard deviations of the sample readings before and after lacquering. Figure 61 shows plot of Q with time of a lacquered HE9 sample bar.

Table 41 shows Q readings taken by removing and replacing the specimen on to the test rig. The variation was very much reduced. Continuous variation of Q present in the unplated samples had cast a lot of doubt regarding the reliability of the instrument during the early part of the instrument development. The standard deviation of the Q values obtained after lacquering showed very small variation and was found to be very consistent. In order to obtain further evidence of surface oxidation HE9 sample bars were anodised and tested.

Table 40. Q readings before and after lacquering.

Sample HE5	As received	1 hour after Lacq.	24 hr. after Lacq.	45 hr after Lacq.	65 hr after Lacq.	69 hr after Lacq.	90 hr after Lacq.	134 hr after Lacq.
Frequency	1003	987	1007	1006	1006	1007	1006	1007
Q 1	6410	2081	2501	2580	2640	2648	2680	2765
2	6428	2070	2512	2611	2635	2631	2695	2761
3	6483	2058	2509	2597	2639	2643	2691	2772
4	6414	2084	2509	2571	2664	2657	2689	2755
5	6423	2074	2495	2601	2631	2653	2685	2671
6	6449	2081	2503	2582	2649	2655	2698	2751
7	6444	2061	2507	2678	2651	2666	2680	2754
8	6482	2083	2499	2583	2628	2658	2687	2778
9	6490	2081	2513	2596	2630	2660	2685	2743
10	6431	2078	2494	2585	2622	2634	2681	2773
Mean	6445	2075	2504	2588	2639	2651	2687	2761
S.d.n-1	30	9	7	12	13	11	6	11

Figure 61 shows Q plot with time of a unpolished HE9 sample bar after lacquering. The first reading was taken an hour after lacquering and the effect of curing of the lacquer was not evident after 20 hours ie. the changes in Q in the first hour was due to the lacquer drying up (curing). The fluctuation of Q with time after this was almost negligible.

Table 41. Q and Standard deviation of a lacquered sample taken by removing and replacing the test sample from the test rig.

Frequency	1007	1007	1007	1007	1007
Q 1	2076	2068	2082	2081	2088
2	2069	2075	2063	2070	2063
3	2079	2057	2058	2058	2082
4	2075	2078	2061	2074	2088
5	2082	2071	2058	2074	2075
6	2082	2066	2052	2081	2075
7	2067	2078	2078	2061	2075
8	2072	2066	2067	2083	2088
9	2080	2069	2067	2081	2088
10	2080	2079	2070	2078	2086
Mean	2076	2071	2066	2075	2079
S.d.n-1	5	7	9	9	9

Three HE9 samples were anodised as shown in Table 42.

Table 42. Anodising conditions used for anodising 3 HE9 alloy bars.

	Operating Temp.	Time	Potential / current density	Coating thickness
Anodised and sealed,	18°C	45 mins	15.5 V	30 µm
Hard anodised	5°C		3 A / dm^2	20 µm
Anodised (opalized*)	50°C	45 mins	1.5 A/ dm^2	12 µm

* Anodising process of Philips, Eindhoven, The Netherlands.

Figure 62 shows Q plots with time after anodising. These samples also show a considerable percentage drop in Q as coating thicknesses increased (cf.Fig.45). The fluctuation patterns were almost flattened out. Both opalized and the sealed coatings showed slight fluctuations, however, after hard anodising the Q plot was almost horizontal. These observations indicate that the fluctuations in as received aluminium alloy bars were due to surface oxidation, on enveloping the active aluminium surface the surface reactions were remarkably reduced to almost no oxidation state.

Table 43. Q values and standard deviations of HE9 Samples Before Anodising.

Sample	33D	8D	70A
Frequency	995	996	1011
Q 1	6166	6364	5805
2	6189	6339	5824
3	6113	6356	5807
4	6244	6345	5831
5	6178	6386	5836
6	6186	6340	5870
7	6288	6311	5842
8	6252	6355	5794
9	6229	6339	5844
10	6255	6346	5812
Mean	6210	6348	5827
S.d n-1	53	20	23

Fig. 61. Changes in Q after lacquering

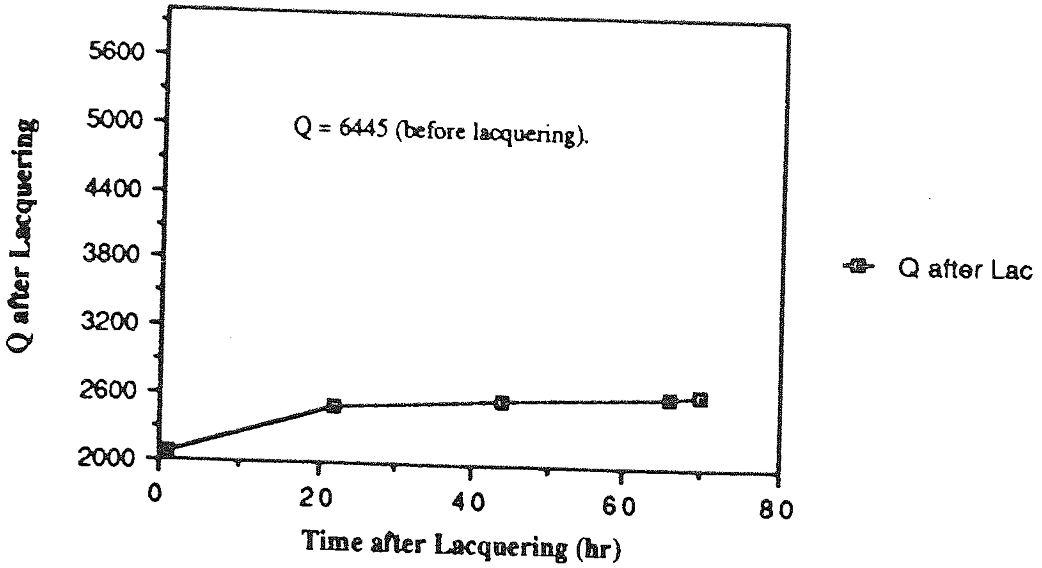
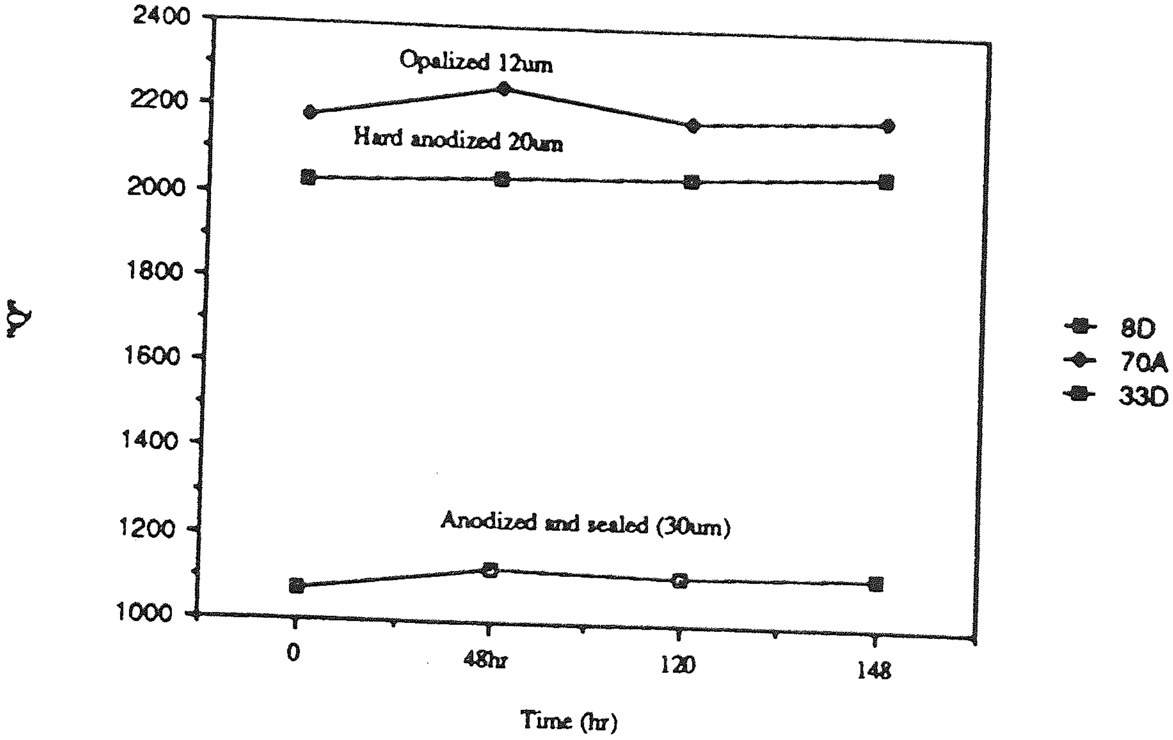


Fig.62. Changes in Q with time of anodised HE9 alloy bars.



CHAPTER 8

8.1 STATISTICAL ANALYSIS

In statistical analysis one has to make decisions about populations on the basis of information obtained by taking a sample from the population. In trying to reach a decision assumptions are made about the populations involved. These assumptions are called hypotheses. Frequently a hypothesis is formulated for the sole purpose of rejecting or nullifying it. For instance if it is necessary to decide if one process is better than another the hypothesis is formulated that there is no difference between the processes, ie.that any observed differences are simply due to fluctuations in samples taken from the same population. Such hypotheses are called null hypotheses and they are usually denoted by H_O.

The purpose of statistical tests of significance is to separate differences which could not easily have occurred by chance from those which could. A difference which could not easily have occurred by chance is said to be statistically significant. The choice of significance level depends upon the nature and importance of the particular investigation being carried out, Table 44 gives the generally accepted divisions.

It is known that if a given population variance is estimated independently from two random samples, drawn from that population, then the ratio of the two variance estimates will be distributed in a particular way, following what is known as the F-distribution. The F-test uses this distribution to compare estimates of population variance and is designed to test whether one population is more variable than another.

Table 44. Significance of Statistical Tests (Brookes, Betteley and Loxston, 1979).

Probability	Conclusion
Greater than 0.1	Not significant, H_O accepted.
Between 0.1 and 0.05	Possibly significant, some doubt is cast on H_O but further evidence sought before rejection.
Between 0.05 and 0.01	Significant, Ho rejected. If the result is very important confirm with further evidence.
Between 0.01 and 0.001	Highly significant.
Less than 0.001	Very highly significant, Ho rejected and it is very unlikely that the conclusion is incorrect.

However, the method used to compare a large number of samples is the analysis of variance. Using this procedure a comparison of variance estimates provides a comparison between mean values. In order to establish the reliability of the Q meter developed it was decided to carry out a statistical analysis using analysis of variance (ANOVA) on a computer on some of the experimental results.

In this analysis there are three types of results and these were obtained using three different instruments :

i. modal analysis,
ii. modified Q-meter and
iii. the decrement Q-meter developed based on impulse technique.

The results obtained using the modal analysis technique showed a lot of variation on visual examination, therefore statistical analysis was only used to show there is a variation in the results. The results obtained using the modified Q-meter also showed a large variation, and the standard deviations were very high.

The standard deviation of the results obtained using the decrement Q-meter (iii) was also very low compared to those obtained by instruments (i) and (ii). Therefore a detailed statistical analysis was carried out.

In any experiment certain experimental conditions can be varied deliberately and the others held constant. There will also be factors affecting the results which cannot be controlled and whose effects cannot be identified separately. Variation caused by such factors are grouped under the heading of experimental error. The experimental error is thus the inherent variability due to random fluctuations and will be measured by the variance of observations made under apparently identical conditions.

Table 45 shows the results obtained after various pretreatments and 15 minutes of plating using the modified Q-meter. It can be seen from the table that the results show a fair amount of variation after any treatment, and this is reflected in the statistical analysis (Tables 46-51). Although the Tables show that the variation is not significant in some observations (Table 47) and that results can be accepted as being consistent in others eg. after acetone cleaning, however, the overall performance shows that the results were statistically very highly significant and therefore cannot be accepted as being consistent. Due to inconsistency in the results and problems associated with vibrating unplated aluminium sample bars a new Q-meter was developed. A statistical analysis of the results obtained using the new Q-meter is discussed below.

Table 52 shows Q values obtained from a unplated aluminium HE9 alloy bar which was cleaned with detergent and acetone swabbed only to remove oil and grease from the surface. The sample was only touched with clean rubber gloves in order to minimise the effect of contamination by chemicals from hands.The table shows four columns; Qc indicates that 100 sample readings were taken continuously without actually removing the specimen from the test rig and the next column Qr shows another 100 sample readings which were taken by removing the sample from the test rig after every 10 readings, the sample was then replaced as close as possible to its original position and the process was repeated 10 times. Table 53 shows statistical analyses of the results shown in Table 52 obtained using ANOVA (analysis of variance) on a computer. The results obtained without removing the sample show that the results are significant ie. cannot be accepted, this differences could not have occurred by chance.

However, Table 54 shows highly significant results which are not at all acceptable as being consistent (prob>F is 0).

The statistical analysis indicate that there is some variation in the result obtained without removing the sample. Removing and replacing has an erratic effect on the Q values. This indicates that there is some variation due to the instrument and also an effect due to removing and replacing the sample, an extra experimental error being introduced.

Table 55 shows Q values obtained from another unplated sample over a period of five days, these readings were taken as in Table 52 by removing and replacing the sample after every 10 readings. Analysis of variance shows (Tables 56 - 60) only on one day (Table 60) results were not significant but on all other days the results were highly significant.

Table 61 shows Q values obtained from another unplated sample over a period of five days, readings were taken as in Table 55. Results of the analysis of variance are shown in Tables 62-66. Analysis shows similar inconsistency as in the earlier unplated sample discussed above.

Table 67 shows Q values taken from a 1/2 hour plated sample in the same way as in Table 61. These results also show statistical inconsistency (Tables 68-72) as has been indicated in earlier samples.

In this analysis, one way analysis of variance was used assuming the only assignable cause of variation was the instrument itself and then the effect of removing and replacing the sample to its original position was studied. Table 53 shows a sample result which was obtained without moving the test bar from its position. Although the standard deviation is only 30.25 the analysis of variance shows that Prob>F is 0.036 which is between 0.01 and 0.05 and according to Table 44 this is significant. Table 54 shows results from the same sample but when it was removed from the test rig and repositioned after every 10 readings, the Prob>F was less than 0.001, ie. the result then became very highly significant. This indicates that repeating/replacing has introduced some extra experimental error. These observations indicate that positioning of the test sample on the test rig is very critical, however, every effort was made to position the sample as close as possible to its original position.

Table 55 shows Q-readings of an unplated sample, the readings were taken by replacing and repeating after every 10 readings on five different days. ANOVA results show only on one day the result was not significant (day 5), results of day 3 could be acceptable but on other days the results were not acceptable. These results confirmed that the instrument shows some variation even when everything was constant, and this variation was continued when readings were taken by replacing and repeating the sample on the same day and also on different days.

However, as no better instrument could be developed the same instrument was used to determine the difference between samples given good and poor pretreatment before plating. This instrument was also used to measure the variation in the Q values due to various heat treatment given to aluminium sample bars, and also after lacquering and anodising.

Table 45. Q values obtained using the modified Q-meter for as received material (HE9) and after various pre-treatments and 15 minutes of plating.

		Ins 1/A							Ins 1/A		
eceived	Qr	Acetone	Qace	Nitric	Q Nitric	Bond Cl 15 s	Qbon cln15s	Bondal Dip	Qb dip	15min Pltg	Q 15minpltg
one	11444	one	10192	one	11585	one	12391	one	11746	one	10557
one	11230	one	10545	one	11677	one	12477	one	11570	one	10112
one	11271	one	10121	one	11666	one	12817	one	11385	one	10427
one	11041	one	10611	one	11730	one	12465	one	11810	one	10311
two	11334	two	10704	two	11691	two	12510	two	11727	two	10414
two	11341	two	10677	two	11901	two	11892	two	11624	two	10219
two	11517	two	10814	two	11811	two	11881	two	11561	two	10271
two	11471	two	10274	two	11954	two	11727	two	11352	two	10311
three	11941	three	10484	three	11891	three	11781	three	12173	three	9427
three	11834	three	10791	three	12014	three	11811	three	11733	three	9407
three	11741	three	10407	three	12012	three	11370	three	12076	three	8881
three	11777	three	10613	three	12104	three	11327	three	11778	three	8701
four	11641									four	8687
four	11247									four	9253
four	11797									four	8671
four	11701									four	8821
five	11615										
five	11651										
five	11825										
five	11841										
MEAN	11563		10519		11836		12037		11711		9654
Dn-1	254		229		167		481		248		737

Table 46. Statistical analyses of the Q values shown in table 45, of as received condition.

Data File: Ins1/A

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Received	878428.50	4	219607.12	9.50	0.000
Error	346595.50	15	23106.37		
Total	1225024.00	19			

Table 47. Statistical analyses of the Q values shown in table 45, after acetone cleaning.

Data File: Ins1/A

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Acetone	142712.67	2	71356.33	1.48	0.279
Error	434586.25	9	48287.36		
Total	577298.92	11			

Table 48. Statistical analyses of the Q values shown in table 45, after nitric acid treatment.

Data File: Ins1/A

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Nitric	232272.17	2	116136.08	14.23	0.002
Error	73452.50	9	8161.39		
Total	305724.67	11			

Table 49. Statistical analyses of the Q values shown in table 45, after electrolytic cleaning in Bondal cleaner.

Data File: Ins1/A

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Bond Cl 15 s	1877738.50	3	625912.83	7.55	0.010
Error	663550.42	8	82943.80		
Total	2541288.92	11			

Table 50. Statistical analyses of the Q values shown in table 45, after 2 minutes bondal dip.

Data File: Ins1/A

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Bondal Dip	321585.50	2	160792.75	4.43	0.046
Error	326444.75	9	36271.64		
Total	648030.25	11			

Table 51. Statistical analyses of the Q values shown in table 45, after 15 minutes plating with nickel.

Data File: Ins1/A

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between 15min PLtg	7380582.25	3	2460194.08	38.99	0.000
Error	757273.50	12	63106.12		
Total	8137855.75	15			

Table 52. Q readings taken of an unplated aluminium sample bar using the new Q-meter. Qc indicates 100 Q-values taken without moving the sample. Qr indicates 100 Q-values taken by removing and replacing the sample to its original position after every 10 readings.

	Continuous	Q c	Column 3	Q r
1	one	6115		6193
2	one	6203		6163
3	one	6179		6176
4	one	6206		6143
5	one	6214		6183
6	one	6222		6175
7	one	6189		6183
8	one	6241		6165
9	one	6218		6157
10	one	6260		6218
11	two	6179		6173
12	two	6247		6184
13	two	6210		6173
14	two	6252		6179
15	two	6227		6172
16	two	6196		6165
17	two	6173		6156
18	two	6214		6153
19	two	6236		6182
20	two	6223		6197
21	three	6197		6151
22	three	6191		6144
23	three	6227		6140
24	three	6208		6127
25	three	6154		6112
26	three	6228		6178
27	three	6238		6186
28	three	6162		6143
29	three	6172		6162
30	three	6235		6162
31	four	6195		6092
32	four	6154		6063
33	four	6160		6097
34	four	6199		6078
35	four	6237		6061
36	four	6178		6087
37	four	6186		6046
38	four	6229		6101
39	four	6132		6088
40	four	6212		6095
41	five	6214		6284
42	five	6202		6242
43	five	6224		6251
44	five	6157		6257
45	five	6179		6251
46	five	6224		6242
47	five	6203		6248
48	five	6232		6173
49	five	6145		6177
50	five	6202		6235
51	six	6191		6093
52	six	6206		6137
53	six	6156		6145
54	six	6238		6119
55	six	6165		6131
56	six	6193		6159
57	six	6191		6126
58	six	6174		6154
59	six	6196		6140
60	six	6236		6124
61	seven	6185		6189
62	seven	6185		6178
63	seven	6215		6193
64	seven	6183		6173
65	seven	6202		6181
66	seven	6184		6141
67	seven	6199		6203
68	seven	6145		6188
69	seven	6175		6182
70	seven	6151		6176
71	eight	6171		6181
72	eight	6172		6189
73	eight	6184		6153
74	eight	6207		6192
75	eight	6169		6193
76	eight	6176		6200
77	eight	6172		6187
78	eight	6179		6173
79	eight	6230		6199
80	eight	6192		6184
81	nine	6259		6208
82	nine	6182		6204
83	nine	6225		6201
84	nine	6189		6180
85	nine	6222		6246
86	nine	6194		6236
87	nine	6182		6216
88	nine	6229		6202
89	nine	6186		6172
90	nine	6210		6203
91	ten	6236		6244
92	ten	6202		6226
93	ten	6262		6171
94	ten	6258		6182
95	ten	6241		6234
96	ten	6176		6182
97	ten	6168		6187
98	ten	6220		6208
99	ten	6207		6150
100	ten	6238		6159
101				
102	Mean	6199.58		6171.11
103	SDn-1	30.25		48.02

Table 53. Satistical analyses of the Q values shown in table 52, without removing the sample from its position.

Data File: Standard Conti

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Qcont	15831.24	9	1759.03	2.12	0.036
Error	74737.40	90	830.42		
Total	90568.64	99			

Table 54. Statistical analyses of the Q values shown in table 52, taken by removing and replacing the sample to its original position after every 10 readings.

Data File: Standard Conti

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Qrep/repl	165795.49	9	18421.72	37.79	0.000
Error	43870.30	90	487.45		
Total	209665.79	99			

Table 55. Q-values of an unplated aluminium (HE9) sample bar taken on 5 different days. 100 Q readings were taken on each day by removing and replacing the sample after every 10 readings.

7/unpl

	Day1	Q1	Day2	Q2	Day3	Q3
1	1	5663	1	5772	1	5641
2	1	5749	1	5816	1	5637
3	1	5698	1	5744	1	5702
4	1	5705	1	5643	1	5696
5	1	5645	1	5703	1	5670
6	1	5640	1	5764	1	5784
7	1	5726	1	5708	1	5664
8	1	5685	1	5715	1	5678
9	1	5678	1	5764	1	5730
10	1	5650	1	5716	1	5732
11	2	5656	2	5711	2	5701
12	2	5661	2	5694	2	5705
13	2	5670	2	5718	2	5677
14	2	5659	2	5695	2	5671
15	2	5702	2	5798	2	5748
16	2	5628	2	5793	2	5688
17	2	5693	2	5807	2	5743
18	2	5636	2	5753	2	5684
19	2	5656	2	5734	2	5650
20	2	5658	2	5708	2	5727
21	3	5671	3	5708	3	5674
22	3	5676	3	5631	3	5694
23	3	5685	3	5739	3	5758
24	3	5679	3	5733	3	5739
25	3	5671	3	5693	3	5645
26	3	5779	3	5677	3	5695
27	3	5670	3	5762	3	5655
28	3	5672	3	5718	3	5730
29	3	5656	3	5825	3	5710
30	3	5647	3	5773	3	5725
31	4	5654	4	5757	4	5642
32	4	5658	4	5644	4	5792
33	4	5641	4	5665	4	5799
34	4	5658	4	5750	4	5766
35	4	5626	4	5708	4	5745
36	4	5661	4	5806	4	5760
37	4	5677	4	5707	4	5681
38	4	5690	4	5737	4	5734
39	4	5651	4	5788	4	5724
40	4	5618	4	5759	4	5703
41	5	5668	5	5740	5	5704
42	5	5657	5	5736	5	5781
43	5	5680	5	5736	5	5768
44	5	5661	5	5763	5	5608
45	5	5671	5	5807	5	5745
46	5	5667	5	5758	5	5680
47	5	5654	5	5673	5	5867
48	5	5666	5	5722	5	5722
49	5	5638	5	5782	5	5780
50	5	5714	5	5756	5	5675

	Day1	Q1	Day2	Q2	Day3	Q3
51	6	5642	6	5735	6	5671
52	6	5651	6	5756	6	5745
53	6	5705	6	5680	6	5710
54	6	5720	6	5764	6	5611
55	6	5690	6	5714	6	5662
56	6	5690	6	5702	6	5706
57	6	5670	6	5739	6	5702
58	6	5651	6	5832	6	5595
59	6	5724	6	5755	6	5764
60	6	5679	6	5727	6	5689
61	7	5654	7	5799	7	5644
62	7	5661	7	5797	7	5604
63	7	5651	7	5823	7	5609
64	7	5773	7	5762	7	5714
65	7	5663	7	5810	7	5590
66	7	5682	7	5755	7	5677
67	7	5722	7	5820	7	5687
68	7	5668	7	5773	7	5679
69	7	5708	7	5756	7	5763
70	7	5666	7	5827	7	5756
71	8	5635	8	5820	8	5774
72	8	5714	8	5756	8	5740
73	8	5724	8	5827	8	5671
74	8	5714	8	5765	8	5709
75	8	5681	8	5746	8	5693
76	8	5747	8	5763	8	5763
77	8	5693	8	5711	8	5674
78	8	5761	8	5794	8	5697
79	8	5732	8	5797	8	5607
80	8	5689	8	5750	8	5661
81	9	5733	9	5739	9	5723
82	9	5729	9	5765	9	5787
83	9	5707	9	5763	9	5664
84	9	5719	9	5771	9	5680
85	9	5733	9	5767	9	5663
86	9	5718	9	5749	9	5667
87	9	5729	9	5758	9	5645
88	9	5706	9	5750	9	5666
89	9	5743	9	5755	9	5734
90	9	5763	9	5726	9	5674
91	10	5708	10	5727	10	5664
92	10	5733	10	5744	10	5718
93	10	5734	10	5768	10	5718
94	10	5705	10	5735	10	5667
95	10	5719	10	5729	10	5661
96	10	5741	10	5731	10	5717
97	10	5715	10	5744	10	5634
98	10	5729	10	5738	10	5617
99	10	5741	10	5688	10	5668
100	10	5745	10	5749	10	5703
101						
102	Mean	5688		5748		5699
103	SDn-1	37		42		51
104						

	Day4	Q4	Day5	Q5
1	1	5739	1	5687
2	1	5735	1	5778
3	1	5771	1	5781
4	1	5750	1	5712
5	1	5809	1	5738
6	1	5740	1	5809
7	1	5741	1	5748
8	1	5769	1	5708
9	1	5739	1	5834
10	1	5746	1	5792
11	2	5726	2	5674
12	2	5705	2	5726
13	2	5768	2	5733
14	2	5738	2	5756
15	2	5751	2	5778
16	2	5783	2	5791
17	2	5793	2	5706
18	2	5713	2	5737
19	2	5734	2	5734
20	2	5764	2	5726
21	3	5802	3	5764
22	3	5759	3	5764
23	3	5756	3	5722
24	3	5760	3	5737
25	3	5745	3	5755
26	3	5778	3	5792
27	3	5779	3	5788
28	3	5757	3	5737
29	3	5770	3	5714
30	3	5750	3	5777
31	4	5695	4	5775
32	4	5753	4	5754
33	4	5688	4	5746
34	4	5755	4	5724
35	4	5761	4	5772
36	4	5728	4	5799
37	4	5740	4	5755
38	4	5750	4	5773
39	4	5736	4	5743
40	4	5751	4	5796
41	5	5696	5	5758
42	5	5721	5	5751
43	5	5696	5	5707
44	5	5722	5	5731
45	5	5756	5	5750
46	5	5734	5	5740
47	5	5722	5	5739
48	5	5757	5	5700
49	5	5759	5	5694
50	5	5726	5	5745
51	6	5703	6	5689
52	6	5716	6	5717
53	6	5696	6	5745
54	6	5741	6	5709
55	6	5742	6	5770
56	6	5731	6	5741
57	6	5719	6	5727
58	6	5754	6	5737
59	6	5714	6	5724
60	6	5718	6	5784
61	7	5755	7	5704

	Day4	Q4	Day5	Q5
62	7	5779	7	5814
63	7	5719	7	5679
64	7	5712	7	5767
65	7	5705	7	5710
66	7	5727	7	5724
67	7	5680	7	5738
68	7	5712	7	5760
69	7	5684	7	5765
70	7	5732	7	5770
71	8	5744	8	5793
72	8	5770	8	5729
73	8	5713	8	5765
74	8	5715	8	5737
75	8	5750	8	5722
76	8	5687	8	5786
77	8	5687	8	5821
78	8	5758	8	5772
79	8	5773	8	5757
80	8	5729	8	5787
81	9	5761	9	5748
82	9	5720	9	5752
83	9	5775	9	5741
84	9	5700	9	5759
85	9	5797	9	5730
86	9	5763	9	5773
87	9	5760	9	5715
88	9	5725	9	5713
89	9	5749	9	5767
90	9	5730	9	5763
91	10	5793	10	5785
92	10	5733	10	5778
93	10	5707	10	5764
94	10	5728	10	5689
95	10	5721	10	5546
96	10	5753	10	5752
97	10	5779	10	5756
98	10	5742	10	5731
99	10	5726	10	5811
100	10	5734	10	5598
101				
102		5739		5746
103		27		41
104				

Table 56. Statistical analyses of the Q values shown in table 55 on day 1, taken by removing and replacing the sample to its original position after every 10 readings.

Data File: 7/unpl

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Day1	59717.24	9	6635.25	8.16	0.000
Error	73152.20	90	812.80		
Total	132869.44	99			

Table 57. Statistical analyses of the Q values shown in table 55 on day 2, taken by removing and replacing the sample to its original position after every 10 readings.

Data File: 7/unpl

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Day2	38023.60	9	4224.84	2.72	0.008
Error	139794.40	90	1553.27		
Total	177818.00	99			

Table 58. Statistical analyses of the Q values shown in table 55 on day 3, taken by removing and replacing the sample to its original position after every 10 readings.

Data File: 7/unpl

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Day3	39341.04	9	4371.23	1.79	0.080
Error	219327.40	90	2436.97		
Total	258668.44	99			

Table 59 Shows statistical analyses of the Q values shown in table 55 on day 4, taken by removing and replacing the sample to its original position after every 10 readings.

Data File: 7/unpl

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Day4	18231.21	9	2025.69	3.05	0.003
Error	59786.50	90	664.29		
Total	78017.71	99			

Table 60. Statistical analyses of the Q values shown in table 55 on day 5, taken by removing and replacing the sample to its original position after every 10 readings.

Data File: 7/unpl

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Day5	20696.64	9	2299.63	1.40	0.199
Error	147558.40	90	1639.54		
Total	168255.04	99			

Table 61. Shows Q-values of a different unplated aluminium (HE9) sample bar taken on 5 different days. 100 Q readings were taken on each day by removing and replacing the sample after every 10 readings.

	Day1	Q1	Day2	Q2	Day3	Q3
1	1	5682	1	5563	1	5402
2	1	5614	1	5587	1	5472
3	1	5681	1	5553	1	5422
4	1	5666	1	5564	1	5473
5	1	5672	1	5542	1	5454
6	1	5681	1	5581	1	5416
7	1	5677	1	5597	1	5426
8	1	5670	1	5524	1	5465
9	1	5687	1	5576	1	5427
10	1	5682	1	5562	1	5454
11	2	5639	2	5512	2	5467
12	2	5679	2	5597	2	5481
13	2	5672	2	5527	2	5478
14	2	5632	2	5528	2	5507
15	2	5655	2	5583	2	5487
16	2	5541	2	5534	2	5471
17	2	5619	2	5599	2	5471
18	2	5645	2	5552	2	5413
19	2	5605	2	5560	2	5460
20	2	5633	2	5537	2	5485
21	3	5591	3	5567	3	5449
22	3	5597	3	5562	3	5483
23	3	5527	3	5552	3	5479
24	3	5536	3	5546	3	5444
25	3	5623	3	5592	3	5415
26	3	5618	3	5586	3	5431
27	3	5574	3	5578	3	5426
28	3	5608	3	5567	3	5452
29	3	5627	3	5550	3	5436
30	3	5591	3	5595	3	5485
31	4	5671	4	5567	4	5343
32	4	5549	4	5562	4	5393
33	4	5561	4	5552	4	5416
34	4	5607	4	5546	4	5403
35	4	5559	4	5592	4	5402
36	4	5583	4	5586	4	5431
37	4	5604	4	5578	4	5405
38	4	5563	4	5567	4	5421
39	4	5560	4	5550	4	5390
40	4	5611	4	5595	4	5419
41	5	5634	5	5501	5	5410
42	5	5582	5	5525	5	5448
43	5	5563	5	5534	5	5462
44	5	5607	5	5557	5	5463
45	5	5555	5	5510	5	5416
46	5	5585	5	5541	5	5462
47	5	5628	5	5504	5	5431
48	5	5553	5	5515	5	5460
49	5	5645	5	5546	5	5445
50	5	5606	5	5527	5	5463

	Day1	Q1	Day2	Q2	Day3	Q3
51	6	5677	6	5573	6	5453
52	6	5655	6	5551	6	5493
53	6	5515	6	5494	6	5440
54	6	5601	6	5503	6	5440
55	6	5580	6	5549	6	5396
56	6	5533	6	5538	6	5430
57	6	5629	6	5572	6	5436
58	6	5639	6	5555	6	5447
59	6	5569	6	5531	6	5426
60	6	5574	6	5532	6	5434
61	7	5614	7	5508	7	5407
62	7	5659	7	5546	7	5411
63	7	5602	7	5540	7	5418
64	7	5628	7	5564	7	5420
65	7	5638	7	5569	7	5415
66	7	5609	7	5510	7	5407
67	7	5645	7	5500	7	5438
68	7	5612	7	5502	7	5441
69	7	5599	7	5526	7	5408
70	7	5634	7	5547	7	5424
71	8	5598	8	5555	8	5479
72	8	5580	8	5568	8	5450
73	8	5585	8	5534	8	5431
74	8	5571	8	5492	8	5455
75	8	5609	8	5595	8	5448
76	8	5591	8	5549	8	5442
77	8	5601	8	5575	8	5433
78	8	5614	8	5515	8	5382
79	8	5600	8	5561	8	5405
80	8	5611	8	5594	8	5405
81	9	5533	9	5525	9	5440
82	9	5579	9	5550	9	5368
83	9	5597	9	5482	9	5434
84	9	5638	9	5497	9	5400
85	9	5587	9	5488	9	5388
86	9	5595	9	5489	9	5420
87	9	5583	9	5491	9	5427
88	9	5576	9	5493	9	5371
89	9	5570	9	5493	9	5408
90	9	5571	9	5506	9	5434
91	10	5570	10	5514	10	5437
92	10	5589	10	5558	10	5444
93	10	5609	10	5531	10	5408
94	10	5609	10	5500	10	5384
95	10	5606	10	5544	10	5386
96	10	5559	10	5542	10	5442
97	10	5562	10	5536	10	5437
98	10	5602	10	5523	10	5393
99	10	5598	10	5516	10	5430
100	10	5600	10	5575	10	5466
101						
102	Mean	5606		5544		5433
103	SDn-1	40		31		31

	Day4	Q4	Day5	Q5
1	1	5550	1	5476
2	1	5573	1	5482
3	1	5546	1	5500
4	1	5594	1	5484
5	1	5507	1	5500
6	1	5556	1	5442
7	1	5557	1	5465
8	1	5508	1	5487
9	1	5602	1	5505
10	1	5573	1	5482
11	2	5574	2	5521
12	2	5566	2	5488
13	2	5549	2	5480
14	2	5536	2	5481
15	2	5540	2	5483
16	2	5541	2	5466
17	2	5534	2	5507
18	2	5594	2	5542
19	2	5604	2	5526
20	2	5527	2	5512
21	3	5559	3	5490
22	3	5552	3	5481
23	3	5525	3	5453
24	3	5522	3	5514
25	3	5571	3	5488
26	3	5548	3	5487
27	3	5553	3	5496
28	3	5555	3	5537
29	3	5551	3	5489
30	3	5515	3	5471
31	4	5560	4	5500
32	4	5517	4	5515
33	4	5528	4	5534
34	4	5588	4	5504
35	4	5537	4	5493
36	4	5543	4	5518
37	4	5574	4	5504
38	4	5581	4	5464
39	4	5523	4	5511
40	4	5548	4	5490
41	5	5543	5	5507
42	5	5566	5	5459
43	5	5557	5	5509
44	5	5529	5	5489
45	5	5545	5	5530
46	5	5557	5	5511
47	5	5547	5	5534
48	5	5586	5	5481
49	5	5537	5	5540
50	5	5512	5	5517

	Day4	Q4	Day5	Q5
51	6	5557	6	5504
52	6	5556	6	5518
53	6	5524	6	5489
54	6	5556	6	5489
55	6	5544	6	5482
56	6	5561	6	5549
57	6	5574	6	5482
58	6	5521	6	5494
59	6	5557	6	5518
60	6	5527	6	5506
61	7	5553	7	5527
62	7	5548	7	5505
63	7	5568	7	5480
64	7	5538	7	5495
65	7	5521	7	5538
66	7	5545	7	5529
67	7	5568	7	5489
68	7	5509	7	5485
69	7	5581	7	5501
70	7	5533	7	5488
71	8	5559	8	5503
72	8	5527	8	5494
73	8	5577	8	5492
74	8	5535	8	5501
75	8	5554	8	5540
76	8	5515	8	5504
77	8	5532	8	5513
78	8	5586	8	5538
79	8	5527	8	5518
80	8	5562	8	5507
81	9	5579	9	5506
82	9	5503	9	5529
83	9	5523	9	5509
84	9	5540	9	5499
85	9	5604	9	5502
86	9	5600	9	5475
87	9	5513	9	5503
88	9	5514	9	5494
89	9	5549	9	5468
90	9	5569	9	5481
91	10	5508	10	5503
92	10	5498	10	5454
93	10	5490	10	5500
94	10	5533	10	5513
95	10	5474	10	5526
96	10	5489	10	5493
97	10	5485	10	5497
98	10	5470	10	5500
99	10	5516	10	5498
100	10	5489	10	5512
101				
102				
103				
		5544		5500
		29		21

Table 62. Statistical analyses of the Q values shown in table 61 on day 1, taken by removing and replacing the sample to its original position after every 10 readings.

Data File: 71/5days

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Day1	69573.45	9	7730.38	7.64	0.000
Error	91093.30	90	1012.15		
Total	160666.75	99			

Table 63. Statistical analyses of the Q values shown in table 61 on day 2, taken by removing and replacing the sample to its original position after every 10 readings.

Data File: 71/5days

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Day2	43339.69	9	4815.52	8.37	0.000
Error	51784.90	90	575.39		
Total	95124.59	99			

Table 64. Shows statistical analyses of the Q values shown in table 61 on day 3, taken by removing and replacing the sample to its original position after every 10 readings.

Data File: 71/5days

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Day3	39082.25	9	4342.47	7.33	0.000
Error	53330.50	90	592.56		
Total	92412.75	99			

Table 65. Shows statistical analyses of the Q values shown in table 61 on day 4, taken by removing and replacing the sample to its original position after every 10 readings.

Data File: 71/5days

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Day4	28074.09	9	3119.34	5.04	0.000
Error	55750.50	90	619.45		
Total	83824.59	99			

Table 66. Shows statistical analyses of the Q values shown in table 61 on day 5, taken by removing and replacing the sample to its original position after every 10 readings.

Data File: 71/5days

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Day5	6279.85	9	697.76	1.63	0.118
Error	38480.90	90	427.57		
Total	44760.75	99			

Table 67 Shows Q-values of a half an hour plated aluminium (HE9) sample bar taken on 5 different days. 100 Q readings were taken on each day by removing and replacing the sample after every 10 readings.

	Day 1	Q 1	Day 2	Q 2	Day 3	Q 3
1	1	4925	1	4954	1	4798
2	1	4956	1	4932	1	4873
3	1	4964	1	4912	1	4884
4	1	4978	1	4947	1	4765
5	1	4925	1	4924	1	4800
6	1	4933	1	4944	1	4809
7	1	4962	1	4951	1	4825
8	1	4927	1	4950	1	4849
9	1	4972	1	4926	1	4799
10	1	4936	1	4988	1	4817
11	2	4926	2	4947	2	4817
12	2	4896	2	4941	2	4855
13	2	4917	2	4940	2	4799
14	2	4914	2	4933	2	4822
15	2	4906	2	4917	2	4854
16	2	4925	2	4923	2	4860
17	2	4898	2	4903	2	4839
18	2	4912	2	4916	2	4872
19	2	4914	2	4920	2	4854
20	2	4930	2	4913	2	4861
21	3	4916	3	4908	3	4793
22	3	4943	3	4960	3	4852
23	3	4906	3	4944	3	4861
24	3	4952	3	4910	3	4832
25	3	4916	3	4923	3	4802
26	3	4880	3	4949	3	4837
27	3	4935	3	4927	3	4820
28	3	4889	3	4915	3	4817
29	3	4935	3	4943	3	4839
30	3	4907	3	4933	3	4822
31	4	4918	4	4919	4	4865
32	4	4936	4	4941	4	4802
33	4	4918	4	4907	4	4799
34	4	4920	4	4930	4	4826
35	4	4933	4	4927	4	4806
36	4	4925	4	4910	4	4826
37	4	4929	4	4910	4	4826
38	4	4921	4	4925	4	4802
39	4	4939	4	4931	4	4818
40	4	4913	4	4918	4	4842
41	5	4906	5	4943	5	4760
42	5	4902	5	4961	5	4839
43	5	4886	5	4930	5	4818
44	5	4913	5	4896	5	4847
45	5	4915	5	4930	5	4820
46	5	4940	5	4906	5	4849
47	5	4891	5	4941	5	4842
48	5	4923	5	4939	5	4823
49	5	4913	5	4927	5	4870
50	5	4904	5	4875	5	4829

	Day 1	Q1	Day 2	Q2	Day 3	Q3
51	6	4901	6	4938	6	4729
52	6	4909	6	4923	6	4800
53	6	4936	6	4945	6	4823
54	6	4861	6	4933	6	4816
55	6	4877	6	4941	6	4837
56	6	4907	6	4938	6	4808
57	6	4920	6	4921	6	4804
58	6	4885	6	4920	6	4850
59	6	4918	6	4919	6	4804
60	6	4895	6	4967	6	4812
61	7	4921	7	4940	7	4821
62	7	4914	7	4958	7	4855
63	7	4939	7	4941	7	4807
64	7	4934	7	4925	7	4819
65	7	4910	7	4969	7	4823
66	7	4919	7	4925	7	4781
67	7	4967	7	4870	7	4834
68	7	4909	7	4957	7	4841
69	7	4924	7	4948	7	4819
70	7	4931	7	4950	7	4829
71	8	4896	8	4896	8	4716
72	8	4932	8	4904	8	4844
73	8	4908	8	4912	8	4825
74	8	4883	8	4890	8	4848
75	8	4895	8	4894	8	4835
76	8	4863	8	4929	8	4841
77	8	4928	8	4940	8	4816
78	8	4897	8	4898	8	4844
79	8	4897	8	4919	8	4804
80	8	4918	8	4900	8	4876
81	9	4910	9	4939	9	4800
82	9	4876	9	4937	9	4798
83	9	4878	9	4904	9	4779
84	9	4921	9	4901	9	4824
85	9	4920	9	4917	9	4813
86	9	4927	9	4911	9	4810
87	9	4941	9	4946	9	4810
88	9	4927	9	4956	9	4819
89	9	4911	9	4921	9	4819
90	9	4915	9	4959	9	4833
91	10	4951	10	4928	10	4843
92	10	4889	10	4900	10	4836
93	10	4891	10	4927	10	4834
94	10	4871	10	4937	10	4851
95	10	4899	10	4921	10	4833
96	10	4868	10	4940	10	4854
97	10	4876	10	4957	10	4863
98	10	4872	10	4947	10	4800
99	10	4880	10	4938	10	4822
100	10	4867	10	4949	10	4846
101						
102	Mean	4914		4929		4823
103	SDn-1	24		21		32

	Day 4	Q4	Day 5	Q5
1	1	4772	1	4876
2	1	4929	1	4889
3	1	4942	1	4912
4	1	4948	1	4864
5	1	4945	1	4812
6	1	4975	1	4883
7	1	4919	1	4942
8	1	4948	1	4896
9	1	4958	1	4905
10	1	4908	1	4932
11	2	4876	2	4880
12	2	4917	2	4867
13	2	4885	2	4829
14	2	4895	2	4884
15	2	4885	2	4861
16	2	4885	2	4838
17	2	4896	2	4908
18	2	4893	2	4866
19	2	4894	2	4904
20	2	4900	2	4874
21	3	4862	3	4875
22	3	4898	3	4846
23	3	4881	3	4914
24	3	4884	3	4869
25	3	4883	3	4842
26	3	4878	3	4914
27	3	4877	3	4928
28	3	4873	3	4883
29	3	4873	3	4866
30	3	4872	3	4859
31	4	4860	4	4884
32	4	4858	4	4901
33	4	4852	4	4916
34	4	4918	4	4897
35	4	4892	4	4921
36	4	4862	4	4910
37	4	4872	4	4909
38	4	4876	4	4862
39	4	4868	4	4861
40	4	4902	4	4905
41	5	4856	5	4892
42	5	4880	5	4846
43	5	4864	5	4920
44	5	4814	5	4907
45	5	4843	5	4842
46	5	4834	5	4850
47	5	4834	5	4881
48	5	4843	5	4882
49	5	4839	5	4916
50	5	4854	5	4884
51	6	4869	6	4863
52	6	4874	6	4893
53	6	4841	6	4890
54	6	4848	6	4881
55	6	4884	6	4911
56	6	4874	6	4908
57	6	4861	6	4873
58	6	4906	6	4884
59	6	4901	6	4866
60	6	4873	6	4893
61	7	4892	7	4881

	Day 4	Q4	Day 5	Q5
62	7	4860	7	4919
63	7	4874	7	4882
64	7	4865	7	4854
65	7	4900	7	4875
66	7	4898	7	4877
67	7	4878	7	4851
68	7	4890	7	4910
69	7	4912	7	4901
70	7	4860	7	4893
71	8	4865	8	4825
72	8	4892	8	4899
73	8	4937	8	4854
74	8	4906	8	4896
75	8	4891	8	4878
76	8	4878	8	4886
77	8	4906	8	4892
78	8	4877	8	4872
79	8	4935	8	4886
80	8	4943	8	4901
81	9	4870	9	4929
82	9	4910	9	4840
83	9	4890	9	4854
84	9	4904	9	4851
85	9	4864	9	4902
86	9	4887	9	4882
87	9	4853	9	4870
88	9	4874	9	4848
89	9	4879	9	4867
90	9	4851	9	4864
91	10	4852	10	4865
92	10	4857	10	4877
93	10	4880	10	4890
94	10	4869	10	4882
95	10	4889	10	4889
96	10	4896	10	4900
97	10	4897	10	4903
98	10	4878	10	4878
99	10	4895	10	4881
100	10	4868	10	4863
101				
102		4883		4882
103		31		25

Table 68. Shows statistical analyses of the Q values shown in table 67 on day 1, taken by removing and replacing the sample to its original position after every 10 readings.

Data File: 50 1/2hr plt

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Day1	25551.04	9	2839.00	7.65	0.000
Error	33387.20	90	370.97		
Total	58938.24	99			

Table 69 Shows statistical analyses of the Q values shown in table 23 on day 2, taken by removing and replacing the sample to its original position after every 10 readings.

Data File: 50 1/2hr plt

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Day2	8569.84	9	952.20	2.57	0.011
Error	33332.00	90	370.36		
Total	41901.84	99			

Table 70 Shows statistical analyses of the Q values shown in table 67 on day 3, taken by removing and replacing the sample to its original position after every 10 readings.

Data File: 50 1/2hr plt

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Day3	15604.24	9	1733.80	1.82	0.075
Error	85565.20	90	950.72		
Total	101169.44	99			

Table 71. Shows statistical analyses of the Q values shown in table 67 on day 4, taken by removing and replacing the sample to its original position after every 10 readings.

Data File: 50 1/2hr plt

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Day4	37851.85	9	4205.76	6.56	0.000
Error	57702.90	90	641.14		
Total	95554.75	99			

Table 72 Shows statistical analyses of the Q values shown in table 67 on day 5, taken by removing and replacing the sample to its original position after every 10 readings.

Data File: 50 1/2hr plt

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between Day5	5820.41	9	646.71	1.02	0.434
Error	57340.90	90	637.12		
Total	63161.31	99			

Notes :

Q_r -	indicates Q readings taken were of as received condition.
Q_{ace}	indicates Q readings were taken after cleaning the sample with acetone.
Q_{Nitric}	indicates Q readings were taken after nitric acid dip for 1 minute.
$Q_{b\ dip}$	indicates Q readings were taken after 2 minute dip in the Bondal solution maintained at room temperature.
$Q_{15\ min\ pltg}$	indicates Q readings were taken after 15 minutes of plating.

CHAPTER 9

DISCUSSION OF RESULTS

9.1 Modal Analysis

Experimental Modal Analysis or Modal Testing is a branch of vibration engineering which was developed in the 1970's. This involves incorporating considerable advances made in digital signal processing and in finite element methods, and provide the means of combining the products of both into a unified tool for studying real structural vibration problems. Using this method it is possible to measure accurately the mode shapes and frequencies of practical structures and display these results in a variety of ways.

Therefore it was anticipated that the modal analysis technique having been fortified with an expensive IBM computer along with a specially prepared software package would be able to detect the differences between good and poor adhesion levels in the plated samples. However, the results obtained were very disappointing. The operation of the system was difficult and time consuming to operate. The software package "SPIDERS" was not properly developed at that stage and very often it failed to calculate the damping values from the data retrieved using the B&K analyser.

Although the position of the accelerometer should not change the damping values, Tables 8-12 indicate a variation due to changing the position of the accelerometer (transducer). The results obtained using the modal analysis technique shown in the above Tables also indicate a fair amount of variation or scatter, even at any given position of the accelerometer. Statistical analyses showed that these results were very highly significant, the variation shown by the results cannot be accepted as occurring by chance alone. Therefore, it was decided to carry on with the Q-meter development using Muaddi's (1982) thesis, as a basis.

One of the problems encountered in this vibrational analysis was the decision about which method of suspension of the sample to use. A sample can be suspended by drilling a hole on one end sample and suspending using elastic bands. It is argued that an elastic band is a very highly damped material compared with aluminium or steel, and therefore would not interfere with the mode of vibration of the suspended material. Another error which can be introduced using this method is by hitting the sample with a regulated hammer to initiate vibration, the hammer used for such purposes was many times bigger than the sample used in this experiment. However, it is claimed that the hammer is programmed to offset any overloading or underloading automatically.

Although vibration experts seem to ignore these variables on small components ie. method of suspension and the use of hammer as not being significant, this development work on Q-meter has cast doubts about the reliability of the results which can have such a big scatter and statistically become unacceptable. On large size components the above variables may have a lesser effect and may be ignored depending on the accuracy of the results demanded by the work.

In this work the precision and repeatability of the results were of primary importance in order to establish any differences due to poor and good adhesion levels in the plated samples. The modal analysis technique could not provide either. It has been established the method of suspension is very important and can be critical. The use of a hammer can be better suited for any vibration analysis instead of an electromagnetic transducer, if the specimen size factor is taken into consideration. The use of a hammer minimises the eddy current effect and also it does not matter if the material is non-magnetic. It has also been established that an improved suspension method is equally important.

9.2 The Modified Q-Meter

As has been discussed earlier [chapter 6] the Q meter developed by Muaddi was based on the equation

$$A_n = A_o \exp(-\pi n/Q)$$

Rearranging the above equation gives

$$A_o / A_n = \exp(\pi n / Q)$$

$\pi n / Q = \ln A_o / A_n$, but $\ln 23.14 = 3.14 = \pi$.

Therefore $\pi n / Q = \pi$, then $n = Q$.

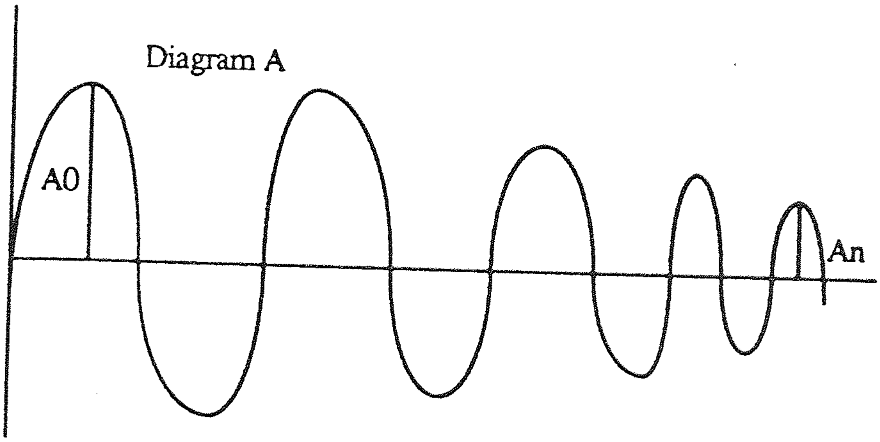


Fig.63. Shows the principle of amplitude measurements.

The constant terms A_o / A_n and π can be removed to give $Q = n$, by ensuring that ratio $A_o / A_n = \ln 23.14$. In order to construct a circuit this ratio must be satisfied for all values of the Q factor. Otherwise it would not be possible to obtain an accurate account of the specimen's Q factor.

As there is no means of recording A_o (the initial amplitude) for the purpose of ensuring the ratio term is satisfied while the Q factor is being measured, Muaddi set up two reference levels (high and low) to achieve this ratio. Providing the signal (damping signal) is sufficient to satisfy the above ratio criterion, the Q factor measured is valid. If the damping signal level fails to satisfy this criterion, the circuit fails to provide a count for Q factor recording. This is illustrated in figure below.

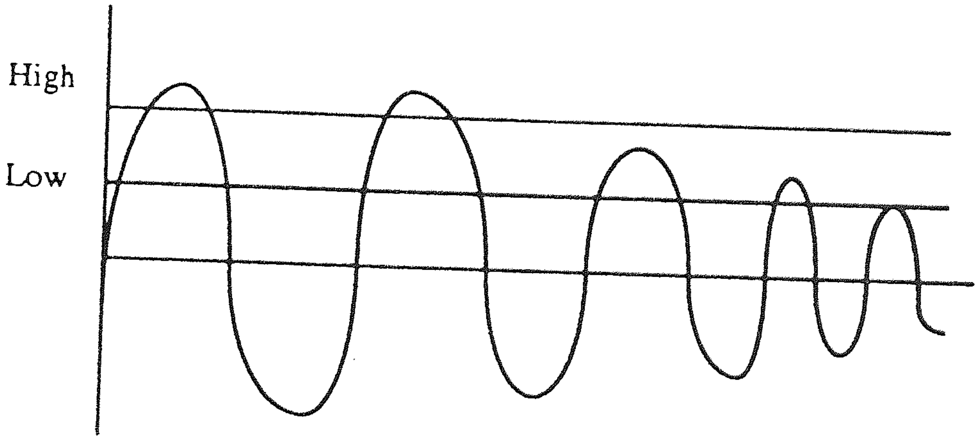


Fig.64. Shows the operation of the reference levels.

In his thesis Muaddi refers to three comparators.The first comparator acts as a zero crossing, while the second and third comparators have high and low voltage respectively. These comparators produce an output only when the amplitude of the input voltage exceeds predetermined reference levels. However, the circuit constructed as per Muaddi's thesis failed to function according to the details given in his thesis as it was not possible to satisfy $Q = n$, in the equation

$A_n = A_o \exp(-\pi n / Q)$ as has been described earlier.

It was not possible to keep the said ratio constant. After constructing the circuit as per Muaddi's thesis, it was discovered that several input parameters as required by the circuit were not highlighted. These were found to be very important parameters relating to the timing of the overall circuit to function as a Q meter. As a result of some experience gained with Muaddi's circuit, a modified version was constructed as shown in Figure 21. As has been detailed in the experimental section [6.5.4.c] the amplified signal is fed to digital Q-meter (Fig.22). The digital Q-meter (Fig.21) has three integrated circuits called monostables, IC1, IC2 and IC3. Figure 22 shows schematically the physical arrangement for electronically vibrating the specimen.

In the modified Q-meter, polystyrene blocks were used for suspension of the test specimens but the major problem encountered was that of vibrating non-magnetic aluminium samples using an electronic hammer. Figure 65 (block diagram) shows the overall operation of the Q-meter. The operation of this meter is further detailed in Fig.66. The pick up signal from the microphone is fed to the amplifiers for amplification.The basic function of the three integrated circuits (monostables) IC1, IC2 and IC3 is to monitor the free oscillation as produced by the material under test producing output pulses until the ratio terms $Ao/An = \ln 23.14$ is no longer satisfied. The ratio of the initial to the final amplitude must satisfy the above criterion for the results to be true ie. $n = Q$. When this is not satisfied the meter stops counting because the amplitude level has fallen below the predetermined lower amplitude level and hence no output is produced.

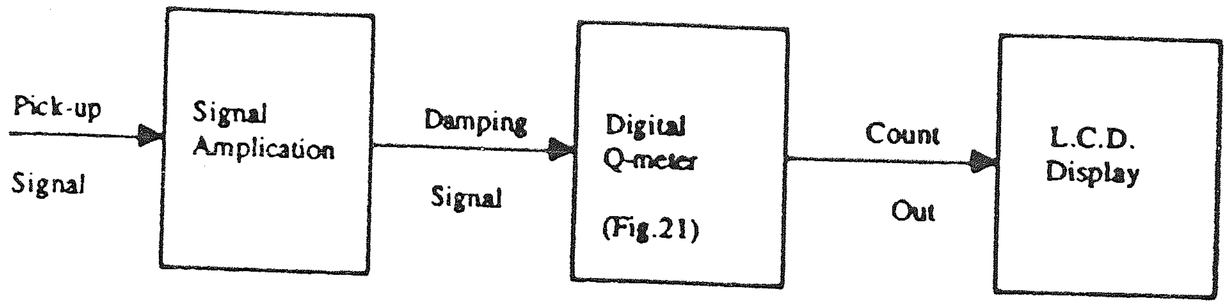


Fig.65. Block diagram showing the overall operation of the modified Q-meter.

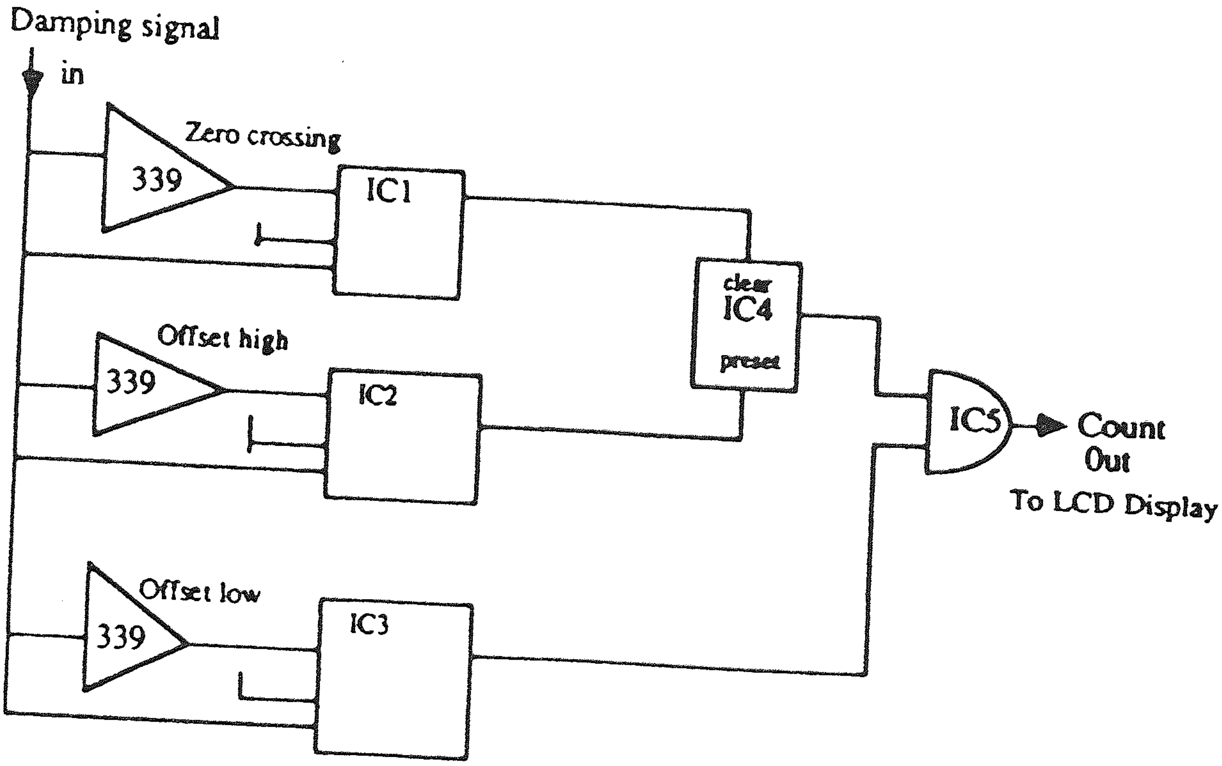


Fig.66. Circuit diagram showing further details of the modified Q-meter.

In order to obtain the above results the three integrated circuits need to be coordinating as a team. The integrated circuit, IC1 is responsible for triggering off the cycle of events, that it has detected the beginning of a cycle, then as the oscillation increases in amplitude it passes over the upper set amplitude level, the function of the IC2 is to referee the event, eventually the amplitude level reaches the lower set amplitude IC3 then witnesses the end of the event, when this has occurred one complete cycle is recorded. This process of counting continues until the vibrational amplitude levels no longer passes through the lower amplitude level ie. is too small for the instrument to count any more complete cycles and then the number of complete cycles counted is reported to the LCD decoder and is displayed as Q on the LCD display (Fig.65). The timing of these integrated circuits IC1, IC2 and IC3 were not clarified in Muaddi's thesis and was the reason for it not working.

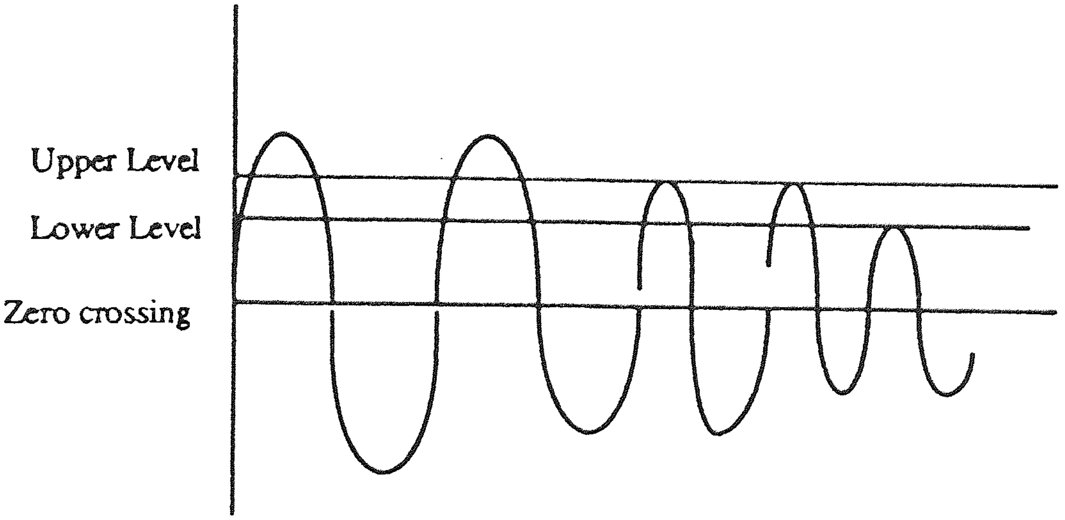


Fig.67. Operation of amplitude levels.

With the modified circuit it was possible to vibrate a magnetic material at its fundamental modes but apparently some inconsistency was observed with the Q values obtained when resonating uncoated aluminium bars, which are paramagnetic, ie. it was found difficult to resonate the specimen sufficiently to obtain consistent/repeatable Q readings. It can be observed from the results obtained (Table 44) that the Q readings were varying quite significantly when polystyrene blocks were used although the nodal points could be easily located by the use of an oscilloscope. Statistical analysis of the Q values obtained from this new modified Q meter indicate that the results cannot be accepted as being consistent or repeatable.

The circuit was found to be very sensitive to external noise and the Q values obtained could easily be altered by someone walking or talking in the room. The noise level was also very high and ear guards needed to be worn. Therefore, this instrument cannot be used in a normal industrial environment ie. has to be operated in a noise free environment.

9.3 The New Q-Meter Based on Impulse Technique

A detailed statistical analysis has been carried out on the results obtained using this instrument. Without the analysis of variance the figures appeared to be fairly consistent. However, the statistical analysis shows that the results obtained using this instrument were not consistent, although not highly significant (a difference which could not have easily occurred by chance is said to be significant) when readings were taken without moving the test piece from the test rig. However, when Q readings were taken by removing and replacing the test piece on to the test rig the analysis of variation shows some of the results were very highly significant ie. the difference could not have occurred by chance alone, and the variations in the results were thought to be due to inconsistency of the instrument. Although the nodal points were calculated and marked on the test pieces and the method of suspension was improved by using fine nylon threads instead of the polystyrene blocks, it is evident that even then it was not possible to obtain repeatable Q readings. Each time the sample was removed and replaced some errors were introduced to the system and this could also have contributed towards the inconsistency of the results obtained using this new Q-meter.

This new instrument was found to be incredibly sensitive, placing a tiny piece of paper on the vibrating sample would show a considerable drop in the Q-values of the test sample indicating a damping effect of the tiny piece of paper on the alloy surface.

It was observed that the Q-values of any given sample could be increased or decreased by altering the position of the microphone. Therefore it was then decided to use an aluminium alloy bar as a standard test piece. A reading was taken using this bar before Q-values were taken of any test samples, and this figure was maintained at one particular Q-value by adjusting the position of the microphone if required.

Although the instrument was found to be inconsistent statistically, it did show significant and consistent differences between plated and as received (untreated) samples, and does not require a statistical analysis to differentiate the effect of plating to be observed. The Q-values dropped dramatically as plating thicknesses were increased and the resonance frequency also dropped with plating thicknesses but this was not as marked as changes in Q.

The Q and resonant frequencies of as received S1C alloy samples were very low compared to those of the HE9 samples and this instrument has very consistently differentiated the differences between the two types of alloys using Q and resonant frequencies as variable criteria. The Q and resonant frequency of any S1C sample were significantly different from that of the HE9's. Another type of aluminium alloy used in this work was also specified as S1C by the supplier (procured from a different source), results obtained using these alloy bars are shown in Table 25. This alloy had the lowest Q values exhibited by any sample. Although no other aluminium alloys were used in this work it is expected that this instrument could be used to distinguish between different alloy types (and given alloys in different metallurgical condition) when compared with standards. Also after plating, these three alloys exhibited different damping levels. After 5 hours of plating HE9 samples showed around 90% damping, which was followed by S1C series 1, showing around 76% damping and the S1C series 2 samples showed only about 58% drop in the Q values, given the same pretreatment sequence (double Bondal, 50% nitric acid dip sequence).

The majority of the work was carried out using HE9 extruded alloy bars as they were available relatively easily. The pretreatments of these samples produced consistent differences after each stage in the sequence. Q in all the samples dropped after electrolytic cleaning but the nitric acid treatment resulted in an increase. After the Bondal dip treatment the Q in all the samples fell below their as received values indicating a damping effect due to the coating, although a very thin immersion coating (approximately 0.25 μm thick) had been applied the instrument was able to detect the presence of a coating on the surface (Fig.30). After nickel plating the instrument also showed an increase in the damping ie. Q decreased dramatically as the coating thicknesses were increased.

9.4 Statistical Analysis of Q readings

Statistical analysis carried out on untreated alloy bars showed a large variation in Q values with time which could not have occurred due to chance alone. Therefore a lot of doubts were cast regarding the accuracy of the instrument in the earlier stages of the instrument development. Also when the instrument failed to detect changes due to good and poor adhesion after plating it was thought that this instrument would be of no use for any application, so further experimental work was carried out on some sample bars after lacquering, anodising and heat-treatment. The results obtained indicate that the instrument is extremely sensitive or super sensitive in detecting surface reaction. Further experimental work carried out using aluminium samples indicates that these fluctuations were not instrumentational errors. Some of the earlier results can now be explained which were thought to be due to instrumentational error and has been discussed in section [9.6].

9.5 Peel Adhesion Test and Surface Analysis

Adhesion refers to the bond, chemical and/or physical, between two adjacent materials, and is related to the force required to effect their complete separation. Cohesive forces are involved when the separation occurs within one of the materials rather than the two.

The adhesion between two different materials is determined by the extent of chemical bonding (which involves the same molecular forces responsible for cohesion); and mechanical bonding due to interlocking, keying action. Because of differences in the mechanical strengths of the alloys, it would be expected that differing percentages of 'perfect ' adhesion between substrate and and coating would be required to obtain the same overall measured level of adhesion. Where the bond between the electrodeposit and substrate is greater than the cohesive forces between atoms within the substrate, that the adhesion value would only depend on the mechanical properties of the substrate provided that the coating can withstand peeling force involved. This corresponds to the 'ultimate ' adhesion attainable.

In this work it has been possible to produce various levels of adhesion. Peel results show that best adhesion was obtained with S1C alloy with double Bondal/HF HNO_3 pretreatment. Single Bondal treatment produced relatively poor adhesion on the same alloy. It has also been possible to produce a very low level of adhesion using HE9 alloy bars which is a difficult to plate alloy due to the presence of silicon as an alloying element. With double and single Bondal treatments it was possible to vary the adhesion levels in the HE9 alloys. The acid etch used was 50% nitric acid and not

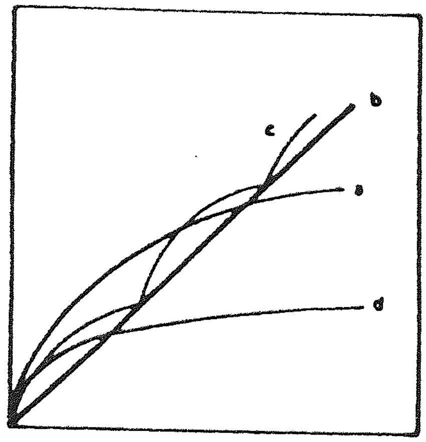
$5\%HF50\%HNO_3$ mixture on the recommendations of Golby and Dennis (1981) who found that hydrofluoric acid treatment reduced the adhesion strength in the case of HE9 alloys although the same pretreatment improved adhesion levels in the S1C alloys.

In this study it was essential to produce various levels of adhesion between the aluminium substrate and the electrodeposited nickel in order to attempt to prove that the Q-meter developed could detect the changes at the interface by producing correspondingly higher damping values due to poor bonding. However, the instrument was found to be insensitive in detecting the changes at the interface ie. between a good and poor bond. It was thought that the weight and moduli of the electrodeposited nickel in the thicker deposits was reducing the sensitivity by causing a much greater change in Q than the poor adhesion effect. Therefore thinner deposits were produced with double and single Bondal treatments in the case of both the HE9 and S1C alloys [7.2]. Even then the Q-meter did not indicate any consistent and significant differences between a good and poor bond although it has been established that it was possible to produce good and poor adhesion levels in this work with thicker coatings.

SEM and XPS examinations revealed that failure surface characteristics are influenced by adhesion level, alloy type and pretreatment. The amount of aluminium attached to the peeled foil increased with bond strength [7.5]. In this work it has been possible to produce very low levels of adhesion, in such cases once a tab was lifted it was then possible to continue peeling by hand without any difficulty. Visual examination of such peeled surfaces showed a dark/grey appearance which looked more like zincated/Bondal coated surface and no white areas showing aluminium was observed. XPS analysis also showed in such cases that there was no aluminium present on either the substrate or on the foil surfaces.

9.6 Fluctuation of the Q-values with time

When the surface of a reactive metal is exposed to an oxidising gas such as dry air or oxygen a thin film of oxide forms over the exposed surface and this slows down the rate of further oxidation by separating the metal from the gas. The rate of oxidation is usually measured by measuring a sample periodically to determine the amount of oxygen taken up. The average film thickness x can then be calculated from known properties of the oxidation product. The oxidation usually develops with time according to one of the curves which are described as logarithmic ($x \propto \ln t$), parabolic ($x \propto t^{1/2}$) or as break-away (repeated rapid parabolic steps giving an overall linear behaviour).



The growth 'laws' of oxidation. (a) Parabolic, (b) rectilinear, (c) quasi-rectilinear and (d) logarithmic.

Fig.68. Shapes of oxidation Curves.

Breakaway effects are observed when something happens to the film, such as cracking or flaking off, which reduces its thickness. Repeated break-away on a fine scale can prevent the protective part of a film from increasing beyond a certain thickness and so give linear oxidation. The plasticity of oxide is important especially at high temperatures because it helps prevent cracking and break-away thus improving the protectiveness of the film.

However, in this experimental work it was not possible to measure such small weight changes with time. The hard anodised aluminium sample did not show the continuous fluctuation in Q-values with time, in case of the sample anodised and sealed the effect was remarkably low. The sample which was coated with lacquer did not show the fluctuation either. This fluctuation was present on untreated aluminium alloy bars and also after polishing operations. Nickel plated samples also exhibited these fluctuation patterns but the gradients were progressively reduced as plating thicknesses increased.

After nitric acid treatment it is known that a passive film is produced on aluminium surfaces and loss or gain associated with this film formation can not be measured. This instrument has shown a rise in Q after nitric acid treatments and after Bondal treatments (which is known to deposit a very thin coating (0.25 μm)) the instrument then recorded a decline in Q (Fig. 30), mainly due to the weight of the coating after the zincate treatment. The fluctuation patterns observed in the as received condition and after various pretreatments indicate that at the initial stages Q goes up due to formation of films and decreases with small weight losses encountered during these stages. It must be mentioned here that after plating, anodising and lacquering Q went down dramatically with increasing thickness. At this stage it can not be explained why Q goes down after both weight losses and gains. However, it can be concluded from these observations in the pretreatment stages that this instrument is extremely sensitive and Q increases with film formation and decreases as weight increased or decreased.

After all the pretreatments the fluctuation pattern was almost similar ie. non linear and constantly going up and then down with time or vice versa, and this was not due to instrumentational error as these fluctuation patterns were not present after anodising. Anodising has reduced the surface activity of the aluminium alloy bars substantially.

In the anodising process the thin invisible film of aluminium oxide which forms naturally on the surface and provides some degree of corrosion protection for the underlying aluminium is increased to a considerably greater thickness. Anodic oxidation is extensively used for the production of protective and decorative films on aluminium. Figure 67 shows the formation of anodic film on the surface of aluminium. In this process the anodised layer is built up from the base of the film. The porous cell structure as illustrated is formed by the solvent action of the acids used in anodising. The thickness of the barrier layer and of the cell walls are proportional to the voltage applied. The size of the pore or cell is dependent on three main inter-related factors :

i) solution concentration

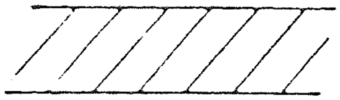
ii) solution temperature

iii) applied current density.

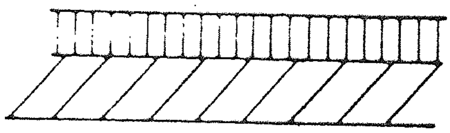
By varying these factors, anodised films are produced for different purposes. For example, the use of a more concentrated sulphuric acid solution and a higher operating temperature gives a more open structure suitable for dyeing, decorative aluminium. On the other hand using lower acid concentration and a lower operating temperature results in the formation of harder films with small pore size which would be suitable for engineering applications.

Sealing involves treating the the anodised articles in boiling water, special salt solutions or in low pressure steam. Under these conditions, hydration of the amorphous oxide is believed to occur becoming the crystalline oxide, $Al_2O_3.H_2O$. This transformation is accompanied by a volume increase which swells the cell walls and effectively closes the pores.

Aluminium surface before anodising.



Anodised surface showing oxide layers.



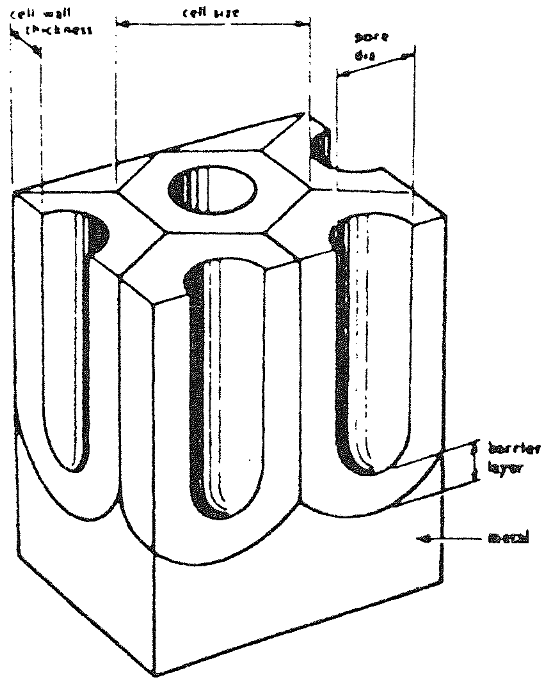


Fig. 69. Microsection of an anodic film showing porous cell structure.

Once the active surfaces were enveloped by lacquering or by the formation of conversion coatings by anodising the instrument reading became very steady and also the variation was reduced dramatically with very low standard deviation and this was not observed on the same samples before anodising and lacquering.

It has been observed that the instrument shows an increase after film formations as after nitric acid etch and also shows a decline with a very small increase/decrease in weight but the drop is dramatic when plated for only 3 minutes with nickel. Therefore this indicates that the instrument is extremely sensitive to surface changes.

The time of wetness of the metal surface due to atmospheric condition determines the duration of the electrochemical process. In case of adsorbed electrolyte layers the water molecules are bound to the metal surface by Van der Waals' forces. It has been estimated that at 55% relative humidity the film on polished iron is just about 15 molecular layers thick. This increases to 90 molecular layers at just below 100% r.h. Such films are capable of supporting electrochemical corrosion processes and these have been studied (Shrier, 1976). The moisture layers become thinner as the humidity is reduced to below 100% then polarisation of the cathodic and particularly the anodic process rapidly becomes enormous and corrosion virtually ceases below about 60% r.h.

However, the relative humidity in this work was found to vary between 65% to 81% during day time measurements. Therefore it can be concluded from the experimental results that in aluminium, when exposed to normal atmospheric conditions at room temperature, oxide films are formed on the exposed surfaces.These films thicken with time and then probably breakdown after reaching a certain thickness and form again and the process continues at room temperature. Although this phenomenon of oxidation of aluminium at room temperatures was not reported in any publications reference can be made to publications by Mott (1946) who put forward one possible explanation for thin film formation at room temperature. Mott suggested positive metal ions at the temperature considered could leave and diffuse through the oxide. At the surface between the oxide and air they will combine with oxygen to form new layers of oxides if electrons too can get through the layer from the metal to the surface. At room temperature electrons can not in principle get through the oxide layer by thermionic emission from the metal into the conduction levels of the oxide therefore quantum mechanical tunnel effect was suggested as the possible mechanism. Another explanation by Mott was based on the following hypotheses :

i) The work function ϕ is small enough to allow the thermionic emission of electrons from the metal into the conduction levels of the oxide. If oxygen is then adsorbed on to the oxide surface and oxide ions are formed, a strong electric field will be set up in the oxide.

ii) The solubility of metal ions in the oxide at room temperatures would be too small for any passage of metal diffusion, under these very strong fields, migration of ions can take place.

Most metals acquire a thin oxide film when exposed to dry air at room temperature. In practice, surface films are heterogeneous. Chemical variations are present not only at the underlying metal, for example at segregated grain boundaries but there are scratch lines, inclusions and sheared edges which are likely to introduce internal stresses in the film. Hence it can be expected that there will be a number of points or 'pores' in the film where it will be less thick, less strong or more permeable than elsewhere. The metal may therefore start reacting at these sensitive points in the presence of a suitable electrolyte. After this three things that are likely to happen are :

i) the film grows again at the pores

ii) localised corrosion continues at the exposed bare metal; or

iii) breakdown extends sideways from the pores until there is no film left.

The continuous changes of Q with time can be due to film breakdown and repair of the and explained with the diagram shown below.

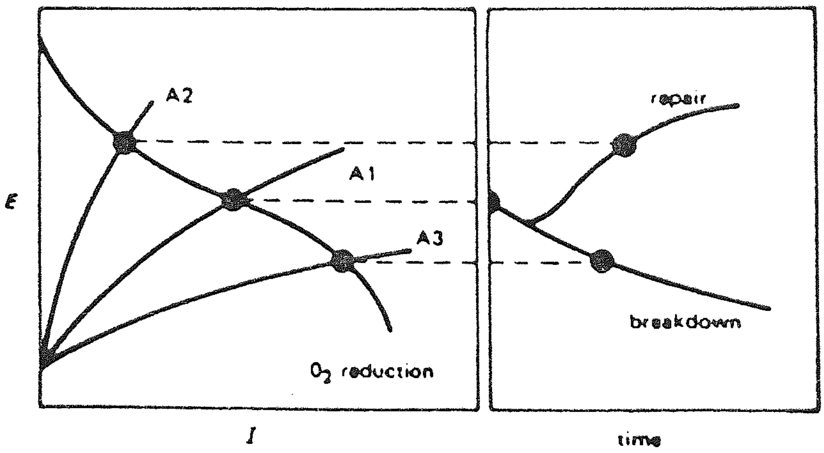


Fig.70. Film breakdown and repair.

The diagram shows film breakdown and repair. A1 the anodic polarisation curve is a composite curve for pores and filmed metal. When the pores are repaired the curve moves to position A2; the curve will move to position A3 if the film breakdown continues. The diagram on the right hand side shows how the corrosion potential changes with time.

At the present time there is no such instrument available for measuring potential changes occurring on bare aluminium surfaces at such sub-microscopic level. However, the present observations confirm that these fluctuations are due to surface reactions and is associated with film breakdown and repair. There was no more time available for further investigation to be carried out using surface analytical techniques.

However, it may be possible using Auger Electron Spectroscopy to confirm this film formation and breakdown behaviour. Study the oxidised layer and then by ion bombardment reduce the surface film to bare aluminium, and the changes associated with the surface with and without the film could be observed.

The nickel plated samples, irrespective of time of plating, demonstrated a similar fluctuation pattern with time. Q was found to be very low immediately after plating, this started to show an increase after less than an hour. The growth pattern continued but with a much reduced gradient. The increase in Q slowly diminished showing a continuous fluctuation pattern.

It can be expected that electrodeposited nickel will be very pure immediately after plating and would be expected to react with the environment ie. free oxygen. A fair amount of hydrogen would be present on the plated object. These adsorbed gases would try to move towards the substrate and some might even diffuse out from the surface. The oxidation of the nickel surface and hydrogen movement would therefore cause a fluctuation in the Q values with time.

9.7 Effect of heat treatment on Q-measurements.

The results obtained after annealing and solution treatment of HE9 and S1C samples were difficult to explain in terms of microstructural changes due to heat-treatment. It is also known that specific damping capacity increases with stress (Hoyt 1952) for example, damping capacity of cast iron has been shown to have gone from 28 to 40 as the stress level was increased from 4,500 psi to 6,700 psi. After annealing HE9 samples should have been relatively stress free with fewer dislocations within the microstructure, very little dissolved elements ie. solid solutions would be present in the pure matrix. The microstructure would contain a small number of large precipitates and hence it would be easy for the vibration to pass through the alloy relatively quickly without much resistance, however, Q dropped after annealing rather than going up. After solution treatment the matrix would be less pure and contain extra alloying elements in solid solution, dislocation density would increase and stress would be expected to have increased slightly due to water quenching. However, Q went up rather than going down after solution treatment. The samples which were precipitation treated did not show much variation after the 4 hour precipitation treatment at 175 ^{o}C (Table 36). After solution treatment Q went up very significantly and also after 24 hour ageing, but a slight drop in Q was observed in all the samples after the first 4 hour precipitation treatment as precipitation treatment time were increased in four hour steps the changes were not very marked but was fluctuating, this was observed with the hardness measurements. After 16 hours of precipitation treatment Q started to show a decline but not a very significant one neither did the hardnesses.

It can be expected that after heat-treatment at 400 ^{o}C a significant oxidation of the aluminium surface would have taken place. The solution treatment at 530 ^{o}C would form even more stable/thicker oxides. After annealing of HE9 samples Q went down but went up after solution treatment. In case of the S1C alloys also the pattern was similar but Q after heat-treatment did not fall below its as received condition. After heat-treatment S1C (commercially pure) alloys would be expected to form films much more rapidly even at 400^{o}C. This instrument has been very sensitive in picking up changes occuring at the surfaces rather than the bulk of the samples, therefore after oxidation of the surfaces the instrument did not respond to the metallurgical changes within the sample bars. Hardness measurements confirmed that metallurgical changes were taking place as would have been expected after various heat treatments.

The object of this research project was to produce a working instrument which would differentiate between good and poor adhesion of plated coatings. A lot of time was spent on actually getting the instrument working due to lack of information in the thesis. After the instrument was developed the fluctuation of Q with time was thought to be due to instrumentional error hence readings were taken over long periods of time and a statistical analysis was carried out . The statistical analysis confirmed the fear that the fluctuations were not due to chance alone ie. probably the instrument was not accurate enough for the job. The instrument also failed to detect changes between samples given very poor treatment and good Bondal treatments. The latest studies on the use of this instrument showed that the instrument is supersensitive to surface changes.

The sponsored research programme had to stop after three years and also the work was not achieving what it was aimed at ie. development of a non-destructive adhesion test method. However, it seems this instrument has opened up a new area in the study of surface metallurgy which was not known to exist. This instrument will be of use to a great number of applications especially in the study of surface oxidations. This instrument is relatively simple to construct and very cheap for studying surface oxidation in terms of high technology equipments that are available in the present day market eg. Auger Electron Specstroscopy.

This instrument can be used to differentiate between different alloys eg. it has differentiated between S1C and HE9 alloys very consistently. It can also be used to measure thicknesses of both anodised and plated coatings non-destructively. However, this instrument would need further development for measuring material properties of practical objects and cannot be used for measuring adhesion levels of electrodeposited coatings.

CHAPTER 10

CONCLUSIONS

1. Although previous work claimed a Q-meter could distinguish between samples given good and poor treatment ie. between good and poor adhesion levels, it was not possible to construct a working instrument from the information provided in the thesis.

2. The Modal testing method is not suitable for such measurements. Accuracy and repeatability of this instrument were very poor. Also the reliability of the software package used was unsatisfactory.

3. A modified Q-meter was developed after several modifications to the earlier design. But then it was not possible to resonate non-magnetic materials, therefore a reasonable comparison could not be made between samples before and after plating.

4. A new working Q-meter was developed based on an Impulse Technique. In this method test samples were vibrated using a miniature hammer and the method of suspension was further improved by using fine nylon threads replacing the polystyrene blocks.

5. This new Q-meter is very sensitive and can detect surface changes after any pre-treatment eg. electrolytic cleaning, nitric acid and Bondal dips.

6. Q drop increases as thickness of the deposited coating increases. It is possible that this instrument could be used for measuring thickness of coatings

non-destructively.

7. It has been observed that the Q of bare aluminium surfaces changes continuously with time.These changes are due to formation of surface oxides at room temperature, which probably forms at weak points, grow and breakaway after a time and this is a continuous process occurring on the surface. This phenomenon has not been reported earlier but theories were put forward in the 1940's by Mott who claimed oxidation of aluminium was possible at room temperatures but could not prove it experimentally.

8. Enveloping the exposed aluminium surface by lacquering, for example, reduced the fluctuation of Q with time very significantly. This was further improved by anodising. After hard anodising fluctuation of Q with time was almost negligible, this is because the surface pores become smaller and eventually reduced free oxygen reacting with the surface.

9. This instrument's results are very repeatable and therefore reliable although the earlier statistical analysis of the untreated aluminium sample bars were misinterpreted and cast a lot of doubt about the reliability of the instrument, which was due to surface oxidation and was not expected to be detected by such a simple instrument.

10. This instrument has very consistently detected major differences between different aluminium alloys that were used eg. HE9 and S1C alloy types, this difference was also maintained in terms of Q-drop as coating thickness was increased progressively.

11. Q of aluminium HE9 sample bars decreased after annealing but went up after solution treatment. In case of the S1C alloys Q went up after both the

treatments. This instrument has been very sensitive in detecting changes occurring on the surface at sub-microscopical level which was not known to be detectable. It was also detecting changes due to high temperature oxidation at the surface rather than the metallurgical changes in the bulk of the material. The surface oxide layer of aluminium would have thickened considerably after heat-treatment, especially after solution treatment. Hence the effect of overall microstructural changes were masked by the activity of oxides on the surface and therefore the observations could not be explained in terms of microstructural changes.

12. The instrument is not adequate to measure adhesion levels of electroplated components but can be used probably for other purposes as indicated in further work section.

SUGGESTIONS FOR FURTHER WORK

1. The present Q-meter can handle aluminium alloy bars of one particular dimension. Therefore this design needs to be improved so that vibration of practical objects and other alloys can be studied.

2. This instrument has consistently distinguished differences between different aluminium alloys that were used. Therefore in order to use it as an analytical tool a calibration work needs to be done with a range of known alloy types.

3. This instrument is a potential non-destructive thickness measuring equipment and this also needs to be calibrated against known thicknesses so that it can measure thicknesses of both anodised and plated coatings.

4. Oxidation of aluminium surfaces at room temperature which is now claimed to be occurring can be further studied using high technology equipment, such as Auger Electron Spectroscopy. It would be possible to study the oxidised aluminium surfaces using AES then strip the oxidised surface by atomic layer by ion bombardment in vacuum until the bare aluminium surface is reached.

5. The metallurgical changes which is known to be present in pure alloys can be further studied, for example, study pure metal without any stresses and precipitation effect and then introduce defects such as stress and precipitation treatment and study changes in Q, if the instrument can pick up these changes, this will open another area of application of the instrument.

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