THICKNESS TESTING OF ELECTROPLATED AND RELATED COATINGS

VOLUME 1

Edited by S.W. Baier

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Volume I

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Contents

Foreword

The purpose of this book is to describe the methods which can be used to measure the thickness of metallic coatings (on both metallic or non-metallic substrates) and of inorganic coatings (such as anodic oxide and phosphate coatings) on metallic substrates, but excluding the measurement of paint or other organic coatings although some of the methods may also be satisfactory for these coatings. The book attempts to give sufficiently detailed treatment of the test methods so that any of those described can be carried out without referring to any other literature, apart from instructions by instrument suppliers on their particular instruments.

For convenience the book has been divided into two parts—Volume 1, dealing with "Destructive Testing Methods" and Volume 2, with methods which in general are "Non-Destructive".

The main destructive methods, apart from the BNF Jet Test, can be considered as "primary" methods, which either measure the coating thicknesses directly (as with microsectioning) or measure the weight of coating on a known area (as with strip and weigh tests or the coulometric method) from which the linear thickness can be calculated provided the density of the coating is known. Although instruments (or apparatus) are obviously needed to carry out these primary methods—e.g., metallurgical microscopes for microsectioning, coulometric instruments for measuring the quantity of electricity to strip a known area of coating, BNF Jet Test apparatus (with a standard jet) or chemical apparatus, including an accurate balance, for strip and weigh tests—there is no need to have "thickness standards" with known thicknesses of coating to calibrate the instrument or apparatus as there is with most non-destructive methods. (Only in the case of the BNF Jet Test, is calibration against known thickness of coating needed. In this case coatings whose thicknesses were measured by microsectioning were used to produce calibration curves, relating the time of penetration by the jet of chemical solution to the coating thickness, and these original published calibration curves are still being used.)

In contrast, most of the non-destructive methods, such as the magnetic, eddy current, beta back-scatter and X-ray spectrographic methods, can only be considered as "secondary" methods as the test instruments must be calibrated, often at frequent intervals, with calibration standards having known thicknesses (measured by primary methods) of the specific coatings on appropriate substrates. However, there are also a few non-destructive (or almost non-destructive) optical and profilometric methods which do not require calibration standards and can, therefore, be considered as primary methods, although except for a few optical methods used for measuring oxide films on aluminium, they are seldom used except for measuring the coatings on calibration standards required for other methods.

Introduction

The Institute of Metal Finishing Industrial and Technical Committee, under the chairmanship of Robert Pinner, realised that a publication giving comprehensive details of the methods which can be used for measuring the thickness of metallic and related coatings would be of great value both to metal finishers and those employing their products. A working party was therefore given the task of producing this book.

The types of coatings for which satisfactory thickness testing methods are available include:

(1) Electroplated coatings on both metallic and non-metallic basis materials—or 'substrates', as they are usually called nowadays when they are considered as the materials underlying the coatings.

(2) Electroless coatings, such as autocatalytic nickel-phosphorus alloy coatings, on both metallic and non-metallic substrates.

(3) Chemical replacement coatings on metallic substrates, such as tin coatings on aluminium.

(4) Hot dipped coatings on metallic substrates, such as zinc (hot-dip galvanized) coatings on steel and hot-dip tin coatings on steel and copper.

(5) Anodic coatings on aluminium and other metals.

(6) Conversion coatings on metallic substrates, such as phosphate coatings on steel and chromate (passivation) coatings on zinc, cadmium or aluminium.

(7) Vitreous enamel coatings on metals.

A number of the methods, especially some of the non-destructive methods are equally applicable to measurement of paint and other organic coatings on metals; but only brief references are made to these applications as they were not considered to come within the scope of this particular I.M.F. working group.

Before giving guidance on the most suitable methods to use it might be useful to consider the basic reasons for carrying out thickness tests. In a few cases, such as building-up worn parts with electrodeposited nickel or chromium, the main reason for thickness testing is to ensure that the dimensions of the coated parts will fit properly when assembled. In this case direct measurements with a micrometer or other suitable gauge, before and after plating, will obviously be the most suitable method rather than any of those given in this book. However, in most cases some definite minimum thickness of coating is required to ensure some specific surface property, such as resistance to wear, corrosion protection, solderability or electrical conductivity (or perhaps insulation in the case of anodic coatings on aluminium).

TESTING FOR MINIMUM THICKNESS

Even with coatings considered as purely decorative, such as decorative chromium or gold plating, it is necessary to have some minimum thickness in order to resist normal wear in handling (except when the coatings are protected by lacquering as is normal with decorative brass coatings over bright-nickel or vacuum evaporated aluminium coatings). On the other hand where considerable resistance to wear is needed—e.g., with hard chromium or hard anodising for engineering purposes—greater coating thicknesses will obviously be needed although for these applications it is also important that the coatings should have a specified wear-resistance, as shown by a direct wear-test and/or by a definite hardness range, as well as an appropriate minimum thickness.

Probably the greatest use of thickness testing is to ensure compliance with specifications for protective coatings. The service life of most decorative and protective coatings is greatly affected by the thickness of the coating and with sacrificial coatings such as zinc and cadmium, which are anodic to the substrate, the life of the coating is directly proportional to its thickness. Even with coatings which are strongly cathodic to the basis metal, the deposit thickness is critical in respect of the porosity of the coating and its ability to withstand pitting corrosion.

A minimum thickness of deposit is, therefore, an essential requirement of most coating standards. The choice of the most appropriate method for thickness testing, as well as being dependent on the particular coating, is also obviously dependent on the purpose for which the test is required. For routine inspection, or quality control, to ensure that production is up to specification thickness, the test method should be as rapid and economic as possible and wherever practical non-destructive methods should be chosen. It is generally considered, especially in American Standards, that accuracies of $\pm 10\%$ are quite satisfactory for this purpose; although for economic reasons, particularly with gold and other precious metal coatings it is often better to get greater accuracy in order to avoid making the coatings of these expensive metals even a few per cent thicker than they need be.

NON-DESTRUCTIVE TESTING FOR MINIMUM THICKNESS

Non-destructive testing is obviously the only way if testing should be required on 100% of the articles being coated and is obviously also the most economic way when large numbers of similar articles have to be tested. However, it should always be realised that non-destructive testing instruments have to be calibrated at fairly frequent intervals with standards having accurately known thicknesses*

(* It should also be realised that the accuracy of any non-destructive method can never be better than the accuracy of the calibration standards and is normally considerably less accurate since the absolut measurement error depends on instrument and operation errors as well, as given by the formu...

$$E_{(abs)} \text{ (Absolute measurement error)} = \sqrt{a^2 + b^2 + c^2}$$

where a = Instrument error
b = Calibration standard error
c = Operational error.

Most instrument manufacturers provide error data for their instruments and calibration standards which they supply, but what cannot be pre-defined is error due to operation.)

of the appropriate coating on the appropriate substrate; and these can sometimes be rather costly to produce or purchase. Therefore, non-destructive testing may not prove really economic when only small samples, or a variety of different coatings, on various substrates have to be tested.

In practice, the two most frequently used non-destructive methods are:

(1) Magnetic methods, which are widely used for measuring non-magnetic metallic (and organic) coatings on iron and steel;

(2) The Eddy Current method which is mainly used for anodic oxide coatings on aluminium.

Many commercial instruments are available for both these methods, from quite cheap, but rather inaccurate, pull-off magnetic gauges to rather more expensive, but more accurate, electromagnetic and eddy current instruments.

A great advantage with both these methods is that plastics foils of known thicknesses can be used quite satisfactorily for calibrating these instruments for the normal ranges of coating thicknesses. For magnetic instruments, simple calibration with foils, placed on samples of mild steel will serve for calibration for testing any non-magnetic metallic coatings, such as zinc, cadmium, tin or copper, or paint or other organic coatings, on almost every type of mild steel; but with eddy current instruments calibration must be done with foils placed on a bare sample of the particular aluminium alloy which has been anodised. (The most recent development in magnetic testing is the production of special proprietary commercial instruments designed for testing nickel coatings on steel—i.e., for testing weakly magnetic coatings, with somewhat variable magnetic properties in the case of electroplated nickel, on strongly magnetic substrates. Such instruments, which are claimed to give very satisfactory results, could be expected to be very useful for routine testing of nickel plated steel articles, although they normally have to be calibrated with accurately known thicknesses of nickel coatings, and not with foils.)

The third very important non-destructive method is the Beta Back-Scatter method, which is now used to a very considerable extent for measuring the thickness of gold or other precious metal coatings, particularly for the electronics industries. Although beta back-scatter instruments are much more expensive than even the best electro-magnetic or eddy current instruments, they are usually well worth using since, on the one hand, it is most important to the electronics industries to be assured that the gold or other coatings they require are up to the thickness specified while, on the other hand, the electroplater wants to be sure that he is not wasting expensive metals by plating any thicker than he has to in order to meet the specifications—a matter which can make the difference between profit and loss. However, calibration of beta back-scatter instruments is nothing like as simple as calibration of magnetic or eddy-current instruments, calibration standards coated with very accurately known thicknesses being needed to enable the instruments to measure the various types of gold coatings or other coatings with the required accuracy. Also it is important that these calibration standards should have practically identical coatings, e.g., bright, dull or alloyed gold coatings, to those on the articles being tested and that the substrate of the standards should correspond to those of the articles. However, since there are no simple alternative methods (either destructive or non-destructive) for measuring the thickness of gold and other precious metal coatings, the beta back-scatter method has to be used wherever there is a call for regular routine testing of these coatings, i.e., except when the number of samples is so limited that microsectioning or chemical stripping might be used instead.

These three non-destructive methods each measure "local"* thickness as is needed to ascertain "minimum"* specified thicknesses on coated articles. In particular the beta back-scatter method is practically the only method, apart from microsectioning, that can be used to measure the local thickness on very small areas, or very small components, as is often required with electrical or electronic components, where it is often only necessary to meet a specified minimum thickness over quite small "significant surfaces".*

DESTRUCTIVE TESTING FOR MINIMUM THICKNESS

Instead of non-destructive methods, destructive methods are often used for measuring local thickness of metallic coatings in cases where only a limited number of components or a rather wide range of components with different coatings and/or substrates have to be tested—e.g., in smaller metal finishing shops or at customers premises where they wish to make occasicnal checks to see that the coatings supplied to them are up to specification. In these cases it can often be shown that it is cheaper to use them than to invest in rather expensive non-destructive instruments and calibrate them for all the various combinations of coatings and substrates which it may be necessary to test. This is particularly true for small articles, where the cost of having to destroy (or re-coat) a small number of samples from each batch is relatively small. The two most popular methods for this purpose are the Coulometric method and the BNF Jet Test, both of which are simple to use and quite rapid.

The Coulometric method has the advantage that the thicknesses can be calculated from the quantity of electricity required to dissolve the coating (as shown on the meter of the apparatus) and the dimensions of the test area ("measuring area" as defined in BS 5411: Part 1) and can, therefore, be considered as a "primary" test method—i.e., not dependent on calibration with thickness standards. Also when the test area can be maintained with sufficient accuracy, the coulometric method can provide a high degree of accuracy, with errors of only between $\pm 2\%$ to 5% of the true thickness. The cost of the coulometric apparatus (or instrument) is normally somewhat less than that of electromagnetic or eddy current instruments and can be used for measuring a great variety of coatings on various substrates, by using the appropriate electrolytes. However, it cannot be used for non-metallic coatings, nor for coatings of gold or the platinum metals; except that proprietary electrolytes, of undisclosed composition, are now available for gold coatings—although it has not always been made clear what substrates are catered for or if calibration against thickness standards might be required when using these electrolytes. (The only practical alternatives to the beta back-scatter non-destructive method for these precious metal coatings is either microsectioning to measure local thickness or "strip and weigh" methods for

* Definitions of these terms, "local thickness", "minimum thickness", "significant surfaces" (and "average thickness") and how they should be measured are given in the recent British Standard, 5411 (Part 1)—"Definitions and Conventions Concerning the Measurement of Thickness".

average thickness, although some of the more sophisticated optical or other methods can sometimes be used if available.)

In contrast to the coulometric method the apparatus for the BNF Jet Test, which was the original rapid local thickness testing method, is much cheaper, but it can only be used for a somewhat limited range of coatings—dull nickel, cobalt, copper, bronze, zinc, cadmium, silver, tin and lead—and it is only claimed to give accuracies within $\pm 15\%$ of the true thickness. (However, it has an advantage in that it can often be carried out at various "awkward" places on articles which the measuring cell of the coulometric test cannot reach.) The reason why only this limited number of coatings can be tested, is that chemical solutions to penetrate the metallic coatings at definite rates, which is the principle of the BNF Jet Test, were only developed and calibration curves drawn up for these particular metallic coatings—the microsectioning method being used as the primary method for producing the calibration curves. This obviously involved quite protracted experimentation for each coating metal, and with the development of alternative thickness testing methods it has apparently been considered too costly to try and develop Jet Test solutions for other metals. However, with the development of the (much simpler) coulometric method there would now seem a more reasonable way of developing further Jet Test solutions and, in fact, this has been done for tin–nickel alloy plating. Re-calibration of some of the original solutions with the coulometric method, which with care can often be appreciably more accurate than microsectioning, might perhaps be useful to see if a better degree of accuracy than $\pm 15\%$ could be obtained. In particular the coulometric method would make it fairly simple to prepare calibration curves for any particular type of "organic" bright nickel coating, since the original calibration curve only holds good for ("dull") nickel coatings free from incorporated "organic" matter (i.e., not containing sulphur and/or carbon). (The rate of penetration of "organic bright nickels" by the BNF Jet Test solution is much more rapid than of "dull" nickel and varies considerably with the particular organic brighteners used in the plating solutions, possibly with the conditions of plating, and sometimes with the actual thickness of the coatings.)

Only in very few cases is microsectioning used as a routine method for thickness testing, largely because of the time and expense involved as well as the complete destruction of the components tested. It should be added that its accuracy is not particularly good, particularly for thinner coatings (for details see the chapter on "Microsectioning") and the results may be completely misleading unless the microsectioning is carried out by operators with sufficient skill and training. Nevertheless, microsectioning may be the only practical method that can be used to get local thickness measurements in a few cases, especially on small parts of complicated shapes, such as gold plated jewellery unless appropriate expensive non-destructive testing instruments, such as beta back-scatter instruments, are available.

In the case of composite (or multi-layer) coatings, such as multi-layer nickel, copper/nickel coatings on steel, or gold on nickel undercoats it is usually necessary to use destructive methods to measure the thickness of each layer although beta back-scatter instruments can be used for the latter whenever the nickel undercoat is thick enough so that it is not penetrated through by the beta rays. Microsectioning can always be used to measure the thicknesses of the various layers, with suitable etching, if necessary, to distinguish between them, e.g., between bright (sulphur containing) and semi-bright (sulphur free) nickel layers. However, in many cases, e.g., with chromium/nickel/copper coatings the coulometric method can be very conveniently used and in a few cases, including copper/nickel composites, the BNF Jet Test can also be used to measure the thickness of the two layers.

REFEREE TESTS

In cases of dispute between the metal finisher and the customer, most specifications give mandatory "referee" methods to be used for local thickness measurement to ascertain the minimum coating thickness. Until recently most British Standards called for microsectioning as the referee method*. However in the last few years it has been realised more and more that microsectioning may not always give as accurate results as most people imagined, especially for thinner coatings.* Therefore, alternative referee methods (or a choice of methods) are frequently given in the more recently published specifications, especially in I.S.O. Standards and it seems likely that, in future, new or revised British Standards may follow suit.

In particular microsectioning cannot be used to measure the thickness of decorative chromium coatings which have minimum specified thicknesses between 0.3 and 0.8 μm (according to the type of chromium) since dimensions below about 0.5 μm are not resolvable by optical microscopes, i.e., these thin coatings cannot be seen in microsections under an optical microscope however high the magnification. The coulometric method, which can measure chromium coatings down to 0.1 μm or less, is, therefore, the referee method for thin chromium coatings and it seems likely that the coulometric method may be specified as a referee method for other metallic coatings to a much greater extent in future.

MEASUREMENT OF AVERAGE THICKNESS

In cases where coatings tend to be fairly uniform in thickness, as on barrel plated work and with hot-dip and sherardized zinc coatings and anodic coatings on aluminium, it would seem perfectly satisfactory to measure the average thickness over reasonably large areas (say, around 10 cm^2) instead of measuring the local thickness over an area of about 1 cm^2 or less. For this purpose strip and weigh methods are obviously satisfactory, although non-destructive tests may be applicable in some cases.

In the case of electroplated threaded components, such as nuts and bolts, the British Standard Specification (BS 3382) calls for a minimum "batch average thickness" on a group of ten components (or rather more with very small components) and so for these components a strip and weigh test becomes the referee test as well as the normal method for routine control, although somewhat quicker but rather less accurate methods, like the "time of gassing" test for cadmium coatings or the measurement of the volume of hydrogen produced

* For details see chapter on Microsectioning.