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Corrosion of metals and alloys — Evaluation of pitting corrosion

Corrosion des métaux et alliages — Évaluation de la corrosion par piqûres

Reference number
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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 11463 was prepared by Technical Committee ISO/TC 156, *Corrosion of metals and alloys.*

Annexes A and B of this International Standard are for information only.

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Introduction

It is important to be able to determine the extent of pitting, either in a service application where it is necessary to estimate the remaining life in a metal structure, or in laboratory test programmes that are used to select pitting-resistant materials for a particular service (see [1] in annex B).

The application of the materials to be tested will determine the minimum pit size to be evaluated and whether total area covered, average pit depth, maximum pit depth or another criterion is the most important to measure.

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Corrosion of metals and alloys — Evaluation of pitting corrosion

1 Scope

This International Standard gives guidance on the selection of procedures that can be used in the identification and examination of pits and in the evaluation of pitting corrosion.

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 8407:1991, *Corrosion of metals and alloys - Removal of corrosion products from corrosion test specimens.*

3 Identification and examination of pits

3.1 Visual inspection

A visual examination of the corroded metal surface with or without the use of a low-power magnifying glass may be used to determine the extent of corrosion and the apparent location of pits. It is often advisable to photograph the corroded surface so that it can be compared with the clean surface after the removal of corrosion products.

3.1.1 If the metal specimen has been exposed to an unknown environment, the composition of the corrosion products may be of value in determining the cause of corrosion. Recommended procedures in the removal of particulate corrosion products should be followed and reserved for future identification.

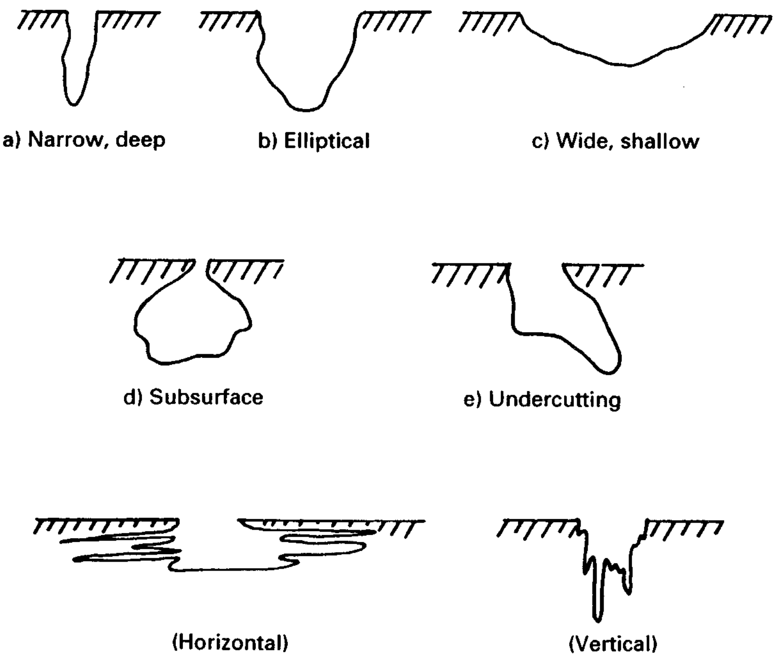
3.1.2 To expose the pits fully, it is recommended that cleaning procedures should be used to remove the corrosion products and avoid solutions that attack the base metal excessively (see ISO 8407). It may be advisable during cleaning to probe the pits with a pointed tool to determine the extent of undercutting or subsurface corrosion (see figure 1). However, scrubbing with a stiff-bristle brush will often enlarge the pit openings sufficiently by removal of corrosion products or undercut metal to make the pits easier to evaluate.

3.1.3 Examine the cleaned metal surface to determine the approximate size and distribution of pits. Follow this procedure by a more detailed examination through a microscope using low magnification (approximately $\times$ 20).

3.1.4 Determine the size, shape and density of pits.

3.1.4.1 Pits may have various sizes and shapes. A visual examination of the metal surface may show a round, elongated or irregular opening, but it seldom provides an accurate indication of corrosion beneath the surface. Thus it is often necessary to cross-section the pit to see its actual shape and to determine its true depth. Several variations in the cross-sectioned shape of pits are shown in figure 1.

3.1.4.2 It is difficult to determine pit density by counting pits through a microscope eyepiece, but the task may be made easier by the use of a plastic grid. Place the grid, containing 3 mm to 6 mm squares, on the metal surface. Count and record the number of pits in each square, and move across the grid in a systematic manner until all the surface has been covered. This approach minimizes eye-strain because the eyes can be taken from the field of view without fear of losing the area of interest. Enlarged photographs of the area of interest may also be used to reduce eye-strain.



f) Microstructural orientation

Figure 1 — Variations in the cross-sectional shape of pits

3.1.5 To carry out a metallographic examination select and cut out a representative portion of the metal surface containing the pits and prepare a metallographic specimen in accordance with recommended procedures. If corrosion products are to be examined in cross-section, it may be necessary to fix the surface in a mounting compound before cutting. Examine microscopically to determine whether there is a relation between pits and inclusions or microstructure, or whether the cavities are true pits or might have resulted from metal loss caused by intergranular corrosion, dealloying, etc.

3.2 Non-destructive inspection

A number of techniques has been developed to assist in the detection of cracks or cavities in a metal surface without destroying the material. See [1] in annex B. These methods are less effective for locating and defining the shape of pits than some of those previously described, but they merit consideration because they are often used *in situ,* and thus are more applicable to field applications.

3.2.1 Radiographic

Radiation, such as X-rays, passes through the object. The intensity of the emergent rays varies with the thickness of the material. Imperfections may be detected if they cause a change in the absorption of X-rays. Detectors or films are used to provide an image of interior imperfections. The metal thickness that can be inspected is dependent on the available energy output. Pores or pits must be as large as 0,5 % of the metal thickness to be detected. This technique has only slight application to pitting detection, but it might be useful for comparing specimens before and after corrosion to determine whether pitting has occurred and whether it is associated with previous porosity. It may also be useful to determine the extent of subsurface and undercutting pitting (see figure 1).

3.2.2 Electromagnetic

3.2.2.1 Eddy currents may be used to detect defects or irregularities in the structure of electrically conductive materials. When a specimen is exposed to a varying magnetic field, produced by connecting an alternating current to a coil, eddy currents are induced in the specimen and they in turn produce a magnetic field of their own. Materials with defects will produce a magnetic field that is different from that of a reference material without defects, and an appropriate detection instrument is required to determine these differences.

3.2.2.2 The induction of a magnetic field in ferromagnetic materials is another approach that is used. Discontinuities that are transverse to the direction of the magnetic field cause a leakage field to form above the surface of the part. Ferromagnetic particles are placed on the surface to detect the leakage field and to outline the size and shape of the discontinuities. Rather small imperfections can be detected by this method. However, the method is limited by the required directionality of defects to the magnetic field, by the possible need for demagnetization of the material and by the limited shape of parts that can be examined.

3.2.3 Sonics

In the use of ultrasonics, pulses of sound energy are transmitted through a couplant, such as oil or water, on to the metal surface where waves are generated. The reflected echoes are converted to electrical signals that can be interpreted to show the location of flaws or pits. Both contact and immersion methods are used. The test shall be carried out from the non-pitted face. The test has good sensitivity, although it is unlikely to detect pits of less than 1 mm diameter or within 1 mm of a non-pitted face, and provides instantaneous information about the size and location of flaws. However, reference standards are required for comparison and training is needed to interpret the results properly.

3.2.4 Penetrants

Defects opening to the surface can be detected by the application of a penetrating liquid that subsequently exudes from the surface after the excess penetrant has been removed. Defects are located by spraying the surface with a developer that reacts with a dye in the penetrant, or the penetrant may contain a fluorescent material that is viewed under ultra-violet light. The size of the defect is shown by the intensity of the colour and the rate of bleed-out. This technique provides only an approximation of the depth and size of pits.

3.2.5 Replication

Images of a pitted surface can be created by applying a material to the surface which conforms to the shape of the pits and can be removed without damaging its shape. This method will not work however, for pits of subsurface or undercut type. The removed material contains a replica of the original surface which, in some cases, is easier to analyze than the original. Replication is particularly useful for analysis of very small pits.

4 Extent of pitting

4.1 Mass loss

Metal mass loss is not ordinarily recommended for use as a measure of the extent of pitting unless general corrosion is slight and pitting is fairly severe. If uniform corrosion is significant, the contribution of pitting to total metal loss is small, and pitting damage cannot be determined accurately from mass loss. In any case, mass loss can only provide information about total metal loss due to pitting but nothing about density of pits and depth of penetration. However, mass loss should not be neglected in every case because it may be of value; for example, mass loss along with a visual comparison of pitted surfaces may be adequate to evaluate the pitting resistance of alloys in laboratory tests. Mass loss may also be useful to detect the existence of subsurface metal loss.

4.2 Pit depth measurement

4.2.1 Metallography

Pit depth may be determined by sectioning vertically through a preselected pit, mounting the cross-sectioned pit metallographically and polishing the surface. A better or alternative way is to section slightly away from the pit and slowly grind until the pit is in the cross-section. Sectioning through a pit can be difficult and one may miss the deepest portion. The depth of the pit is measured on the flat, polished surface by the use of a microscope with a calibrated eyepiece. The method is very accurate, but it requires good operator skill and good judment in the selection of the pit and good technique in cutting through the pit. Its limitations are that it is time-consuming, the deepest pit may not have been selected and the pit may not have been sectioned at the deepest point of penetration. The method, however, is the only suitable for the evaluation of the pit shape as in figure 1.

4.2.2 Machining

See [2] and [3] in annex B.

4.2.2.1 This method requires a sample that is fairly regular in shape, and it usually involves the destruction of the specimen. Measure the thickness of the specimen between two areas that have not been affected by general corrosion. Select a portion of the surface on one side of the specimen that is relatively unaffected; then machine the opposite surface where the pits are located on a precision lathe, grinder or mill until all signs of corrosion have disappeared. Some difficulty from galling and smearing may be encountered with soft metals and pits may be obliterated. Conversely, inclusions may be removed from the metal thus confusing examination. Measure the thickness of the specimen between the unaffected surface and subtract from the original thickness to give the maximum depth of pitting. Repeat this procedure on the unmachined surface unless the thickness has been reduced by 50 % or more during the machining of the first side.

4.2.2.2 This method is equally suitable for determining the number of pits with specific depths. Count the visible pits then machine away the surface of the metal in measured stages and count the number of visible pits remaining at each stage. Subtract the number of pits at each stage from the count at the previous stage to obtain the number of pits at each depth of cut. Count at the previous stage to obtain the number of pits at each depth of cut.

4.2.3 Micrometer or depth gauge

4.2.3.1 This method is based on the use of a pointed needle attached to a micrometer or calibrated depth gauge to penetrate the pit cavity. Remove surrounding corrosion products or debris thoroughly then zero the instrument on an unaffected area at the lip of the pit.

Insert the needle in the pit until it reaches the base. The distance travelled by the needle is the depth of the pit. It is best to use constant-tension instruments to minimize metal penetration at the base of the pit. It may be advantageous to use a stereomicroscope in conjunction with this technique so that the pit can be magnified to ensure that the needle point is at the bottom of the pit. The method is limited to pits that have a sufficiently large opening to accommodate the needle without obstruction. This eliminates those pits which have undercutting or strong directional orientation.

4.2.3.2 In a variation of this method, attach the probe to a spherometer and connect it through a microammeter and battery to the specimen (see [3] and [4] in annex B). When the probe touches the bottom of the pit, it completes the electrical circuit and the probe movement is a measurement of pit depth. This method is limited to very regularly shaped pits because contact with the side of the pit or conductive debris would give a false reading.

4.2.4 Microscopy

This method is particularly valuable when pits are too narrow or difficult to penetrate with a probe type of instrument. The method is amenable to use as long as light can be focused on the bottom of the pit. This would not be possible in the case of example (e) in figure 1.

4.2.4.1 Use a metallurgical microscope with a magnification range from × 50 to × 500 and a calibrated fine-focus knob (for example, 1 division ≙ 0,001 mm). If the latter is not available, a dial micrometer can be attached to the microscope in such a way that it will show movement of the stage relative to the microscope body.

4.2.4.2 Locate a single pit on the metal surface and centre it under the objective lens of the microscope at low magnification (e.g., × 50). Increase the objective lens magnification until the pit area covers most of the field under view. Focus the specimen surface at the lip of the pit, using first the coarse and then the fine-focusing knobs of the microscope. Record initial readings from the fine-focusing knob, refocus on the bottom of the pit with the fine-focusing knob, and record the reading. The difference between the initial and the final readings on the fine-focusing knob is the pit depth.

4.2.4.3 Repeat the steps in 4.2.4.2 to obtain additional measurements or until satisfactory duplication has been obtained. The repeatability of pit depth measurements on a single pit at four magnifications is shown in annex A.

4.2.4.4 A variation of this technique employs the use of an interference microscope. A beam of light is split and one portion is projected on to the specimen and the other on to the surface of a reference mirror. The reflected light from these two surfaces is recombined, and interference fringes are formed that provide a topographical map of the specimen surface. These fringes can be used to measure vertical deviations on the metal surface. However, the method is limited to the shallower pits, that is, less than 25 µm, because the number of fringes increases to the point where they are difficult to count.

5 Evaluation of pitting

5.1 General

There are several ways in which pitting can be described, given a quantitative expression to indicate its significance or used to predict the life of a material. Some of the more commonly used methods are described in this clause, although it is often found that no single method is sufficient by itself.

5.2 Standard charts

See [3] in annex B.

5.2.1 Rate the pits in terms of density, size and depth on the basis of standard charts, such as those shown in figure 2. Columns A and B relate to the extent of pitting at the surface of the metal (that is, column A is a means for rating the number of sites per unit area and column B a means for showing the average size of these sites). Column C rates the intensity or average depth of attack. A typical rating might be A-3, B-2, C-3, representing a density of 5×10^4 pits/m², an average pit opening of 2 mm² and an average pit depth of 1,6 mm.

5.2.2 This method offers an effective means of communication between those who are familiar with the charts and it is a simple means of storing data for comparison with other test results. However, it is tedious and time consuming to measure all pits and the time is usually not justified because maximum values (e.g. pit depths) usually have more significance than average values.

5.3 Metal penetration

5.3.1 Measure the deepest pit and express metal penetration in terms of the maximum pit depth or the average of the ten deepest pits or preferably both. This type of measurement is particularly significant when the metal is associated with an enclosure for a gas or liquid, and a hole could lead to a loss of fluid.

5.3.2 Metal penetration may also be expressed in terms of a pitting factor. This is the ratio of the deepest metal penetration to the average metal penetration, determined from mass loss, as shown in the following relationship.

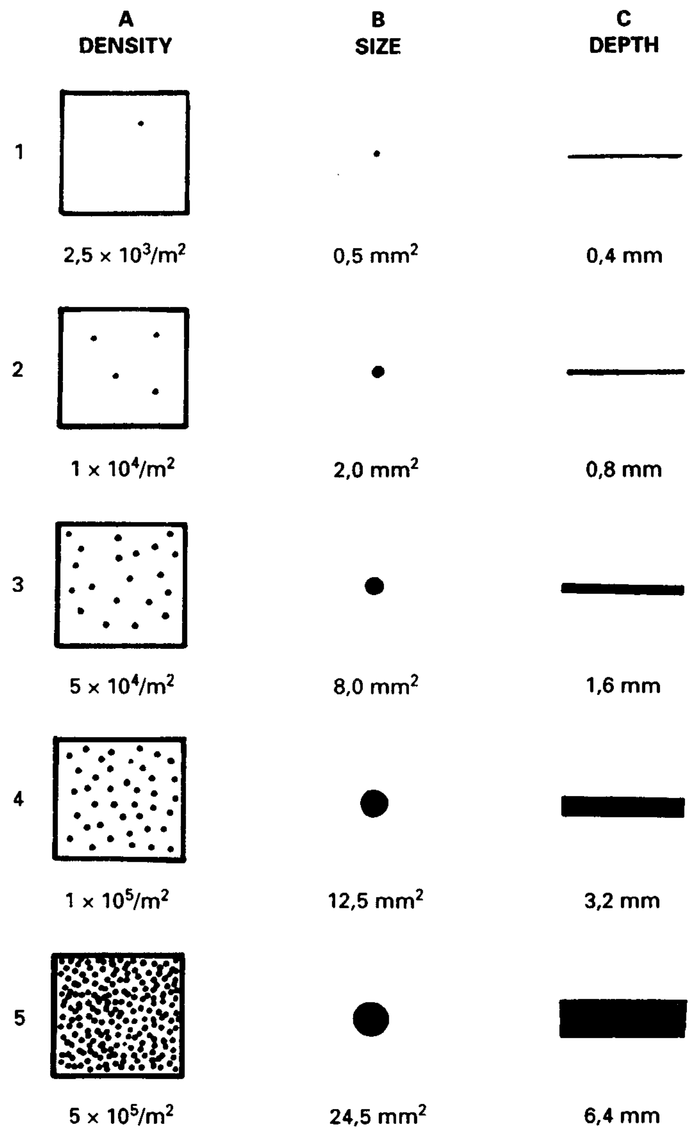


Figure 2 — Standard rating charts for pits

$$\text{Pitting factor} = \frac{\text{deepest metal penetration}}{\text{average metal penetration}}$$

A pitting factor of 1 represents uniform corrosion. The larger the number, the greater the depth of penetration. The factor does not apply in those cases where pitting or general corrosion is very small because values of zero or infinity can readily be obtained when dealing with a ratio where one number approaches zero.

5.4 Statistical

5.4.1 The application of statistics to the analysis of corrosion data is discussed briefly in this document to show that statistics have a bearing on the evaluation of pitting data. More detailed information can be obtained from other publications (see [11] and [12] in annex B).

5.4.2 The probability that pits will initiate on a metal surface is dependent on a number of factors, such as the pitting tendency of the metal, the corrosivity of the solution, the specimen area and the time of exposure. A pitting probability test can be conducted to determine the susceptibility of metals to pitting, but it will not provide information about the rate of propagation and the results are only applicable to the conditions of exposure. The pitting probability, P, in % after the exposure of a number of specimens to a particular set of conditions can be expressed as follows:

$$P = \frac{N_p}{N} \times 100$$

where

N_p is the number of specimens that pit;

N is the total number of specimens.

See [5] and [6] in annex B.

5.4.3 The relationship between pit depth and area or time of exposure may vary with the environment, the metal exposed and other variables. The relationships cited in 5.4.3.1 and 5.4.3.2 are examples that have been found to apply under certain exposure conditions.

5.4.3.1 The following relationship was found between the maximum pit depth, D, and the area, A, of a pipeline exposed to soil.

$$D = bA^a$$

where a and b are constants derived from the slope and the y-intercept of a straight line curve obtained when the logarithms of the mean pit depth for successively increasing areas on the pipe are plotted against the logarithms of the corresponding areas.

See [7], [8] and [9] in annex B.

The dependance on area is attributed to the increased chance for the deepest pit to be found when the size of the sample of pits is increased through an increased area of corroded surface.

5.4.3.2 The maximum pit depth, D, of aluminium exposed to various waters was found to vary as the cube root of time, t, as shown in the following relationship:

$$D = Kt^{1/3}$$

where K is a constant that is a function of the composition of the water and alloy.

See [5] and [10] in annex B.

This relationship has been found to apply to several aluminium alloys exposed to different waters.

5.4.4 Extreme value probability statistics (see [11] and [12] in annex B) have been successfully applied to maximum pit depth data to estimate the maximum pit depth of a large area of material on the basis of examination of a small portion of that area (see [3], [5] and [10] in annex B). The procedure is to measure specimens that have pitted, and then arrange the pit depth values in order of increasing rank. A plotting position for each order of ranking is obtained by substituting in the relation, $M/(n+1)$, where M is the order of ranking and n is the total number of specimens or values. For example, the plotting position for the second value out of 10 would be $2/(10+1) = 0,1818$. These values are plotted on the ordinate of extreme value probability paper versus their respective maximum pit depth. If a straight line is obtained, it shows that extreme value statistics apply. Extrapolation of the straight line can be used to determine the probability that a specific depth will occur or the number of observations that must be made to find a particular pit depth.

5.5 Loss in mechanical properties

If pitting is the predominant form of corrosion and the density of pitting is relatively high, the change in a mechanical property may be used advantageously to evaluate the degree of pitting. Typical properties that are considered for this purpose are strength, impact resistance and burst pressure (see [13] and [14] in annex B).

5.5.1 The precautions that must be taken in the application of these mechanical test procedures are covered in most standard methods, but it must be stressed that it is important to use as nearly replicate specimens as possible for both the exposed and unexposed specimens. Thus, consideration should be given to sample geometry and edge effects, direction of rolling, surface condition, etc.

5.5.2 Representative specimens of the metal are exposed to the same conditions, except the corrosive environment. The mechanical properties of the exposed and unexposed specimens are measured after exposure. The difference between the two results is attributed to corrosion.

5.5.3 Some of these methods are more properly suited to the evaluation of other forms of localized corrosion, such as intergranular or stress corrosion, so their limitations must be considered. The often erratic nature of pitting and the location of pits on the specimen can affect results. In some cases the change in mechanical properties due to pitting may be too small to provide meaningful results. Probably one of the most difficult problems is to separate the effects due to pitting from those caused by some other form of corrosion.

6 Report

The report should include as much detailed information as possible, such as the following:

a) material composition and product form, supplier and production details, metallurgical treatment of the metal, surface preparation and final surface finish before exposure to test or to service;

b) environmental conditions and duration of exposure;

c) appearance of the corroded surface before and after cleaning;

d) identification of corrosion products and distribution;

e) characterization of pits including: size, shape, density, uniformity of distribution, depth (average and maximum) and location of pits with reference to microstructure, face, edge, crevice, etc.;

f) change in mechanical properties as the result of corrosion and the method by which determined;

g) statistical information.

7 Additional information

More detailed information on evaluation of pitting corrosion is contained in the literature listed in annex B.

Annex A
(informative)

Repeatability of measurements by use of a microscope

A.1 Repeatability of pit depth measurements on a single pit at four magnifications is shown in Table A.1.

A.2 The data in Table A.1 indicate that as the magnification is increased (that is, from × 65 to × 370), the average pit depth that is measured decreases from 0,174 mm to 0,151 mm. Repeatability of measurement improves with magnification, and, as will be shown in A.3, accuracy also shows marked improvement.

A.3 The pit used for measurements in Table A.1 was cross-sectioned and photographed at × 100 through a microscope with a micrometer reticle. As shown in Fig. A.1, the depth measured in cross-section is 0,152 mm. This result is in excellent agreement with that found under high magnification and shown in Table A.1.

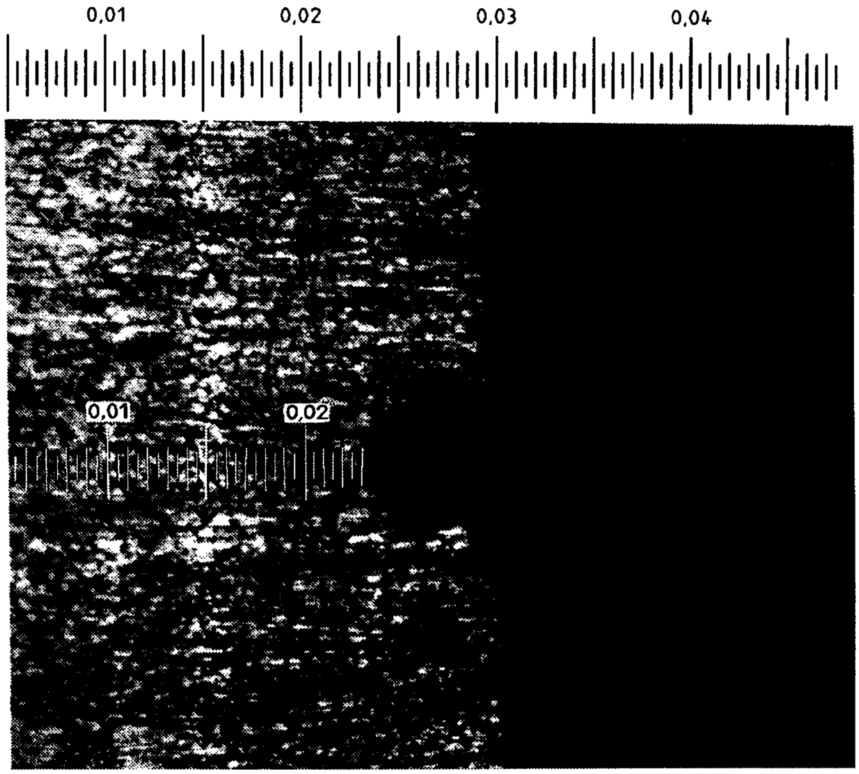
A.4 Pit depth measurements were made over the range from 0,04 to 0,34 mm.

The only limitation to this method is that associated with the range of movement of the calibrated focusing knob on the microscope.

Table A.1 — Microscopic pit depth

Magnification	Pit depth (mm)
65	0,183 0,159 **0,179** 0,174 average
132	0,159 0,16 0,155 **0,159** 0,158 average
200	0,149 0,157 0,15 **0,153** 0,152 average
370	0,151 0,151 **0,152** 0,151 average

Each scale division corresponds to 0,000 5 in (13 µm)



NOTE — Use with × 10 fixed focus objective.

Figure A.1 — Cross-section of pit used for depth measurements in table A.1

Annex B
(informative)

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