

FROM THE DEPARTMENT OF MEDICAL PHYSICS (HEAD: DOC. P. PETERSEN)
OF THE INSTITUTE OF PHYSIOLOGY, UNIVERSITY OF LUND (CHIEF: PROF.
G. KAHLSON) AND THE ORTHOPAEDIC CLINIC, UNIVERSITY OF LUND
(CHIEF: PROF. G. WIBERG)

THE FERROXYLE TEST AS A GENERAL TEST OF THE
CORROSIVENESS OF SURGICAL APPLIANCES MADE
FROM STAINLESS STEEL OR CO-BASED ALLOYS OF
STELLITE-TYPE, MAINLY VITALLIUM AND NEUTRILIUM

By

PETER PETERSEN and HANS EMNÉUS

After the report in 1947 of *Venable & Stuck* on the corrosiveness of modern materials for surgical appliances the manufacturers have used mainly the two alloys considered most reliable, namely acid resistant stainless steel 18 % Cr, 8 % Ni, 2.5 % Mo and Vitallium 65 % Co, 30 % Cr, 5 % Mo. Neutrilium, which in contrast to Vitallium contains Ni and tungsten, has also found some use.

It is known that the stellite-alloys, namely Vitallium and Neutrilium are significantly more resistant to corrosion than acid-resistant stainless steel. However, owing to some of its mechanical properties, such as workability and corrosiveness under stress, stainless steel is still often preferred.

The selection of suitable alloys for surgical appliances is difficult and the current laboratory methods for testing the corrosiveness of such materials are by no means fully significant. In general, it may be stated that there exist a number of different methods, each of which can demonstrate or measure one or at best some of the factors causing corrosion.

The simplest method is weighing before and after exposure to a corrosive medium. This may give a fairly good general idea about the corrosiveness, but seldom allows localization of the process, and usually requires a series of tests, because the weight loss is often too small to be significantly demonstrated by a single measurement. Moreover, if the material has been inserted in an animal or a human being, it is

difficult to clean if the appliance is of complicated shape, and the results will often be erroneous.—Such a method is therefore of little help for ascertaining the presence or absence of corrosion in a given case.

Clarke & Hickman have claimed (1953) and also demonstrated that a measurable factor called “the back electromotive force” can be used as a sort of indicator on the general nobility or inertness of pure metal or an alloy. The back EMF ranges from about +1.5 volt over 0 to roughly —1.5 volt and the measurement is made against a calomel electrode as a reference cathode¹. As a result the elements or alloys measured can be inserted in an expanded detailed voltage chain ranging from plus to minus. The rule is that the more positive a material is, the greater is its nobility or inertness. This is, however, not completely true, because this overall-method hardly demonstrates any change for small local foci of corrosion, and the validity of back EMF is thus rather obscure in materials whose inertness is due to the passive state of the surface layer. This applies to stainless steel and probably also to vitallium. Their actual corrosiveness in a given biological environment is due mainly to local disturbances in the protective surface film and local irregularities which may cause such disturbance are hardly measured by the overall values of their anodic back EMF.

The nature of some such local causes of corrosion has been physically analyzed to some extent in a previous paper by *Emnéus & Petersen* (1958) and investigated further by *Emnéus & Stenram* (1960) in another paper based on biological testing.

Biological tests have also been performed by *Clarke, Hickman & Jennings* in 1958 and their work seems to have demonstrated that there is at least a general statistical correlation between the corrosiveness observed in their tests and the back EMF of the material used.

C. O. Orville, A. B. Ferguson & P. G. Laing (1959) in their monograph on “Metals and Engineering in Bone and Joint Surgery” give a full revue of the whole field, describing the different metals and alloys in use or available and the tests in use for their selection. They also give a survey of the current literature and of earlier work in this field.

From this monograph it is evident that the choice of a suitable metal or metallic alloy is an intricate question, and that no single method available can demonstrate the actual corrosiveness in Loco of a *single appliance*. Besides, there is no method described of such a nature that it might easily be practised in a surgical ward or in a non-specialized laboratory. The need for a good and simple test seems urgent.

¹ For details: see the work of *Clarke & Hickman* quoted above.

However, the literature contains a description of an old test, called the ferroxyle method, which has been used to some extent for testing the porosity of galvanic deposits, such as Ni- or/and Cr-coatings. The Swedish surgeon Prof. Sven Johansson at Gothenburg (1940, 1941) described and used a method which to some extent resembled the ferroxyle test, and he used it for quantitative determination of the rate of corrosion on iron material. The fundamental idea of the ferroxyle method depends on the fact that almost every type of corrosion (with the exception of the so-called "season cracking" and the nucleation or so called "dry corrosion") depends on certain differences between metallic structures in electrical contact. Such differences between structure exposed to an electrolytical environment, tend to create electromotoric forces between the structures in question. Electrolysis will then occur, whereby metallic material at the anode goes into solution. The main corrosive problem is encountered in iron or iron-based alloys. The dissolution of solid iron into ionized form can easily be demonstrated through the presence of ferricyanide ions which immediately combine with Fe to ferrocyanide, which has an intense blue colour. (Turnbull blue). This is in fact the so-called Turnbull reaction, which is also used to visualize and demonstrate iron pigment in tissue.

To perform the ferroxyle test the material to be investigated is immersed in an electrolyte, which originally consisted of a 3 % solution of NaCl. To this about 2 % (by weight) of the ferricyanide of K was added. In such a medium corrosive action is easily and almost instantly observable as blue spots or areas, due to secondary reaction of iron ions with ferricyanide at the anodic corrosive focus. The method gains very much in differentiation if the testing fluid is made viscous by the addition of some suitable neutral substance such as dextrane, pectin or similar organic material. It can even be gelatinized, and in most routine testing this is preferable, because the test specimen immersed in the test environment can then easily be handled and even turned upside down without risk of stirring or spilling. In addition the localization of corrosive spots or areas shows up much more clearly.

After we had tried this test for some time and also modified it somewhat, we found it to be a most useful *general* test for almost every kind of corrosion in stainless steel. It demonstrates not only site of the process but also the intensity. By magnification (working microscope) even very small foci, such as the interaction between structures in an etched surface can be detected.

The test is normally performed by embedding the material to be

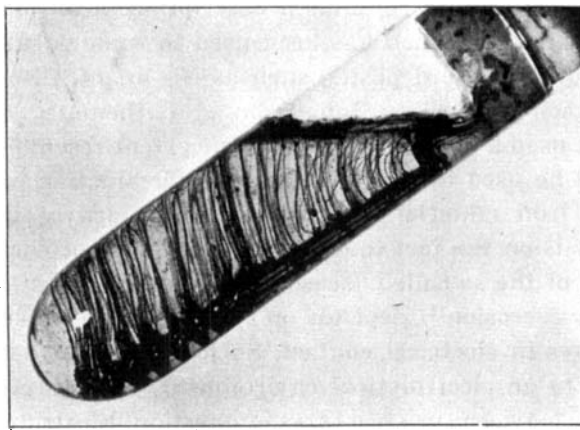


Fig. 1.

Wing screw, Sven Johansson design, manufactured from simple chromium steel. The picture of vivid corrosion was evident 30 min. after the screw had been placed in the ferroxyle gel. The photo was taken 2 hours after commencement of the test.

studied in a ferricyanide-containing, transparent indicator jelly with NaCl as the electrolyte. The material to be tested should be placed in a glass or perspex vessel and the jelly be warmed to about +45° C and poured over the test material until it completely covers the latter. In the ferricyanide environment the corrosion centres are clearly indicated by a colour reaction around the active anodic points. Figs. 1, 2 and 3.

The composition of the jelly was as follows:

NaCl in aq. dest.	10/1.000 g.	1 %
Gelatin	50 g.	5 %
Potassium ferricyanid	20 g.	2 %

The result is a product that is fluid at above 40° C and soon sets at room temperature. pH range is bestween 5.5–6.0. The solution is yellow. Corrosion of an Fe-containing test object in such a jelly will be demonstrated by a reaction between the released Fe-ions and the ferricyanide radical, which gives the blue colour (Turnbull reaction). The intensity is impressively indicated by the rapidity of growth in each focus. The surface often becomes passive and the spots stop growing.

The method is fast and medium active centres of corrosion can usually be detected within two or three minutes.

While working with the ferroxyle test on stainless steel it was con-

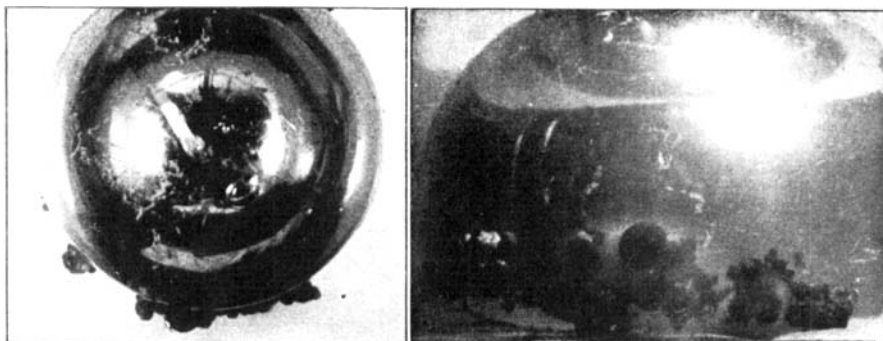


Fig. 2.

Fig. 3.

Figs. 2 and 3.

Fig. 2. Smith-Petersen cup, made of 18-8-stainless steel. The cup was removed from a patient because of luxation from its position in the acetabulum. There were many small scratches all over the sphere, possibly made on removal; corrosion was shown by the ferroxyle test only in a few places, as seen in the fig. The colour of the bubbles was blue, resembling that of Turnbull blue.

Fig. 3. Lateral view of the same Smith-Petersen cup as in fig. 2. Each bubble indicates one anodic area.

sidered worthwhile to try the method also on non-ferrous alloys Co-Cr-Mo and Co-Cr-Ni alloys.

Addition of cobalt salts to potassium ferricyanide causes a black-brown-violet precipitation.

On addition of nickel salts to potassium ferricyanide a yellow-brown precipitate is formed.

Actual tests clearly demonstrated that it was in fact possible to demonstrate corrosion products from cobalt and nickel alloys by the same simple method. Co-Cr-Mo-alloy (vitallium) is very resistant to corrosion. *Bowden, Williamsson & Laing* have, however, shown the presence of Co in the tissue round vitallium appliances. Co-Cr-Ni-alloy without tungsten has been used in dentistry together with vitallium. Such an alloy, called alloy S, was tested by *Hickman & Clarke* and it had a back EMF of 750 millivolts, thus 100 millivolt better than vitallium.

Experimentally we could demonstrate local action-corrosion of Co-Cr-Ni-alloy, but not on genuine vitallium manufactured by Austenal.

To bring about galvanic corrosion Co-Cr-Ni-alloy and Co-Cr-Mo-alloy (vitallium) were put in good contact by electric spot welding. When testing this system with the ferroxyle test rich precipitation around active foci was demonstrable. See Fig. 4.

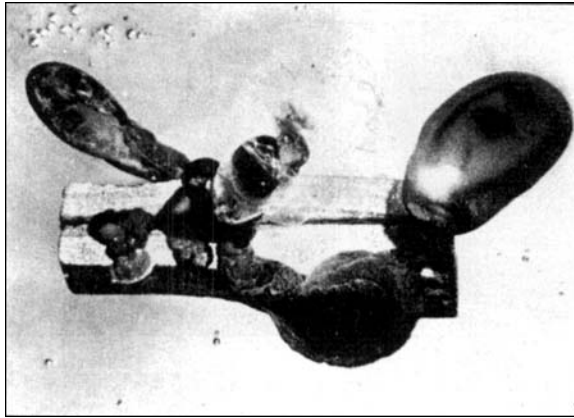


Fig. 4.

Two pieces of slightly different cobalt-chromium alloy, spotwelded together and exposed in ferroxyle gel. One is the ordinary vitallium with Co 65%, Cr 30% and Mo 5%. The other is the so-called soft vitallium, which is composed of Co 52%, Cr 19%, Ni 28% and Mo 0.5%. The bubbles indicate galvanic corrosion with the "soft vitallium" as anode. The colour of the bubbles is dark brown to violet and with a yellowish tint in some places. The photo was taken 24 hours after commencement of the test.

The precipitate was identified as Co and Ni salts with dominance for Co by roentgenspectrographic analyses.

As said above, the process of indication is fast and corrosion centers may often be detected two or three minutes after exposure to the indicator jelly has started, and is as a rule marked after some hours or a day (Fig. 1).

When examining corrosion of non-ferrous alloys containing cobalt it was always necessary to prolong the test period over at least several hours, in many cases a day or more.

The transparency of the medium and of the vessel, makes it possible to observe all parts of the object. The stiffened jelly fixes each process in position and at the same time permits inversion of the vessel for inspection.

Even protracted reactions which are mainly found in cobalt alloys, can easily be observed by the aid of this test method. If desired the time of observation at room temperature may be prolonged to at least two weeks. After that time there is a risk of infection and growth of microorganisms which usually destroy the jelly. Very long-term observation therefore requires a closed vessel and aseptic conditions which

can, however, be readily obtained. It is also possible to prolong the observation time by the addition of a suitable antiseptic with a low electrolytical activity, i.e. a low dissociation-rate.

The ferroxyle method has been found to have some essential characteristics which should be emphasized.

1. The aggressiveness of the test depends to a large extent upon the electrolyte concentration. In our test-case (surgical prosthesis) 1 % NaCl was chosen because of its relative similarity to the electrolyte system of the body. A ringer solution may also be used, and regularly give similar results. The 3 % NaCl-solution is by far more aggressive, and is not necessary for our purpose. For industrial tests such a concentration is, however, recommended. In addition other electrolytes corresponding to specific corrosive environment may be used in such a case.

2. The ferroxyle-test in 2 % ferricyanide is *provocative* and therefore over-sensitive. In the relatively strong ferricyanide, the reaction with the heavy metal results in the formation of a semipermeable membrane, a Traube cell, that tends to prevent diffusion from the interior into the surrounding jelly. Inside the cell the reaction products raise the osmotic pressure and the cell therefore tends to grow not only as a direct result of electrolytic action but also owing to water absorption caused by osmosis. The result is a bladder, which tends to grow relatively rapidly and which behaves as "a corrosive isolate" created over the point or area of initial corrosion (Fig. 3). Such an isolate tends to prevent the occurrence of a passive state in stainless steels. Once started under such circumstances the corrosion may therefore continue to increase even after the corrosive type of material in the corrosive nucleus is fret away.

3. The provocative properties of the test can be modified by the use of a more diluted ferricyanide. At 0.2 % the formation of Traube-cells, acting as corrosive isolates, is very slight and at this concentration the sensitivity appears to be crudely tuned to a "biological level" which appears suitable for general testing of stainless steel appliances of unknown material which should not be appreciably damaged by the test.—It should be stressed, however, that a really good quality stainless steel ought to tolerate also the more severe 2 % ferricyanide test.

4. It is possible to test the effect of different environments around the same test object. For instance two concentrations of electrolyte can be used in two different zones of the object. Moreover, pH and the type of electrolyte may be kept at different levels in different areas.—The gaseous environment can also be controlled. It is thus possible to work



Fig. 5.

100 rods with a diameter of 2 mm, and a average length of 20 mm, were cut from two qualities of stainless steel wire, 50 rods, thus 100 cut ends of each quality. The upper 50 is the ordinary 18-8-steel. The lower 50 is of a higher quality. When cutting wires like this there will always be some deposition from the cutter and a rough and deformed surface easily susceptible to corrosion is formed. This picture will illustrate how easy it is to get a statistical evaluation of differences in a special corrosion resistance between two stainless steel qualities by means of the ferroxyle test. There is a reaction in at least 99 of 100 cut ends of quality 832 M, but only in 29 of 100 ends of quality 832 SL.

in either an oxygen-rich or an almost oxygen-free atmosphere and also in an atmosphere rich in CO_2 . These conditions may be achieved over only a part of the object or over the whole of it. Such local differences in environment are common in living tissue. They may cause corrosion just as well as differences in the material tested. It is, of course, highly valuable that the test can imitate all the different conditions in living tissue. This can even be done fairly easily in most cases.

5. The products of the corrosion are to some extent fixed in position by the jelly and may therefore be made the object of analysis, either directly by chemical methods or by beam spectrography. On the other hand a quick process protrudes through the jelly like a spear with the result that an intensive reaction at any active point is very impressively indicated by the growth in one direction (Fig. 1).

6. The methods of choice for obtaining objective results in this test method are either photography (mostly in colour) or statistical methods on a large number of objects in the same jelly. The number of corrosive points in any given, representative test population, can thus easily be determined and compared with other materials (Fig. 5).—By photography at intervals not only *localisation* but also *intensity of growth* can be investigated. For demonstration purposes a film with compressed time factor can thus be made very impressive. It is a great advantage that the method can easily be adapted statistically because fifty or even 100 specimens of the same sort can be tested at the same time in one tray. Comparison between two materials, even statistically, is not time-consuming.

7. The method is useful for the study of combinates made from two materials (e.g. two different brands of stainless steel) and also for the investigation of maltreatment such as overtension, compression, torsion and deposition through tools etc. of small amounts of some different metal. In all such cases a great number of test objects can easily and quickly be handled in one vessel and the result be photographed for comparison. Note: In comparison it is evidently necessary to keep *not only time but also temperature uniform*.

SUMMARY

A study has been made to find a suitable general test method for the surgical prosthesis of metallic material, mainly stainless steel or vitallium. It is emphasized and demonstrated that the so-called *ferroxy-le-method* is useful for such a purpose. This technique is described and discussed, and some essential features of the method are stressed and analysed. The method is cheap and simple and is recommended for routine use not only in the research institutes but also as a means of control in a hospital if there is any doubt concerning the reliability of the material in use.

RESUME

Une étude a été faite en vue de trouver une méthode générale d'essai appropriée pour les prothèses chirurgicales de matière métallique, principalement d'acier pur ou de vitallium. Il est souligné, avec exemples à l'appui, que la méthode dite "ferroxy!" est utile dans ce but. Cette technique est décrite et discutée et certains faits essentiels de la méthode sont relevés et analysés. La méthode est peu coûteuse et simple

et elle est recommandée pour usage routinier non seulement dans les Instituts de Recherches, mais aussi comme un moyen de contrôle dans les hôpitaux s'il y a un doute quelconque concernant la confiance que l'on peut avoir dans le matériel utilisé.

ZUSAMMENFASSUNG

Eine Untersuchung wurde vorgenommen um eine brauchbare Methode einer allgemeinen Prüfung von chirurgischem, metallischem Prothesenmaterial, hauptsächlich rostfreiem Stahl oder Vitallium zu finden. Man hebt an Hand von Beispielen hervor, dass die sogenannte *Ferroxyl-Methode* für ein solches Vorhaben verwendbar ist. Diese Technik wird beschrieben und besprochen und einige wesentliche Züge der Methode werden betont und analysiert. Die Methode ist billig und einfach und wird zum Routinegebrauch nicht nur in Forschungsinstituten, sondern auch als ein Kontrollmittel an Krankenhäusern empfohlen, wenn irgendwelcher Zweifel hinsichtlich der Verlässlichkeit des gebrauchten Materiales besteht.

REFERENCES

- Bechtol, C. O., Ferguson Jr., A. B., Laing, P. G.:* Metals and engineering in bone and joint surgery. The Williams & Wilkins Company, Baltimore, 1959.
- Bowden, F. P., Williamsson, J. B. P. & Laing, P. G. J.:* J. Bone Jt Surg. 37 B: 676, 1955.
- Clarke, E. G. C. & Hickman, J.:* J. Bone Jt. Surg. 35 B: 467, 1953.
- *Ibid.* 40 B: 799, 1958.
- Corrosion in Action:* The International Nickel Company, Inc. New York 5, N.Y.
- Emnéus, H. & Petersen, P.:* Nord. Med. 1958: 59: 593.
- Emnéus, H. & Stenram, U.:* Acta Orthop. Scand., in press.
- Evans, U. R.:* Metallic Corrosion Passivity and Protection, Edvard Arnold and Co., London 1946.
- Johansson, Sven:* Jernkontorets annaler Årg. 124: 629–631, 1940.
- *Ibid.* Årg. 125: 599–613, 1941.
- Laing, P. G. J.:* J. Bone Jt. Surg. 40 A: 853, 1958.
- Tödt, Frits:* Korrosion und Korrosionsschutz. Corrosion of ferrous materials involving the absorption of oxygen.
- Uhlig, Herbert H.:* The corrosion handbook, John Wiley and Sons, Inc. New York, New York, U.S.A. 1948.
- Venable, C. S. & Stuck, W. G.:* J. B. Jt. Surg. 30. A: 247, 1948.