From: The Department of Pathology I
(Head: Professor *C-M. Fajers*), the
Medical School, Umeå and the Royal
School of Dentistry, Umeå, Sweden.

STANDARDIZATION, BY MEANS OF ULTRASONIC TREATMENT, OF TEST SAMPLES FOR LABORATORY STEAM-CORROSION TESTS

by

LARS G. HOLMLUND

One important condition for investigations of corrosion attack is that a satisfactory procedure for the standardization of the test material has been developed (*Uhlig* 1948, *Evans* 1960). In the present work, the primary aim was to study the corrosion inhibition caused by the addition of various substances to the corrosive medium. In studies on corrosion and its inhibition during the sterilization of surgical and dental instruments of carbon steel in the autoclave, relatively short experimental periods are necessarily employed. The amount of corrosion products formed per unit surface area is therefore small and thus an accurate standardization of the test material is especially important. For this reason the instruments were replaced by test samples prepared in different groups, each group corresponding to a particular type of dental or surgical instrument made of carbon steel. The dimensions, composition and pretreatment of the samples were the same in each group. However, during preliminary investigations, it was found that test samples from the same group exhibited considerable differences despite careful cleaning with ether and repeated rinsing with de-ionized water. The reason for this may have been, among other things, that the surfaces were oxidized to different degrees and that the surface crystals were probably cold-deformed to different extents during

the final polishing. Pickling of the test samples in diluted acids containing pickling inhibitors gave a surface of uneven quality. The sand blasting of metal surfaces prior to laboratory corrosion tests is considered to result in a consistent corrosion pattern but is liable to leave particles of sand embedded in the materials. (*Evans* 1960, *Freedman, Drawincks & Ostroffsky* 1960.)

Osterman (1959), *Koontz & Amron* (1959) and *Gollmick* (1962) maintain that, for the electroplating of metal surfaces, a mechanical cleaning by ultrasonic treatment gives better results than any known chemical method. In the present work, the effect of a pretreatment of test samples by means of ultrasonics was therefore more closely investigated.

MATERIAL INVESTIGATED

The material used for the test samples was made by Sandvikens Jernverk, and the samples themselves were manufactured by AB J. Sjöding, Stockholm. The shape of the samples was cylindrical, 45 mm long and 5 mm in diameter. Analytical data etc. are given in Table 1.

Table 1

Analysis in % of steel sample

Group 1	C	Si	Mn	Cr	W	V	Pb	Structure	Corresponding instrument
Sandvik 21T10P	1.25	0.15	0.3	0.25	1.7	0.1	0.2	Martensite	Dental burr

APPARATUS

A Narda ultrasonic apparatus*) was employed. It consists of a generator, cleaning tank and a transducer built into the bottom of the tank. Electrical impulses from the generator are converted by the transducer into mechanical vibrations. This causes

*) Ser. 600. Generator: Model 60 1. Frequency: 40 KC. Power input: 117 V, 50/60 cps, 2.0 amp. Transducerized Tanks: Model 602 Type Titanate. Frequency: 40 KC. Compartment Dimensions: 5×9¼×6 in.

the bottom of the tank to vibrate and produces cavitation in the liquid in the tank, *i.e.* the rapid collapse of thousands of microscopic bubbles within the solution. The bubbles grow in size until they collapse violently with the production of high local velocities and pressure (*Noltingk* 1959). The cavitation occurring during ultrasonic cleaning, however, causes erosion (sometimes accompanied by corrosion) to take place on the metal surfaces of the probe (*Rheingans* 1958).

PRINCIPLE OF STANDARDIZATION TECHNIQUE

If a number of test samples, which are similar as far as composition and method of production are concerned, are placed in separate test tubes containing the same cleaning liquid and if the tubes are then immersed in an ultrasonic tank in definite positions, chosen so that each tube is subjected to the same treatment during the ultrasonic cleaning, then after a certain time the surfaces of the samples will become more "similar" to each other than they were in the beginning. If this "cleaning time" is divided up into a number of equal cleaning periods, in which each sample is placed, before each new cleaning period, in a new tube (containing fresh cleaning liquid) in the same place in the tank as before, then it is possible to study quantitatively the effect of the ultrasonic cleaning by analysing the cleaning liquid for dissolved Fe. When the amounts of Fe in the cleaning liquid become constant, one can consider the surfaces of the different samples to be standardized and mutally similar and thus similar with respect to their way of reacting to this treatment. One condition is of course that the cleaning method itself is accurately standardized and that the cleaning system is not overloaded.

In order to produce, as far as possible, an effective and constant cleaning procedure and a suitable surface state for the subsequent investigation of these test samples, the ultrasonic cleaning was standardized with respect to:

(1) Frequency and plate current,
(2) Amount of water in the cleaning tank,
(3) Temperature of the water in the tank,

(4) The cleaning tubes and their positions,

(5) Cleaning liquid,

(6) Cleaning time.

(1). The frequency was 40 KC and the plate current 60—80 scale divisions. A voltage stabilizer was connected between the mains and the generator.

(2). The amount of water in the tank was 1800 ml (tap water). The dissolved gases in the water were removed by subjecting it to caviation for 4 min(degassing).

(3). In order to avoid too great an increase in the temperature of the water in the tank, it was considered advisable to replace the water every 14th minute. The water temperature was registered after gas removal (i.e. after 4 min) and after each fifth 2 min shaking period (see section 6 below). The temperature after degassing was 14—15° C and after five 2 min shaking periods 18—20° C.

(4). After rinsing in ether, the samples were placed in flat-bottomed pyrex tubes containing de-ionized water (*i.e.* cleaning liquid) (see section 5). The dimensions of the tubes were: height, outer 100 mm, inner 98.5—99 mm; diameter, outer 13.5—14 mm, inner 11—11.5 mm. During the ultrasonic cleaning, the tubes were placed directly over the transducer and were immersed to a depth of 2 cm from the bottom of the tank. The surface of the tank water was thus above the level of the cleaning liquid in the tube. The tube holder was clamped to the edge of the tank in such a way that its lower surface was just above the liquid level in the tank. (Fig. 1).

Preliminary experiments showed that the cleaning effect is reduced if the tubes are placed in the holder so that they are in contact with the bottom of the tank immediately above the transducer. In order to obtain reproducible results in ultrasonic experiments on the kinetics of the oxidation of ferrous iron, *Miller* (1951) also found that it is essential to maintain the "cell" in a fixed position with respect to the source of sound.

(5). The cleaning liquid consisted of 5 ml de-ionized water in which the samples were completely immersed during the ultrasonic treatment. In order to remove dissolved gases, the liquid

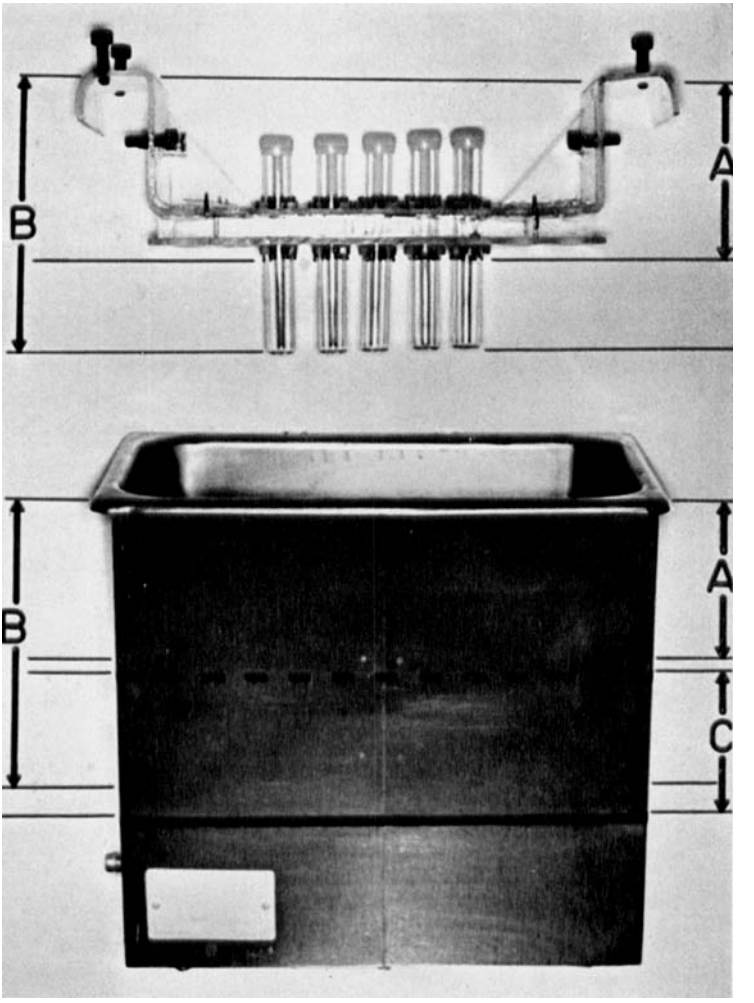

Fig. 1. Cleaning tank and tube holder. The full line indicates the internal bottom surface and the dashed line the water level in the tank. The distance A shows how the lower surface of the holder is situated relative to the water surface in the tank while B indicates how the tubes are placed in relation to the bottom of the tank. C is the height of water in the tank.

was allowed to cavitate for 4 min immediately before the sample was immersed in it.

(6). A temperature increase in the cleaning liquid can also result in increased erosion and corrosion attacks on the surface of the sample (*Rheingans* 1958, *Osterman & Santa Lucia* 1960). For this reason, the ultrasonic treatment has been divided up into 2 min cleaning periods. At the beginning of each new cleaning period, the sample was shifted to a fresh tube containing 5 ml de-ionized water (see section 5). Each sample was altogether subjected to 10 cleaning periods, *i.e.* it was ultrasonically cleaned for 20 min.

DETERMINATION OF IRON

The amount of dissolved Fe in the cleaning liquid was determined by a modified ortho-phenanthroline method (*Holmlund* 1963). Duplicate determinations were performed for each sample and cleaning period. The amount of dissolved iron is given as $\mu g/cm^2$ test sample surface area. The error in the method was found to vary between $\pm$ 0.01(3) and $\pm$ 0.02(8) μg Fe/cm^2.

PROCEDURE IN THE PRESENT INVESTIGATION

In a preliminary series of experiments with an increasing number of test samples, it was found that the effect on the surface of the ultrasonic treatment described above was still apparently similar when 5 test pieces, placed directly over the transducer built into the bottom of the tank, were cleaned simultaneously. For this reason and since five samples was a satisfactory number for the investigations planned, it was decided that the studies in this work would comprise 12 series with 5 test samples in each, each sample being ultrasonically cleaned as described above for a total of ten 2 min cleaning periods.

RESULTS

Fig. 2 shows the amount of dissolved Fe/cm^2 test sample surface area for each cleaning position in the ultrasonic apparatus and also how the amount of dissolved Fe varies both with re-

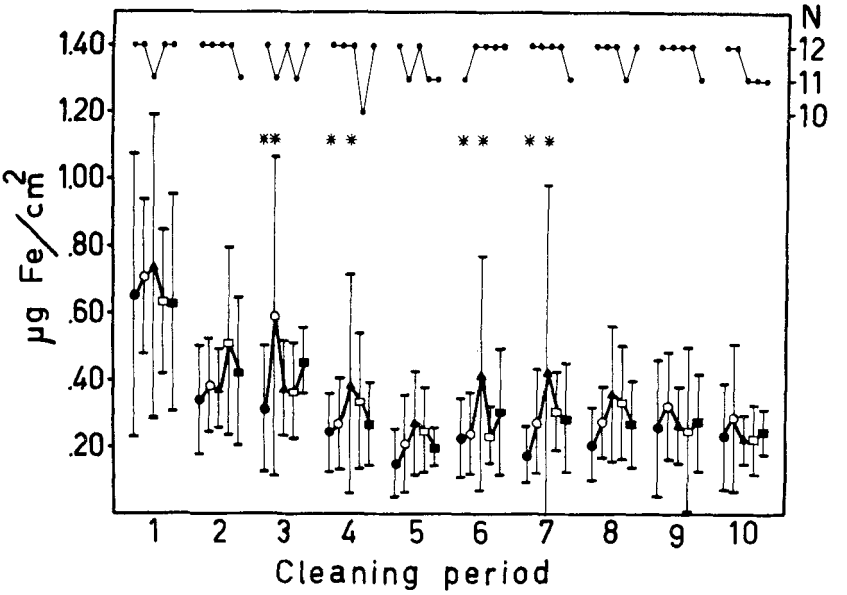

Fig. 2. Amount of dissolved Fe/cm² test sample surface area for each cleaning position during the different cleaning periods. The asterisks indicate the occurrence, during the cleaning period, of significant differences in the amount of dissolved Fe/cm² between the cleaning positions thus indicated. The other symbols denote:

● Mean value, cleaning position 1
o „ „ „ „ 2
▲ „ „ „ „ 3
□ „ „ „ „ 4
■ „ „ „ „ 5

I = Standard deviation

N = number of test samples per cleaning position.

spect to the different cleaning positions in the apparatus during each cleaning period and also with respect to the different cleaning periods. Significant differences in the amount of dissolved Fe are observed between the different cleaning positions during cleaning periods 3, 4, 6, and 7 whilst the remaining cleaning periods do not exhibit any such significant differences, neither with respect to the mean values nor to the standard deviations. It is also clear from Fig. 2 that the mean values for the amount of dissolved Fe for the different cleaning positions become successively more and more similar with increasing number of cleaning periods.

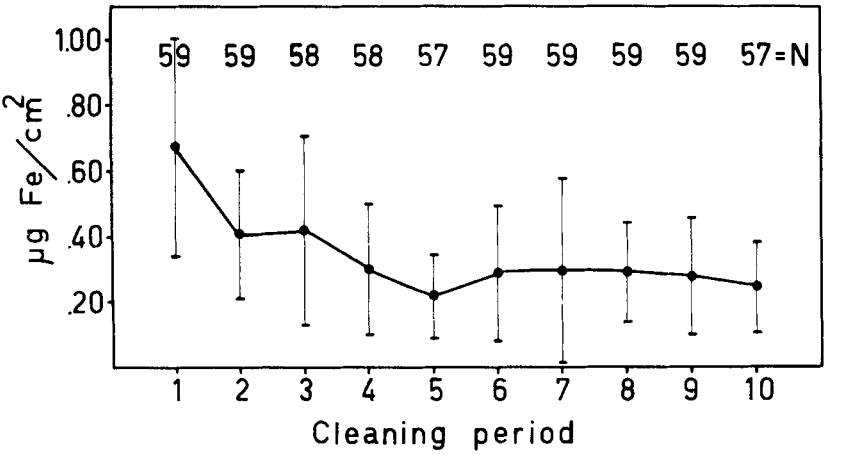

Fig. 3. Amount of dissolved Fe/cm² for all test samples and each cleaning period. The full line indicates the mean values and the vertical lines the standard deviations. N denotes the number of test samples per cleaning period.

If, however, the variation in the amount of dissolved Fe with respect to cleaning period is considered, then it is seen (Fig. 3) — as is also apparent from Fig. 2 — that this quantity decreases up to cleaning period 5 but remains steady thereafter. Moreover, the SD also mainly decreases with increasing number of cleaning periods (Fig. 3).

DISCUSSION

Preliminary investigations on the possibility of standardizing various surgical and dental instruments made of carbon steels, in order to study during relatively short periods the susceptibility to corrosion and/or corrosion inhibition, indicated large variations from experiment to experiment. Even after the instruments were replaced by test samples made from the same material as the instruments, difficulties were encountered in obtaining, despite careful standardization during manufacture, the experimental material sufficiently uniform. Mechanical cleaning by means of brushing and washing did not give a sufficiently homogeneous starting material, and pilot studies indicated that

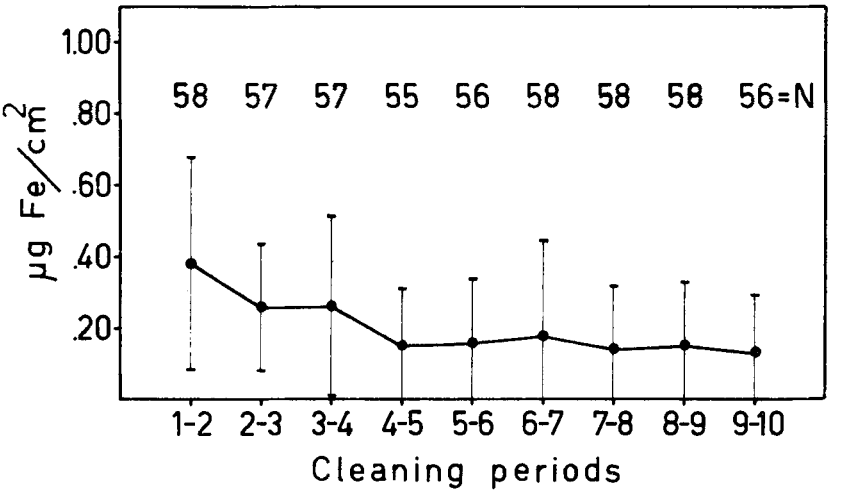

Fig. 4. Mean values (full line) ± standard deviations (dashed line) for the differences in the amount of dissolved Fe/cm² for each test sample between two successive cleaning periods for the whole experimental material. N = number of test samples for which this difference was calculated.

standardization using diluted acids containing pickling inhibitors results in a far too variable surface destruction and a far too large dissolution in comparison with the surface attack occurring during the actual corrosion test. Since good results had been obtained by the ultrasonic cleaning of metal surfaces subjected to electroplating (*Osterman* 1959, *Koonz & Amron* 1959, *Gollmick* 1962, *Barber* 1963), this method was tried for the standardization of the surfaces of the test samples.

Fig. 2 and perhaps more particularly Fig. 3 indicate that two different stages occur during the cleaning process. Cleaning periods 1 to 5 must represent a mechanical cleaning of the samples in which loosely attached impurities and also surface crystals that have been cold-deformed to different extents during the final surface polishing are primarily removed. The curve for cleaning periods 6—10 is mainly horizontal and the standard deviations decrease. During each of these latter cleaning periods, the aqueous medium contains about the same amount of Fe, this amount probably representing mainly corrosion products formed during the cleaning process. If, for each separate sample, the

amount of Fe/cm² dissolved out during two successive cleaning periods is constant, then this means that the surface of the sample under the experimental conditions operating here gives the same amount of Fe/cm² when it is subjected to the same action.

Fig. 4 shows the mean values ± SDs for the difference in the amount of dissolved Fe/cm² from one and the same test sample between two successive cleaning periods for the whole of the experimental material. From this curve it is apparent that, up to cleaning periods 4—5, the amount of Fe dissolved out per cleaning period decreases but thereafter remains fairly constant as far as the mean value is concerned while the SDs becomes smaller towards the end of the curve, *i.e.* with increasing number of cleaning periods. Significant differences in the amount of dissolved Fe/cm² did not occur, for the test samples in the different cleaning periods, between cleaning periods 8, 9, and 10. Moreover, the amount of dissolved Fe/cm² does not differ significantly for the samples in the different positions in the ultrasonic tank during these cleaning periods (Fig. 2).

The surfaces of all the test samples reacted uniformly during this stage of the ultrasonic cleaning, *i.e.* the different surfaces had now reached a state of dynamic equilibrium. This would therefore indicate that the material can be considered to be well standardized and thus suitable for corrosion investigations.

SUMMARY

A method for the standardization, by means of ultrasonics, of test materials for corrosion investigations is described.

Test samples corresponding to one type of dental instrument made of carbon steel were employed. Their dimensions, composition, and pretreatment were the same in all cases. After preliminary cleaning, they were standardized by means of ultrasonic treatment. To do this, it was necessary to standardize the various stages of the ultrasonic process.

The results show that this treatment gives a well standardized material with a surface which is sufficiently uniform from a corrosion point of view and thus suitable for corrosion investigations.

RÉSUMÉ

STANDARDISATION, À L'AIDE DE TRAITEMENT PAR ULTRA-SONS, DES ÉCHANTILLONS POUR TESTS DE CORROSION À LA VAPEUR AU LABORATOIRE

L'auteur décrit une méthode employant les ultra-sons pour la standardisation des matériaux d'essai pour recherches sur la corrosion.

Des échantillons d'épreuve correspondant à un type d'instrument dentaire fait d'acier au carbone ont été utilisés. Leurs dimensions, leur composition, et le traitement préliminaire ont été les mêmes dans tous les cas. Après un nettoyage préliminaire, ils ont été standardisés au moyen d'un traitement par ultra-sons. Dans ce but, il a été nécessaire de standardiser les différentes phases du traitement ultrasonique.

Les résultats montrent que ce traitement donne un matériau bien standardisé, dont la surface est suffisamment uniforme du point de vue de la corrosion, et par conséquent appropriée aux recherches sur la corrosion.

ZUSAMMENFASSUNG

STANDARDISIERUNG DES MATERIALS FÜR EXPERIMENTELLE DAMPF-KORROSIONSTESTS MIT HILFE VON ULTRASCHALL

Es wird eine Methode zur Standardisierung des Versuchsmateriales für Korrosionsuntersuchungen mit Hilfe von Ultraschall beschrieben. Dentalinstrumente eines bestimmten Types aus Karbon-Stahl (Hartmetall) wurden in der Versuchsreihe angewandt. Ihre Dimensionen, Zusammensetzung und Vorbehandlung waren in allen Fällen die gleichen. Nach vorausgegangener Reinigung wurden sie mittels Ultraschallbehandlung standardisiert. Hierzu was es nötig, die einzelnen Stadien des ultrasonischen Prozesses zu standardisieren.

Die Ergebnisse zeigen, dass man durch diese Behandlung ein gut standardisiertes Material erhält mit einer Oberfläche, die hinreichend gleichartig ist im Hinblick auf die Korrosion und sich daher für Korrosionsuntersuchungen eignet.

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