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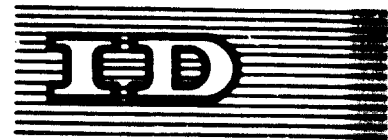
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D04683



United Nations Industrial Development Organization

Distr.
LIMITED

ID/WG.152/1
14 March 1973

ORIGINAL: ENGLISH

Seminar on Food Processing
and Packaging

Guatemala City, Guatemala, 7 - 12 May 1973

RAPID TEST METHODS FOR CHARACTERIZING
PRODUCT/CONTAINER REACTIONS WITH
TINPLATE AND ALUMINIUM CONTAINERS^{1/}

by

Dr. Gerd Habenicht
General Manager
Research and Development
Schmalbach-Lubeca-Werke A.G.
Braunschweig
Federal Republic of Germany

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1. Introduction

(1) As long as metal containers have been used for commercial packaging of food, non-food and cosmetic products, the industry has tried to predetermine potential product/container reactions quickly by so-called rapid test methods. To obtain such information by way of storage tests under normal field conditions is often time-consuming and expensive. Running tests under field conditions means that an adequate number of containers - often several hundred units - have to be filled with the product to be tested, stored for up to two years and controlled at regular intervals.

(2) These conventional storage tests can hardly be dispensed with for the study of basic problems. The demand for reliable rapid test methods, however, has increased in recent years, since manufacturers want to benefit from market prospects for new products quickly and products are frequently modified for differentiation. If, in former times, the demand for rapid test methods for product/container reaction was a well-reasoned desire, it is now, in most instances, a real necessity.

(3) Everybody who starts working on rapid test methods for metal containers will soon recognize the multitude of problems involved. The objective of this paper therefore is to report, under current aspects, on some major rapid test methods, their application, advantages as well as their inherent risks.

2. Defined objectives of rapid test methods

(4) No matter whether a rapid test method or a conventional long-term storage test is concerned, a clear definition of the objectives in the planning phase is an essential factor for the quality of the final results.

(5) The term "product/container reaction" implies that the mechanism is one of potential reciprocal action. The more data are available about reactivities and potential reaction results for the two factors product and container, the better can a plan for the execution of the test be set up and the more reliable is the evaluation of the results. This is particularly true for rapid tests.

(6) If, for instance, the laboratory staff concerned have special knowledge of packaging materials, they will have a hard time to carry out the test and evaluate the results unless they have adequate knowledge of or detailed information on the product. On the other hand, if the laboratory staff are purely product-oriented and have inadequate knowledge of the specific container material properties, they will invariably run the risk of an inappropriate test setup and poor evaluation of the results.

(7) The saying "You can gather the more knowledge the more you know already" is fully true for this case as it is for a variety of other aspects.

(8) With reference to rapid test methods, this means also that the safety of a rapid test result will be the better the more experience is available of similar or comparable product/container combinations. With

such background at hand, the objective of the rapid test may at best be confined to the clarification of one specific detail. This offers considerable advantages over a situation where many unknown factors are involved and where the definition of the objectives of a rapid test is a risky game. What these problems look like in practice will be explained below in connection with the individual rapid test methods.

2.1. Negative selection by rapid tests

(9) An essential objective of rapid tests may be to gain a survey of the conditions rather than to obtain accurate detailed information. Instead of a clear "yes" or "no", the objective of the test will, in the first instance, be an overall distinction between poor and positive prospects for success. Such a screening by rapid test methods is very common and particularly useful in cases where a great number of variations are to be tested. For instance, if this screening by rapid test methods showed that eight of ten theoretical variations have little chances of success, work on the resulting two, more promising versions can be intensified.

(10) This negative selection is therefore frequently applied for determining the adequateness of a specific package for a specific product. One of the major reasons for this is the fact that several rapid test methods give more reliable results for the exclusion than for the adoption of a product/container combination.

2.2. Consideration of reference standards in rapid tests

(11) Another major objective of test methods is the comparison of performance properties under extreme conditions, but with inclusion of reference standards. This is a useful method whenever several unknown factors are involved and clarification is sought first where to march for realistic solutions.

(12) One should not overlook in this connection that the economic side is an important factor in the evaluation of product/container combinations. The price of the package in relation to the product to be packed has to be considered in the determination and establishment of container target values, and comparative tests are often a helpful means for finding out the justifiable and not too expensive ideal solution.

2.3. Product analysis as a means for rapid evaluation

(13) Product analysis is one of the most important and most rapid methods yielding data for evaluating the suitability of a product/container system. Mostly, an expensive quantitative analysis of all components is not required, but various characteristics have to be examined, and a comparison with corresponding data for similar materials may be highly informative.

(14) The type of characteristic data to be determined may, of course, vary widely with the product type.

(15) For food products, the determination of the following data ranks foremost:

- pH as a general criterion for acidity,
- the concentration of free or combined acids, such as acetic acid, lactic acid, citric acid, malic acid, ocalic acid, sulphuric acid or phosphorous acid,
- salt, fat or sugar content,
- nitrite and nitrate content,
- phosphates,
- presence of metal traces in the product, especially copper.

(16) If these test data are available for a food product, its behaviour can be predetermined to some extent and hence container specifications can be established.

(17) Non-food and cosmetic products may be even more problematic. If the products are based on organic solvents, requirements on the container are mostly clear. If, however, anorganic or organic hydrous systems are concerned, general information by means of analytical data will be of limited use for defining the chemical and technological requirements on the container specification.

(18) Of course, information on pH, acid or chloride content will be valuable also in this case. Slight modifications of a formula, however, which can hardly be determined by analytical methods, may change the product/container reaction so radically that simple characteristic data will be insufficient. Even a detailed knowledge of the composition of the product will often be inadequate for assessing its overall reactivity, so that a performance test will be the only reliable means for an evaluation of the product.

3. Chemical/physical analytical test methods for the predetermination of product/container performance

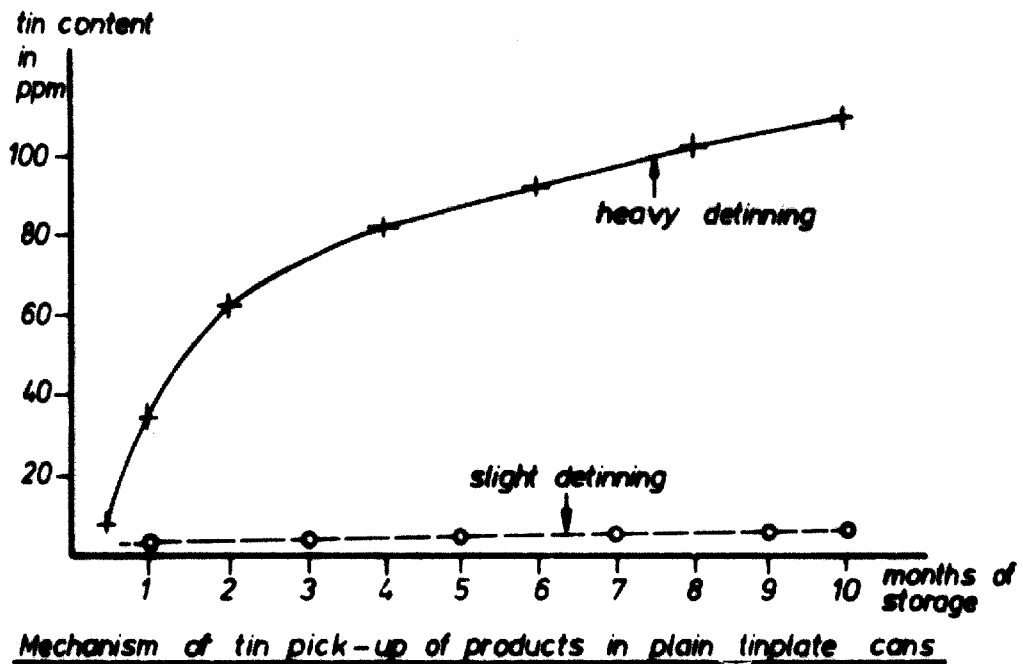
3.1. Early determination of product/container reactions by chemical or physical analysis

(19) A product/container reaction which is assumed to occur in the course of storage should be assessable by appropriate analytical testing of product and packaging material or by determination of the reaction products. It will be a question of economics what personnel and instrumental expenditures will be justified for determining minute changes by analytical testing.

(20) It has been common practice for many years to obtain additional information on product/container reaction through storage testing of food in tinfoil cans by determining the so-called iron and tin pick-up values. A graphical evaluation of a great number of such measuring results makes obvious that the metal pick-up curves follow more or less the same pattern (see figure 1).

(21) Although the data of individual packages will scatter, a precise determination will be possible with a sufficiently large number of test cans.

Figure 1



(22) If the curve for the metal pick-up of a specific product or container type is known, a relatively reliable extrapolation for the metal pick-up over considerably longer storage times will be possible on the basis of one or two months' storage data.

3.2. Product analysis by means of atomic absorption spectrophotometry

(23) A prerequisite for rapid analytical testing is the availability of reliable test methods for quantitative determination of the element in question at a concentration of 1 ppm or even smaller. The atomic absorption spectrophotometry may be considered as a suitable analytical method for determining various

metals which may play a role in metal packaging problems, for instance iron, tin, lead, aluminium, chromium or copper. A laboratory with such equipment will be able to carry out a great number of trace analyses per day with low personnel expenditure, so that within few weeks of storage essential information about the storage performance can be provided.

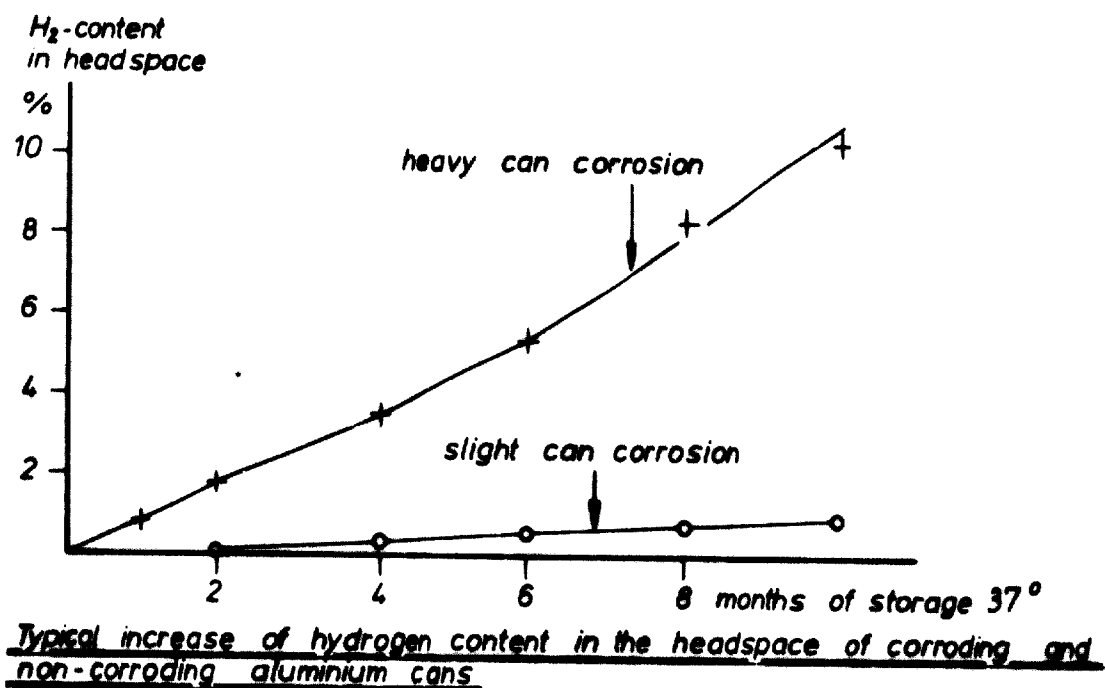
(24) As samples for analysis can be small, only few grams or millilitres, it will often be possible to determine the early metal pick-up values for a single packaging unit periodically by mounting a suitable dispensing device on the package. Irritating scatter of data from one package to the other can thus be eliminated.

3.3. Gas chromatographic headspace analysis

(25) Gas chromatography is another analytical method which is applicable for the early determination of product/container reactions on account of its accuracy. The method is based on the principle that a dissolution of iron or aluminium normally releases equivalent quantities of hydrogen gas in the package. The final stage of a can failure under these conditions is the familiar hydrogen swell.

(26) Whilst such failure could formerly be determined in a relatively advanced stage only by measuring the internal pressure increase, the gas chromatography permits today much earlier identification of failures by determination of small amounts of hydrogen in the headspace (see figure 2).

Figure 2



3.4. Analytical assessment of product changes

(27) The analytical methods described so far are applied for early identification of reactions between the product and the container, but chemical analyses are equally applicable for the determination of product changes. In many cases of product/container reactions it is not the packaging material which is negatively affected, for instance by corrosion, but the product itself undergoes undesired changes in the course of storage. Problems of this kind may arise in connection with a new filling technique; in such cases the test objective will not primarily be the compatibility of product and container but rather the appropriateness of the new process.

(28) Unacceptable oxidative changes of the product, for instance as a consequence of a poor gassing technique, can be assessed by analytical methods after relatively short time. Discoloration of the product due to contact with metal or oxygen, turbidity or variations in consistency can often be determined and measured by chemical and physical analytical methods at concentrations far below the threshold of sensory perception.

4. Accelerated storage test

(29) One of the most common methods for quick results on product/container reactions is the acceleration of the reaction by increased temperature. As a rule of thumb, a temperature increase by approx. 10° C will about double the rate of chemical reaction in the package.

(30) In a very rough estimate it can be said that, if the normal storage temperature were about 20° C, a storage test for one month at 30° C would correspond to two months' storage under normal conditions. The result of a one-month storage test at 40° C would even be comparable to the results of four months at 20° C.

(31) A further extension to six months of storage at 40° C would correspond to two years at normal conditions. In practice this would mean that a test period of about six months, which is acceptable in most cases, will yield data for the long-term performance of a product.

(32) The question may be justified why storage temperatures of 50, 60, 70 or even 80° C are not generally applied, since storage for one week at 80° C would correspond to 64 weeks or more than a year at normal conditions.

(33) The fact that storage temperatures above 40° C are applied in exceptional cases only makes clear that the temperature increase rule is not considered fully reliable. Actually, the temperature increase as a means for rapid testing has its limitations and should be applied with principal reservations only. The reasons are obvious. The acceleration of a chemical reaction by an increase of the temperature is applicable to a uniform reaction mechanism only. At elevated temperatures, however, the reaction mechanism of product and container may be entirely different. The product - no matter whether it is a food or a non-food product - may, and often does, change its consistency, dissociation and especially its texture.

(34) In the case of the packaging material tinfoil, which consists of tin and steel, the electrochemical potentials of the individual metals will shift with increasing temperature, depending on the type of electrolyte. This means that the reaction at 50° C may be basically different from that at 20° C. Hence the product/container reaction under severely changed temperature conditions may give completely different results, either positive or negative, than might be expected on account of the above time/temperature calculations.

(35) Even the storage tests at 40° C may yield false results, either extremely negative or, rather often, too positive.

(36) Nevertheless, the accelerated storage test maintains its importance as a rapid test, but it will be reliable only if the objective of the test falls within the tester's competence. If the result is a vital factor for a decision, the 40° C storage test should always be paralleled by a storage test at room temperature to back up the first result of the 40° C storage test by the subsequent 4 months' test at 20° C. For testing the product/container reaction with aerosol cans, for instance, the system: two months at 40° C and six months at 20° C in parallel, has proven useful as a rapid test method.

(37) It will be essential with such short-term tests to subject each package of the test series to a minute test procedure. Sometimes it is indispensable to test each square centimeter of the container inside under the surface microscope or to compare the product carefully with the reference sample after the storage test. After all, the objective is to identify the first indications of a product or container change. The greater the tester's experience, the more reliable will be his findings.

5. Simulating test procedures using model solutions

5.1. Rapid evaluation of containers by weak spot reactions

(38) For various reasons on the material and technology side, the metal container has certain areas where product/container reactions are most likely to occur. Such areas are, for instance, the side seam of a soldered or welded body, the reinforcing beads in a top or bottom end, the drawing radii of drawn bodies or the

crevice between body wall and end chuck wall where the container material is subjected to considerable load during double seaming, especially at the juncture. Any pore in a tin coating or lacquer film is, of course, also a weak spot for early product/container reaction. If the cans are not spray-lacquered after their fabrication, the presence of pores, which may reach down to the steel basis, is unavoidable in commercial production and should normally not cause can failure.

(39) As the areas most liable to failure are known, the evaluation of storage test results will focus on these points, which will show first whether surface or pitting corrosion develops, whether there is filiform corrosion or discoloration of the product in these areas.

(40) Since such weak spots have always to be expected, it is a logical consequence to include containers with a large number of artificially induced weak spots in rapid tests. On one hand, this facilitates the subsequent testing of containers, because the areas demanding special attention are known and, on the other, it ensures that the test series includes containers representing the theoretical lowest container quality standard.

(41) Such artificial weak spots can be produced in various forms, depending on the test objective: either the coating is damaged by deep scratches, or particularly deep beads are produced in a can, or sub-standard coating film weights are applied on part of the test cans. It may often be recommendable to include different weak spots in the various elements of the test series in order to assess the mutually effective factors.

(42) Of course, it would be unrealistic to apply artificial weak spots on an excessive scale, since the results might not be in line with the principal reaction pattern. If applied deliberately and on a modest scale, such artificial weak spots may considerably improve the value of rapid test results either at ambient or accelerated temperature.

5.2. Rapid test methods using model solutions

(43) In the same way as the product/container reaction can be accelerated by artificial weak spots, this can be done by increasing the aggressivity of a product in normal cans. Such a method may be advantageous if the resistance of different container specifications is to be compared. It is the method of choice for testing inside coatings for specific product groups.

(44) It is common practice in the application of this method to use so-called model solutions, which stand for a specific aggressivity, instead of using original products with increased aggressivity through addition of particular substances.

(45) If, for instance, the acid resistance of various inside coatings is to be determined, acid solutions based on either acetic acid, lactic acid or citric acid are produced, which are comparable with the acid type of the original product. Through relative increase of acid concentration and use of further additives, such as cooking salt, a reproducible model solution of increased aggressivity may be synthesized which is suitable for comparative rapid tests.

(46) These model solutions can, of course, be varied in all directions. Many aggressivity features can thus be simulated for determining the container resistance against acids, alkalines, fats, detergents, softeners, acetone, alcohol, sulphur and many other substances.

(47) A vital point is, however, to keep in line with the properties of the original product so as to warrant realistic results.

6. Rapid electrochemical test methods for products and containers

(48) In view of the fact that the corrosion reactions in a metal container are electrochemical processes, several laboratories have tried in recent years to determine type and extent of the reaction mechanisms and to predict the product/container reaction by measuring the corrosion current and potential.

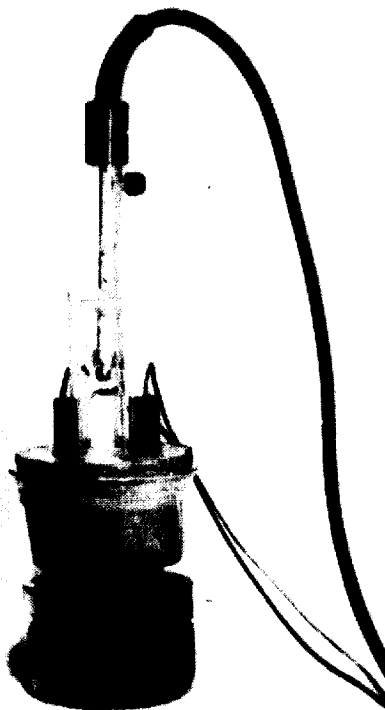
(49) The measuring accuracy and the sensitivity of the respective instruments is excellent, so there was a real challenge to benefit from the scientific knowledge in routine laboratory work.

(50) The first electrochemical corrosion measurements date back as far as twenty years, but they yielded such interesting and informative results with reference to metal containers and were improved in the meantime to such an extent that it seems worthwhile to discuss these methods in more detail.

6.1. The corrosivity test

(51) Emphasis will be laid on those methods which have gained significance in compatability testing of products and containers. Among these, the corrosivity test ranks foremost.

Picture 1



Test cell
for corrosivi
test

(52) Resin-embedded and transversely polished electrodes corresponding to the tinplate can materials - iron, tin and solder metal - are immersed into the product to be tested. Anaerobic or aerobic conditions are simulated

by injecting either nitrogen or air into the test cell during the measuring procedure. Over a period of several days the individual potentials of the metals as well as their short-circuit currents were measured. The anodic or cathodic behaviour of the individual metals was derived from the position of the individual potentials. The values of the short-circuit currents permit conclusions on the corrosion rate.

(53) Although this test method yielded many useful results, some substantial shortcomings became obvious in the course of time. The question arose, for instance, what would be the right size of the individual electrode areas and the right ratio to give polarization conditions during the coupling period which would actually resemble practical conditions.

Picture 2



Transversely polished
metal electrodes embedded in plastic

(54) After all, the ratio of areas is an essential point in a static-reactive test setup with regard to the potentials resulting at the individual metal electrodes. The results could be improved by using different electrode area ratios within one test series, but in many cases they remained unsatisfactory.

6.2. Modified corrosivity tests

(55) The corrosivity test was modified in various respects in the course of time. Instead of resin-embedded, transversely polished electrodes, some laboratories started using metal sheet electrodes in clamping devices. Others tried to simulate practical conditions more reliably by including a complete can in the test system. In that case the test can was filled with the product to be tested, and additionally separate electrodes of tin, steel or solder metal were immersed into the product. Over a test period of days or even weeks, the potentials of the separate electrodes to the can and the short-circuit current were measured and evaluated in accordance with the principles of the corrosivity test.

(56) Although this method gave reliable results in several instances, it had similar shortcomings as the original corrosivity test. Moreover, one should decide before designing an electrochemical test setup whether the electrochemical principle of reaction testing of individual metals should be strictly adhered to and the relation to practical conditions should be achieved through interpretation of the results, or whether complete cans should be included thus providing a composite galvanic cell in the test circuit as an approach to practical conditions.

(57) In the first case, the mode of interpretation may cause problems, whilst the principle of the measuring technique is maintained, that is the assessment of the reaction kinetics of the individual elements. In the second case, where complete cans or composite galvanic cells are included in the test circuit, there will often be a lack of clarity about the reaction elements responsible for the data obtained.

6.3. Application of the current density potential curve for product/container evaluation

(58) Let us now turn to the measuring techniques which do not in the first place relate to the mutual polarization of electrode pairs but rather to electrochemical reactions caused from outside. The major methods are the galvano-dynamic and the potentiodynamic measuring techniques. The underlying principle of these two methods is to force the electrodes into a reaction direction and to examine their behaviour rather than awaiting the mutual electrochemical effect of the electrodes immersed into the product to be tested.

(59) Whether the galvano-dynamic or the potentiodynamic method is chosen for these electrochemical tests, is irrelevant, because either has certain pros and cons.

6.4. Design of test cells

(60) How are these methods carried through?
In the first instance, a test cell of chemically inert and non-conductive material provided with bores for the electrodes is required for accepting the product to be tested. Openings for injection and discharge of

gases have to be provided, so that the test can be run under aerobic and anaerobic conditions. For aerosol products, special test cells are offered which permit testing under varying propellant pressure conditions (see picture 1).

6.5. Materials for working electrodes

(61) The working electrodes to be tested are to be produced of the materials of which the test cans are composed. It is imperative that the electrode material is of exactly the same composition and condition.

(62) If an extruded Monobloc aluminium can is to be tested, the aluminium test electrode should be of the same chemical composition and structure as the can, it should best be cut from the can proper. If a drawn aluminium can or an aluminium easy-opening end are to be tested, analogous alloys should be used, also preferably cut from the respective can components.

(63) The same applies to tinfoil can materials. Tin and solder metal electrodes are invariably to be made of precisely the same metal type. The steel electrode should be made of the same grade as the can, either common end or body stock, a deep-drawing quality, double-reduced plate or other.

(64) It happened more than once that faulty test results were only due to the fact that the material qualities used for the production of electrodes did not exactly correspond to those of the respective containers.

6.6. Electrode types

(65) The electrodes are prepared in a similar manner as for the corrosivity test method described above. Sometimes material bars or strips are embedded in resin and polished transversely, but surface electrodes are used likewise.

(66) Both types have their merits and shortcomings. The advantage of the resin-embedded, transversely polished electrodes is their long service life. As the material dissolution during the measuring processes is insignificant, it is sufficient to polish a few tenth of a millimeter down to have clean material surfaces for the next test. The reproducibility of the electrode surface condition is achieved by using always one and the same polishing method. The small surface of these electrodes may sometimes be disadvantageous. Care must also be taken that the formation of crevices between the electrodes and the resin is avoided. This defect can be largely eliminated by applying adhesion lacquer to the metal electrodes before they are embedded in the resin and by using resins with good adhesion properties, low curing shrinkage and high inertness. Nevertheless, checking for crevice formation between electrodes and resin is essential before reusing transversely polished electrodes.

(67) The use of surface electrodes in clamping devices is more expensive in time and labour, since such electrode plates can be used only once.

(68) To warrant reproducible surface conditions, the electrodes have to be treated chemically before use. On the other hand, surface electrodes offer more latitude in the measuring process.

(69) Another substantial advantage of the clamped surface electrode is its appropriateness for overall surface testing of the container plate, from which the electrode is cut, for instance for studying the effect of different surface passivations of tinplate or aluminium on the product/container reaction or for testing coated areas under specific reaction conditions.

6.7. Measuring, testing and evaluation

(70) As far as instruments for galvano-dynamic or potentiodynamic tests are concerned, a description need not be given here, since there is abundant literature on potentiostats, potential measuring instruments or recorders and they are commercially available in large number and various designs.

Picture 3



Measuring set for the determination of the potentiodynamic or galvano-dynamic current density potential curve

(71) A more significant point is, rather, the aspect under which the measurements are to be carried out, which values are to be determined and what is to be evaluated.

(72) As an example, let us consider a typical measuring process: It is intended to test a product of unknown aggressivity for its compatibility with a soldered tinfoil can; electrodes of pure tin, solder metal, can steel as well as the reference and counter-electrodes will be inserted into the measuring cell. Then the product is filled into the measuring cell. Normally, two measuring cells will be set up in parallel, one being flushed with nitrogen and the other with air during the entire testing period, so as to determine whether the presence or exclusion of oxygen is significant for the product/container reaction to be investigated.

(73) Before the current density potential curve can be measured, the individual metal electrodes should approximately have reached a reaction equilibrium, that is, a more or less constant rest potential at the non-coupled electrodes. This may take several hours.

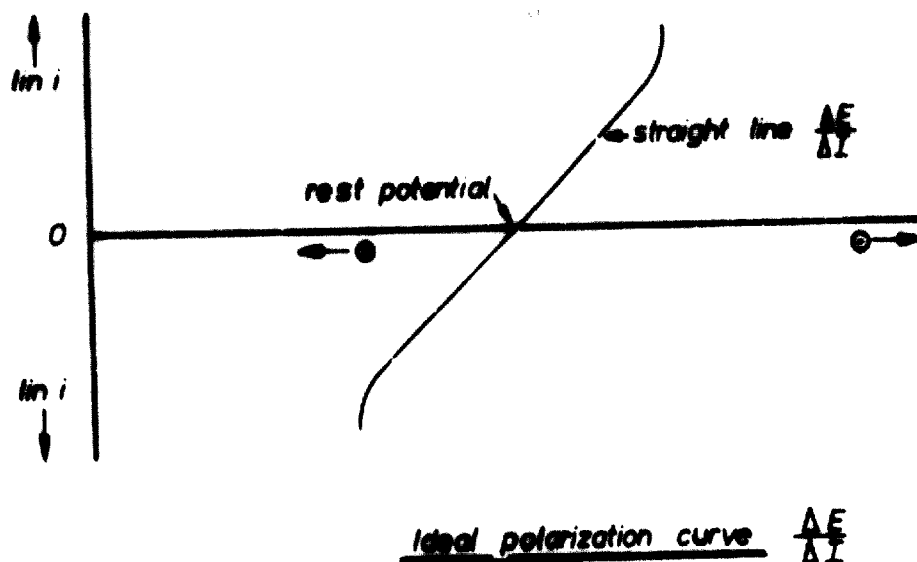
(74) If several measurements have confirmed that constant rest potentials have formed at the electrodes and their values have been measured, the first step of the test objective has been completed. The position of the rest potential makes evident which metal part is anodic and which is cathodic. This gives an indication whether a detinning reaction is to be expected or corrosion in the form of iron dissolution or even solder metal dissolution.

(75) The dissolution rate is still unknown, of course, as the current flowing between the electrodes is required for determining this factor. To this end the current density potential curve is determined for each electrode.

6.8. Polarization conductance as a measure of the corrosion rate

(76) The current density potential curve can be evaluated in different ways. A common method for characterizing the corrosion current intensity is the determination of the so-called polarization conductance $\Delta I/\Delta E$ in terms of $\mu\text{A}/\text{mV}$. It is based on the fact that the current density potential curve is linear within a range of about ± 30 mV from the rest potential and that the slope of this line is governed by the corrosion behaviour. This method has the advantage that a short part of the current density potential curve has to be determined only.

Figure 3

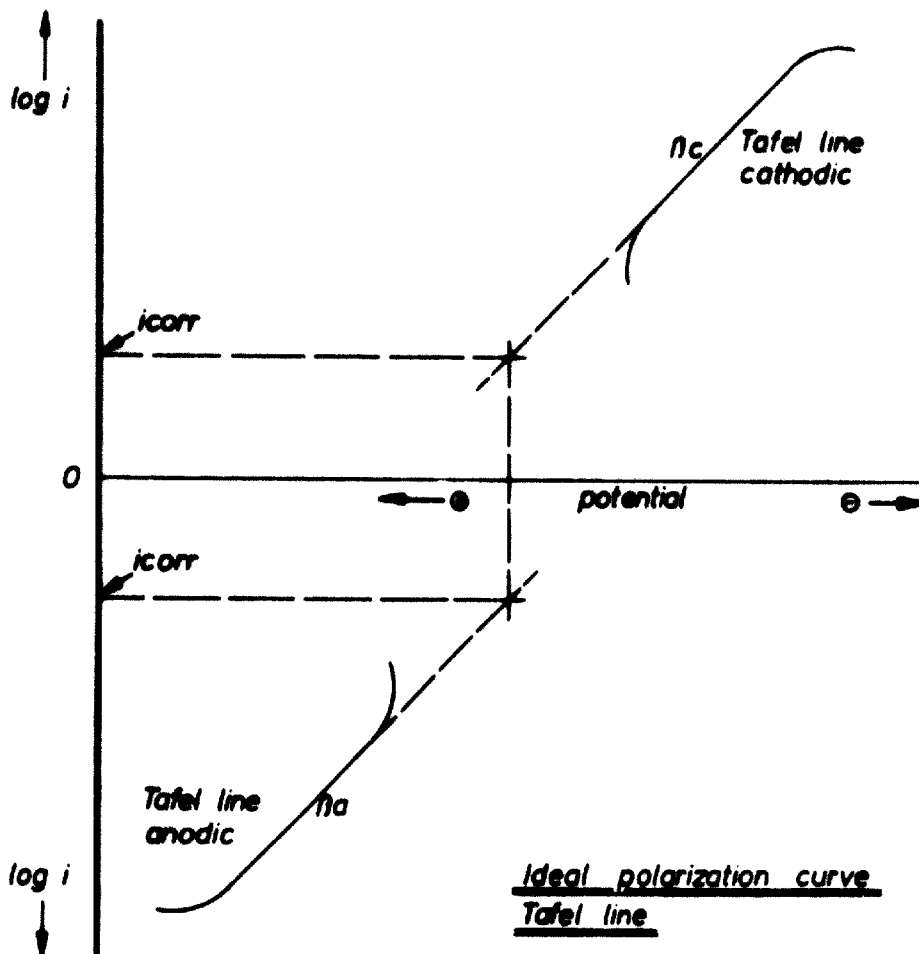


7. Practical consequences and interpretation of electro-chemical test data

7.1. The application of Tafel lines for the determination of the corrosion current

(77) Another method for a direct determination of the corrosion current is the extrapolation of the so-called Tafel lines from the cathodic current density potential curve with reference to the rest potential. It is based on the fact that the cathodic current density potential curve, if plotted semi-logarithmically, is more or less linear at about 100 - 120 mV above the rest potential. Lacking the ideal conditions of a straight line, the approximate calculation method is applied.

Figure 4



(78) Furthermore, the corrosion current can be determined as the point of intersection of the measured current density potential curves for the respective metals. Depending on the position of the rest potential, one metal turns anodic and the other cathodic.

(79) An essential factor of this method, which was mentioned in connection with the corrosivity test, is the relative size of the electrode surfaces and their concurrence with the relations in the can. However, these can be calculated approximately, too.

(80) It would exceed the scope of this paper to discuss the various evaluation methods for such cases where more than three metal components are combined in a container, but methods applicable for this problem do exist.

7.2. Direct interpretation of measuring data

(81) In reviewing the measuring techniques using the current density potential curve one may conclude that the various measuring and evaluation methods certainly represent considerable progress in the reliability of product/container reaction evaluation. A major problem remains unsolved with these methods, namely the simple question

"Which corrosion current value corresponds to how many months or years of storage"?

(82) Many laboratories will have established empirical values on the basis of their experience of various measuring methods and comparisons with conventional storage tests. In many cases - and this seems still more important - it will do to have the rapid test

result for predicting whether a product can be considered as safe, critical or hazardous under the aspects of product/container reaction. Such a classification is possible today for a number of product groups and container specifications.

(83) On the other hand, one should not overlook that the described electrochemical methods neglect several factors of the product/container reaction in the original package or assess them only unadequately. The role of an inside coating in a can with regard to the potential, for instance, is still undefined. The corrosive effect of the iron-tin alloy in tinfoil containers should not be underrated, and the current methods often do not consider this appropriately.

7.3. Pitting corrosion and its evaluation by means of current density potential curve measuring methods

(84) The most serious problem in the use of cans is, no doubt, the fact that pitting corrosion occurs during normal storage of various products, although the position of the rest potential gives no reason to assume this and the corrosion current data classify the product as safe. Typical products of this category are water-based aerosol products. Failure through pitting corrosion was observed, although the electrochemical corrosivity test and the current density potential curves had classified them as safe products.

(85) Seeking an explanation for this phenomenon, one should first review the conditions of an inside coated can. With standard inside coatings, a certain degree of porosity of the coating film is inevitable. If

aggressive products are packed in such cans, type and degree of corrosion in the pores will vary, that is, only few of them will undergo deep pitting corrosion, whilst all the other pores show little attack.

(86) We should also remember that a certain portion of a storage test series with highly aggressive products often fails rather early due to pitting corrosion, with few defective cans following thereafter, whilst the rest of the storage test series can be stored over extremely long periods without any further failure from pitting corrosion. One may safely assume in the case of such storage test series that the product filled into the cans was more or less of the same composition and that the can specifications were identical for all cans involved. Hence the product in a can reacts in a different manner with the coating pore A than it does with the coating pore B, and some cans remain perfect over long periods although there is every likelihood that pores do exist in the coating.

(87) To explain this phenomenon, some time ago the terms "active" and "passive" pores were established, and it was tried to determine the specific conditions of the pores, either active or passive, by measuring methods. The results published so far were generally unsatisfactory.

(88) Now the question is up how the current electrochemical corrosion measuring techniques can be applied for assessing the different active-passive conditions of an exposed basic steel pore in a can and how the results can be considered in the overall evaluation. This is certainly the key to the reliability of the rapid electrochemical corrosivity test

using the current density potential curve. No relevant publications have been issued to date with respect to the electrochemical testing of product/container reactions.

(89) We understand that several laboratories have been working on these problems in recent times with promising results. In general, the current density potential curve of the individual measuring electrodes is measured by the hysteresis technique after pre-activation or pre-passivation of the surfaces. The results obtained by this method with regard to potential scatter and corrosion current changes will substantially improve the value of the prediction on the product/container performance.

8. State of the art

(90) Naturally, the electrochemical test methods for a rapid predetermination of the compatibility of product and container have not been developed to the optimum as yet, but conventional storage tests will hardly be required in a great many cases if a well-equipped electrochemical laboratory is available.

(91) A rapid and economical predetermination of the product/container performance is only one of the advantages of these electrochemical rapid test methods, a better determination of the causes of material-induced reactions is another one. If, for instance, a common storage test showed that a specification did not give satisfactory product/container performance results and cans failed in some way or other, the cause of the failure is still uncertain. It may take long to find the solution to the problem, often by running further expensive storage tests.

(92) Electrochemical measuring results, however, often permit direct conclusions on the cause of the failure: a suitable can specification can be determined at once, or the product can be reformulated under defined aspects. Further measurements will rapidly disclose whether the modification of the product yielded the desired result. Especially for chemical and technical products permitting addition of corrosion inhibitors, the electrochemical measuring technique may be the method of choice for assessing the type and extent of the effect of an inhibitor by one test series at short sight.

(93) Finally, one may safely predict that the electrochemical test methods will achieve significance as rapid tests for product/container evaluation in the future. On the other hand, experience calls for a warning to all concerned not to adopt any published measuring method for one's own operations without thorough previous study. Even if the method was successful in specific cases, several failures may have been experienced side by side, which are hardly mentioned in the publication. The electrochemical test results should not be used as the only evaluation method, unless extensive experience in the handling of the method is available and the problems involved are known. Unless such precautions are taken, this would only add to the many cases of disappointment in the extrapolation of rapid test results. On the other hand, one should not easily give up, if a new method does not readily yield the expected success. The rapid test demands much of your time, patience and accuracy until you master it, but then it will save you time in return.

9. Typical applications of the test methods to selected products to be packed

(94) In respect of the practical application of the tests described in this report, three basic fields of testing are indicated below. The following table lists examples for the various fields and the respective test methods applicable.

Field of testing	Examples	Tests applicable
Development of basically new cans.	Cans with easy-opening systems. Use of tin-free steel instead of tinplate.	The conventional long-term storage test is required for final testing, but during the development phases rapid tests are really advantageous for appraising individual criteria.
Gradual changes of can specifications.	Slight changes of tin coating weight. Testing of different inside coating systems. Changes of can geometry, e.g. new end profiles or body beading.	Use of synthetic test solutions is possible, rapid tests applying analytical testing of metal pickup and of metal pickup mechanism during storage, headspace analysis, etc. Very careful visual inspection of cans for reaction with the product at weak spots. Comparative testing of previous and new can specifications.
New products in familiar or unchanged can specifications.	Food cans: Changes of recipes for ready meals, new recipes for pickles, etc.; use of coated instead of plain cans for fruit and vegetable juices, other products from different growth areas, if effects on product properties may be expected.	Analytical data, electrochemical testing of products for corrosivity, accelerated storage tests at 30-50°C; long term storage tests in exceptional cases only.

(95) Some explanations on the foregoing table should be given:

(96) All fundamentally new developments should include long-term storage tests to confirm the test results obtained by rapid methods. The container manufacturer carries a high responsibility and cannot afford to use specifications of which he has inadequate knowledge. In the various development stages, however, rapid tests can be applied for testing new or modified can specifications.

(97) For gradual changes of can specifications, a packaging test laboratory will normally have sufficient experience to appraise their suitability by means of rapid tests. Comparative storage of previous and new can specifications with various products is an appropriate method. If the coatings are to be modified, the wide experience in coating performance testing with various test solutions should be helpful.

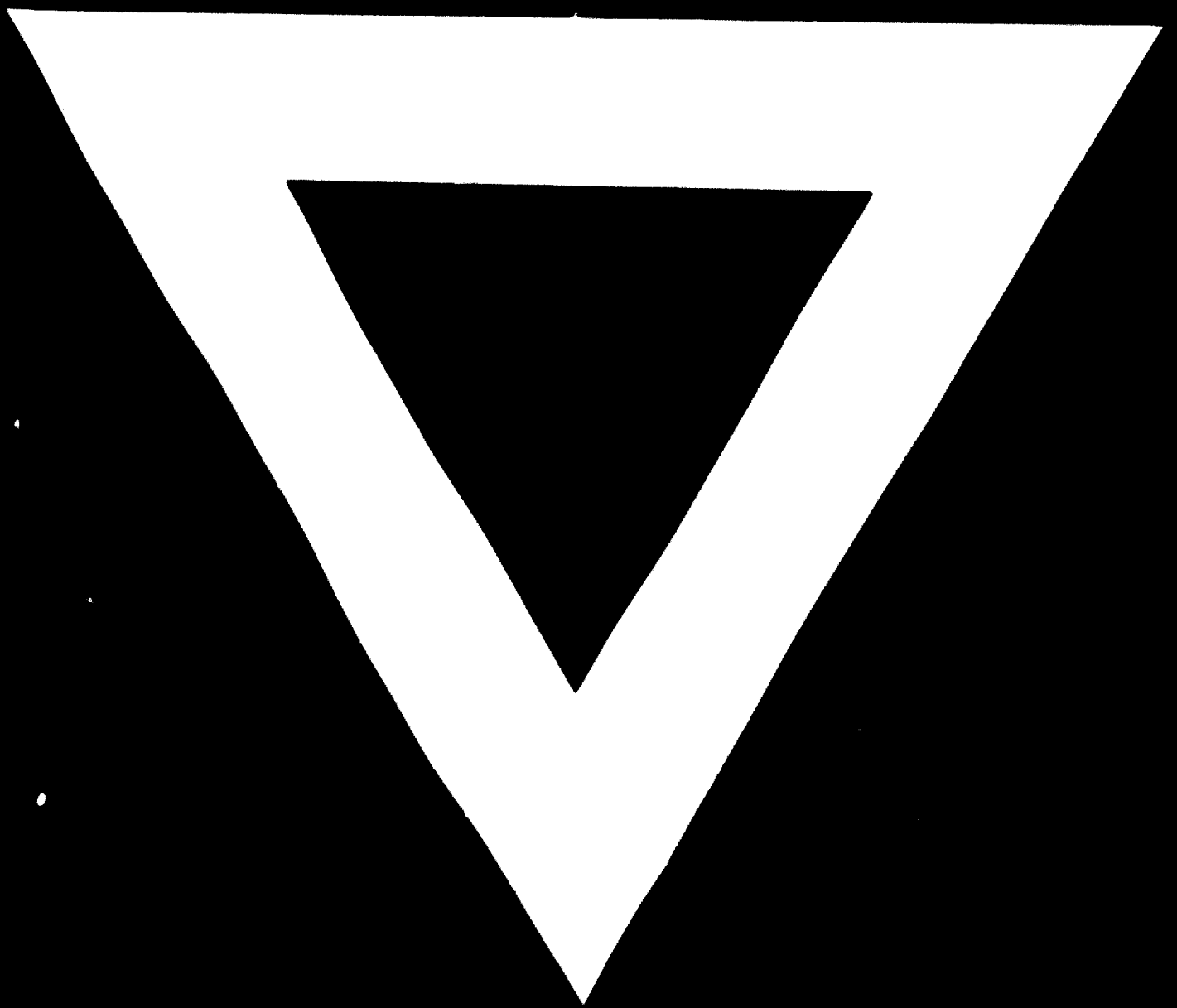
(98) If new products are involved, analytical data should first be determined to make sure to what extent the new product deviates from the familiar comparable product. pH, analytical data on salt, nitrite, nitrate, phosphate content, etc. will provide a sound basis. A relatively large amount of laboratory service has to be provided in these cases, but electrochemical product testing methods will help to save time. In any case we recommend to include a corrosion laboratory in a packaging test laboratory.

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