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APPLICATION OF OTHER THAN TIN MATERIAL USED FOR COATING OF STEEL IN PACKAGING 1/

by

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Contents

1. Introduction

(1) It is public property that tinplate - in the beginning hot-dipped tinplate, later electrolytic tinplate - has been used as food and non-food packaging material for more than 150 years and, judging from the billions of cans and containers, tinplate has proved its universal usability. Even though the tinplate production methods have changed over the decades, the combination steel + tin is, now as before, one of the most suitable material combinations offering an optimum solution with regard to the strength of the container, based on the properties of the steel, and with regard to the protection of the product and against exterior influences, based on the properties of the tin. For more than 100 years, when talking about tinplate, one knew only of hot-dipped tinplate. The hotdipped tinplate is in little use today. Hot-dipped tinplate is used only where electrolytic tinplate has not made its way yet for various reasons. The main characteristic of hot-dipped tinplate is that it is covered with an extremely high amount of tin. Further, the tin coating weight fluctuates heavily. The former can production methods, with the exception of the lap-seam soldering - which have been replaced by modern procedures today - embodied practically no problems

which influenced the can quality due to this heavy fluctuation in tin coating. Improvement of the procedure made it possible - even though not to the exactness as reached with the electrolytic tinning procedures of today - to effect a more even tinning. The major disadvantage of the hot-dipped tinplate was, contingent upon the procedure, that a larger quantity of tin was used for the intended purpose in can production than actually required for the majority of packages. Since, in addition, tin is a relative costly material, it is not surprising that, in the course of time, one thought up a procedure to reach, with similar good properties, more even and thinner surface coatings, which answer the exact purpose. The principal object was to reduce the tin coating weights. A decisive advancement was made in 1930 - 1935, when the first electrolytic tinplate was produced. The old method of dipping the plate into the tin and subsequent squeezing of the surplus tin was replaced by a new method utilizing electro-chemical laws, according to which a known quantity of current separates an equivalent quantity of metal. This method, based practically exclusively on the factors current density, time, concentration and temperature of respective tinning baths, made it possible to produce surface coatings which showed a high degree of evenness and the thickness of which could be controlled according to specification. Much has been written about this procedure, and it is not the object of this report to repeat information which is public property. Development continued. There was parallel development of can production machinery. Both made it possible to produce cans of electrolytic tinplate, without that the container resistance toward the product changed considerably as compared to hot-dipped tinplate. An important factor in this development was, without doubt, the parallel development of suitable organic surface coatings - lacquers offering with the tinplate a maximum of protection against corrosion. Statistics show that the average tin coating weight per m^2, measured on both sides, was reduced from 25 - 25 g/m^2 to 5 - 10 g/m^2 during the last decades. On the average, only 20 - 30 % of the earlier tin coating weight is used today for food can production.

(2) It is not surprising that this trend caused investigations to derermine whether it would not be possible to replace tin by some other coating material. Another factor in favor of such investigations is that world politics make tin more and more a subject of strategic and political considerations. It goes without saying that one tried to find ways and means to produce food packages without this metal successfully used for 150 years.

(3) A material, which has been in parallel use with tinplate, is regular blackplate without surface treatment, as produced by the rolling mills. This material which was used in 1940 - 1945 for the production of three-part welded food cans is used today for non-food containers. This material has the disadvantage that it has low resistance to corrosion, in particular to atmospheric corrosion. When coated with lacquers specially developed for the intended purpose, however, the material comes up to expectations.

(4) For years, investigations have been conducted with regard to the production of the material and the suitability of the material after corresponding surface treatment to give the plate a better resistance to corrosion. Above all, phosphate-carbonate treatments were used which were carried out in alkaline agents. These methods and material, however, did not push through as of this day. There were no optimum results with regard to lacquer adhesion and product suitability.

(5) In the beginning of the sixties, a worldwide development was started in Japan with the object to produce a material which, on one side, did not require tin as surface coating material and, on the other side, did not have the disadvantages of regular plate and the disadvantages of the other surface post-treatment methods mentioned. After systematic investigatione it was decided to use chromium as surface coating material making use of the extensive world-wide experience in the field of electro-chemistry and, in particular, electrolytic separation of chromium in "true" chromium-plating processes.

(6) It was not possible to employ "true" chromium-plating proceseee for the intended purpoee, as it is difficult to com-

bine metallic chromium with the basic blackplate without providing corresponding intermediate layers. In addition, they would not provide a surface, which would meet the mechanical stress of deformation and profiling because of the brittleness. On the other hand, it had to be tried to control the thickness of the surface coating, giving consideration to universal usability, in such a way to make an economical production of the material for packaging purposes possible. The essential progress today is that the surface coating is not limited to metallic chromium only, but includes suitable combinations of metallic and oxide chromium. This method is, in principle, the method which made its world-wide success from Japan.

(7) As always with new developments, which have been solved "on principle", additional work began concentrating on the production of other surface coatings. Mention is made, in particular, of the use of aluminium, both plated and vacuum coated. The packaging industry, however, was not able to make use of the latter procedure until this date because of technical problems and questions of economy.

(8) The present report will concentrate, therefore, on the properties and applicability of the so-called chromium-plated plates which, as mentioned before, deviate in surface structure depending on production process used, but which, in principle, have similar properties. It is object of this report to point out the present state of the art and which main points must find consideration in evaluating the usability of these materials for the various purposes. This covers food as well non-food containers.

(9) In the foreground is the main question which prerequisites must exist to produce packages from this material, how such containers are to be treated and, finally, which features are to be expected on principle. Special value is being attached to point out cases of distinct differences in the usability as compared to conventional containers of tinned material. The author is trying to treat the subject as detailed as possible. It must be pointed out, however, that enormous

development work continues in this field, so that it is extremely difficult to keep up with the most current state of development.

(10) To make sure that the following relates to that material which is generally known under "chromium-plated blackplate", here is a brief definition of the term. Today, chromium-plated blackplate is a material, which is led in coil form through cleaning baths and surface treatment baths and which, after running through these devices, has a surface coating of varying composition of metallic and oxide chromium and phosphates, depending upon the procedure. The basic blackplate is, with regard to its technological properties, identical with the material which is used for the production of tinplate. Most of the various materials on the market because of their different construction of equipment, show certain differences in the surface. These differences are, however, not so serious that one could not speak all in all, for the purpose of this report, of one material with regard to the properties in processing and with regard to the performance of finished containers. TFS (Tin Free Steel) in this report is a material which, in international terms, is CCO (Chromium-Chromium-Oxide) or CPT (Chromium-Phosphate-Treatment). The deposition on the surface is done both in cathodic and anodic-cathodic manner.

2. Present situation and properties of chromium-plated sheets

2.1 Production of material

(11) The basic set-up of all chromium-plating lines is the same and is, in principle, the same as of electrolytic tinning lines. The set-up is as follows:

- Coil feeding

(12) The electrolytic chromium-plating is done in a continuous device. An endless coil must be used, as a constant speed must be maintained in the surface treatment section. Two uncoilers are required, the end of the first coil to be automatically welded to the second coil. A twinshear with subsequent welding machine

is used for this. In addition, there is the so-called loop pit or loop tower, from which the surface treatment section is fed with coil during standstill for the welding process. Subsequently, the coil edges are trimmed.

- **Pretreatment section**

(13) Prior to the surface treatment, the coil surface must be freed from oil and dirt particles. This is done in the de-greasing section. For better results, the "Mittelleiter-Verfahren" is used. The coil is led through an electrolytic bath (2 - 3 % silicate solution) between cathodic and anodic electrodes arranged in series. The hydrogen, which is released, blows off the oil particles.

(14) After de-greasing, the coil is running through a brushing machine. With the addition of water, the coil surface is brushed before the coil moves into the pickling bath. The pickling is done at room temperature in hydrochloric acid without current (just dipped). The pickling is necessary to remove, on one part, the residues from de-greasing and to etch, on the other hand, the steel surface for the surface treatment process. After pickling the coil is thoroughly cleaned in a rinsing and brushing device.

- **Surface treatment**

(15) Here electrolytic depositing takes place on the surface.

- **Post-treatment**

(16) To begin with, the coil runs through a rinsing device to catch the acid and, after that, through a drying device. The last step is that the surface is greased with diootyl sebacate - mostly by electrostatical means. The greasing weight is extremely low. It ranges from 10 - 15 mg/m^2 for both sides. The stations required for tinning, as for instance flow-melting, quenching,

cleaning and passivation, are not required.

- <u>Grading and shearing section</u>

(17) Depending upon the type of installation the coil is reeled and, if desired by the customer, cut to sheets on a special inspection and cutting device or, with slower moving devices, is graded directly in line and distributed. With the "in line" operation, the sheet is running again through a loop pit and, thereafter, through the inspection section with pinhole detector and thickness measuring device. They are then aligned in a leveller and, thereafter, cut into the format ordered. At the end of the installation is the stacking device for the cut and graded sheets. It need not be mentioned that the material may come in coil form, too.

2.2 <u>Surface</u>

(18) Since the essential difference of this material as compared to tinned material is the surface and not the basic material used, it seems expedient to treat this point first.

(19) The total surface coating on the blackplate which, as mentioned before, was applied electrolytically, has a thickness of approx. 0.05 μ (1 micron = 1/1000 mm).

(20) It must be mentioned that the chromium-plated materials have, on principle, a different appearance than the tinned sheets with their very shiny surface. Depending upon quality and production method, the visual appearance ranges between blue grey, shiny grey, brown grey and silvery grey surface. The appearance of the surface is dependent upon roughness of the steel surface and, essentially, on the varying portion of metallic as compared to oxidic chromium as well as the possible presence of phosphates.

(21) At the beginning of the developments, the difference between qualities was, in general, dependent upon their portion of metallic as compared to oxidic chromium. It is important to

note that the surface thickness as compared to electrolytic tinplate of the tin coating weight of 0.25 lbs/b.b. (5.6 g/m^2) is essentially lower and is within the range of approx. 1/10 of this thickness.

(22) The essential requirements to be met by such a surface are optimum corrosion resistance, minimum number of pores, good mechanical deformability and very good lacquer adhesion. Further, the efficiency of the production must be optimum. The current efficiency for separating chromium is essentially lower than for separating tin, due to the uncontrolled side reactions, in particular the undesirable release of hydrogen, so that it was not possible to reach, at the beginning, the same line speed as reached with tinning. In order to increase the line speed it was necessary to change from originally high chromium coating weights to lower ones, as this reduced the depositing time. To obtain an optimum of properties, the first production processes were devided into two steps. In the first step, the metallic chromium was separated electrolytically, in the second step, which may be parallel or "in line", it was passivated in corresponding solutions. This passivation process produces an oxide coating on the metallic chromium. The true improvements made were that the electrolytic deposition process permitted an essential increase of line speed by corresponding bath composition and control of the current density. Line speeds of 450 m/min (approx. 1500 feet/min) are presently being obtained.

(23) Analysis of the surface coatings deposited on the steel surface is done with most modern physical-chemical methods today, the X-ray spectroscopy and electrons beam deflection outranking electro-chemical methods of potential measuring. In addition, optical evaluation of the surface is done by electron microscopes. The portion of chromium oxide versus chromium metal, formed during the chemical process, varies extremely with the bath composition. This is the real know-how for the production of such material. It is further of essential importance whether the chromium deposition comes

from alkaline or acidic solutions. From the above mentioned analysis it was found that the main components present on the surface are:

$$Cr - Cr_2O_3 - Cr_3O_4 - CrO(OH) - Cr(OH)_3 \times 3\ H_2O - Cr_x(PO_4)_y$$

(24) Generally speaking, the surface coating has an amorphous structure which has a specific weight of approx. 2.1 - 2.2 g/cm^3. The composition of a hydrated chromium oxide coating is close to the formula $Cr(OH)_3 \times 3\ H_2O$ and the content of elementary chromium in this oxide coating is between 0.20 - 0.55 mg/dm^2. These surface coatings offer an excellent basis for good corrosion resistance and lacquer adhesion . Both points will be covered by this report later. Tests conducted during the last years showed that this surface, with regard to further aging, is extremely stable and superior to tinned material in this respect. Lacquer adhesion and corrosion resistance toward atmospheric influences are maintained over a long period of storage under normal conditions.

(25) The liability to aging of the surface is examined, in addition to using other methods, by testing the influence of increased temperatures upon the surface appearance. Temperature application of 250 °C (480 °F) for approx. 12 minutes upon the plain surface should not lead to brown-yellow coloring of the heated sample.

2.3 Corrosion resistance

(26) A common means for testing the corrosion resistance is the salt spray test. The samples to be tested are placed in a closed chamber and diluted NaCl solution is sprayed into the chamber. The time until rusting occurs, i.e. until brown-reddish iron oxides are formed through the chromium-plated surface, is the measure for corrosion resistance. This test is carried out with both non-deformed and deformed components in order to assess the effect of mechanical stress on the surface finish.

(27) Another testing method is the iron solution test. It is a valuable aid for quantitative assessment of the iron porosity, especially for determining the most favourable formulation of the CCO layers. Flat samples are used at first for the test which are subsequently deformed to an increasing extent, in order to determine a possible increase of iron pores.

(28) We know from test results with plain stock that the corrosion resistance depends to an essential degree on the portion of oxide chromium, the proportion between corrosion resistance and oxide chromium content being directly linear. As, on the other hand, other material properties such as lacquer adhesion and deformability decrease with an excessive oxide layer, it will be necessary to find an optimum here. For one of the common material types, a chromium oxide layer of approx. 0.03 - 0.2 mg per dm^2, calculated as metallic chromium, has been determined as an optimum coating weight.

(29) The essential advantage of TFS materials over conventional blackplate, even disregarding the major influence of the manufacturing process, is their considerably better corrosion resistance during storage. As mentioned already, the surface is so stable that the normal atmospheric components like oxigen, water vapour and carbon dioxide do practically not change the surface. It is directly comparable with electrolytic tinplate, if the influence of the storage on the lacquer adhesion proper is disregarded. Lacquer adhesion of electrolytic tinplate decreases more rapidly with storage than that of TFS plate, because the electrochemical situation is basically different. The use of TFS for the manufacture of bottom ends for beer and beverage cans, for which electrolytic tinplate with a tin coating weight of 5.6 g/m^2 had been used previously, showed that the performance of these two surface types is quite comparable.

(30) Now, this material offers a substantial advantage over conventional tinplate, because it may be transported over long distances, even in comparatively unfavourable climates,

without becoming unserviceable.

(31) As already mentioned, the TPS surface is liable to scratching. Under the aspect of potential corrosion this means that, contrary to tinplate, any scratch in the TPS surface finish will, with utmost probability, make that area sensitive to rust or corrosion. The performance of a CCO or CPT finish differs definitely from that of a tin coating. The first category provides an inactivation of the steel plate, with as little porosity as possible; like a lacquer film, they impart a "passive protection to corrosion". Tin or aluminium coatings, on the other hand, provide an "active protection to corrosion", because they "co-react" in the corrosion mechanism as sacrificial anodes.

2.4 Behaviour of TPS materials towards lacquers

(32) The first test samples which were produced several years ago showed already that chromium-plated materials have a better adhesion for the lacquer types used in the packaging industry than tinplate. The main reason should be sought in the principally different polar forces, which have a substantially more positive effect on the lacquer adhesion with chromium-plated material than with other surfaces. It is generally assumed today that the strength of the hydrogen bond between the polar zones of the surface and the individual groups of organic coatings is the main factor in this positive performance.

(33) Before going into detail with regard to lacquer adhesion, it should be mentioned that chromium-plated stock which is plain on either side can hardly be converted because of its surface structure, which is much harder than that of a tin coating. This harder surface is highly sensitive to scratching, and with the present state of the art, plain materials may not be used, or in accurately defined exceptional cases only, for instance with heavy surface greasing, or with a small contact area of the deforming tools with the plate surface.

(34) The amount of chromium oxide is not only decisive for the corrosion strength but also for the lacquer adhesion. Too

thin or too thick chromium oxide layers reduce the lacquer adhesion. An optimum is reached with a coating of approx. 0.2 - 0.5 mg/dm^2, again with reference to a common CCO type.

(35) An essential advantage, which should be mentioned in the discussion of coating problems, is the elimination of the so-called sulphur staining with TFS plate, which is a familiar phenomenon with tin-coated surfaces. During sterilization of protein-containing, sulphur-separating products, tin-coated cans produce blue-black marbling stains consisting mainly of compounds of tin and organic sulphur compositions. As this intermediate layer is formed between lacquer film and metallic tin during sterilization, lacquer adhesion may possibly be reduced and the coating film may be removed. This phenomenon has not been observed with coated TFS plate up to now.

(36) Whereas specially developed deep-drawing lacquers must be used for the manufacture of drawn electrolytic tinplate cans, one may assume that normal lacquers without special deep-drawing properties may be used on TFS plate for the manufacture of deep-drawn containers because of the excellent adhesion properties of TFS. If the same lacquer qualities are used on electrolytic and TFS plate, TFS is superior to conventional tinplate. Cans of identical specifications made of tinplate and TFS plate for comparison proved, that the tinplate cans showed heavier porosity and lacquer removal in the areas which had been subjected to mechanical stress. This refers more or less to all lacquer types used in container manufacture, most of which are epicote-phenolic-resin-based modifications. It should be mentioned that the lacquer adhesion is considerably reduced by fingerprints on the plain TFS surface caused by manual feeding of individual sheets into coaters and printing machines. It will, therefore, be reasonable to convert TFS plate on fully automatic equipment in order to eliminate this shortcoming.

(37) The excellent lacquer adhesion of TFS was one of the reasons for its application in crown cork manufacture. Lacquer adhesion is of vital importance for this product. The subject

will be discussed later on. It was further observed during seaming of top and bottom ends of TFS plate that damage to the coating film by seaming rolls is considerably less with TFS plate than with conventional tinplate, a true advantage offered by TFS.

(38) The excellent lacquer adhesion is further proved by the methods commonly used for the determination of the lacquer film weight. Lacquer removal by electrochemical treatment in soda solution, which is applied for removing the coating film from tinplate substance, is not suitable for TFS materials. The same refers to the so-called Scotch tape test which is used for lacquer adhesion testing. Even if the coating film is cut cross-wise, it is hardly possible to remove the coating from the surface. To summarize, one can say that TFS offers definite advantages over tin-coated material wherever a stock with outstanding lacquer adhesion is needed for special applications.

(39) In developing new coating systems for this new material, which does not have the bright surface of electrolytic tinplate, it was tried to impart a favourable effect to the appearance of the finished coating. In this connection, special developments should be mentioned which use polymerization compounds with a strong gold coloration effect for improving the appearance of the TFS surface. It was furthermore necessary with pigmented coatings, for instance white coatings for stamped components, to achieve an even better coverage with lowest possible dry coating weights. Non-pigmented coatings which impart an appearance to TFS plate which is similar or nearly comparable to coated tinplate have not appeared up to now, and the development over the past few years showed that there is no actual demand for such coatings. A comparison of one lacquer type on these two different substrates makes obvious that coating weights must be higher for TFS because of its darker surface, if the same optical effect is to be achieved as with tin-coated material. Similar considerations as those mentioned in connection with outside white coating apply to printing. To achieve a similar optical effect, more printing

ink will be required. Especially in case of white printing inks, sometimes additional passes through the printing press will be required in order to get a similar appearance. A colourless prime coat and other printing processes, e.g. dry offset printing, lend themselves to improve the overall result.

(40) An essential advantage of TFS over tin-coated surfaces is its suitability for much higher lacquer baking temperatures. It will be generally known that the melting point of tin at 232 °C (450 °F) limits the baking temperature, which results in relatively long baking times of 10 - 12 minutes for polymerizing lacquers. Baking of coatings on TFS substance may be handled by the high-temperature-short-time principle - provided that adequate equipment is available - i.e. few seconds at temperatures of approximately 350 °C (660 °F). The length of drying ovens may therefore be considerably reduced.

2.5 Conversion of TFS plate to containers

(41) The conventional body manufacturing process by soldering is no longer applicable for chromium-plated materials. As a consequence, TFS was used in its initial stage of introduction for those items which did not require a body joining process. This refers particularly to bottle closures, for instance crown corks, and containers or container components which are seamless, such as drawn cans and top and bottom ends for cans. Drawn cans were mainly used for fish products. Corresponding storage tests were carried out before.

(42) In order to find applications for this new material in cases where bodies need a rigid joint such as a lap or lock and lap seam, research work was done to adapt bonding methods already used in the packaging industry - welding, gluing, lock-seaming and cementing with side seam cements - for this material. The problems involved in welding of TFS on conventional machinery by normal methods, which are caused by its particular surface characteristics, have not been definitely cleared away for commercial production, at least the plate

cannot be converted in the condition as supplied. If, however, the chromium/chromium oxide or phosphate layer is removed from those areas which are to be welded - a mechanical process, either milling or brushing - welding of TFS containers on high-speed equipment is no longer considered as a technical problem. Problems are caused, on the one hand, by the detrimental effect of surface components on the electrode material and, on the other hand, from the resulting non-uniform contact between electrode and weld seam. A compromise is therefore made for the time being. As already indicated, the plate is weldable if the surface finish is removed. Normal blackplate is then available which may be welded on conventional equipment. With aggressive products or such products which are sensitive to iron pick-up, for instance beer, however, the side seam is the critical area of a container, and the protective function of the original surface finish as well as its excellent lacquer adhesion property are deliberately abandoned by edge cleaning. The new problem resulting now is an efficient coverage of the side seam. Methods commonly used today are the conventional spray-coating process as well as new methods, such as powder side striping.

(43) Apart from welding, other methods such as gluing or locking and cementing lend themselves for rigid bonding. Adhesives for can bodies were successfully developed during the past years, they are mainly based on nylon compounds. Cans with glued lap seams are commercially used for beer. The adhesives used withstand beer pasteurization temperatures without any hazard of micro-leakage in the seam. The glued can is manufactured on similar equipment as that known as "bodymakers" for the manufacture of lock-and-lap seamed cans. The nylon strip required for the bonding process is either extruded onto the blank or applied in-line in the bodymaker. Heat treatment and immediately following quick cooling - to warrant the required production speeds - give the container adequate seam strength. Contrary to the welding process, the surface finish need not be removed for this method, it is

rather required as a lacquer adhesion substrate for the TFS - lacquer - adhesive - system. Up to now, no adhesive materials are available for the manufacture of round food can bodies which would withstand sterilization temperatures above 100 °C (212 °F) for more than one hour. For this field, welding is still the only suitable bonding process. Apart from this gluing process, the conventional sealing of lock-seamed cans with side seam cements is still used. This process is applicable to TFS, tinplate or untreated blackplate without any limitation. Finally, it is mentioned once more that soldering of containers made of TFS plate is not yet possible with the required high production speeds, and it seems doubtful that this process will ever assume practical importance.

(44) In connection with the use of this new material, considerations were repeatedly made as to what extent the very hard surface layer would cause increased wear of cutting tools, e.g. in stamping and slitting, compared with the previous tin coatings. Thorough investigations of this subject showed that the cutting tools are worn earlier, but no case has come to notice where, for this very reason, the use of TFS material was excluded, because tooling costs were too high and production economy was detrimentally affected. Tools subject to special wear would be, for instance, slitters, scroll shears, and die rings in the press tool.

(45) It should be mentioned here that whenever the manufacture of drawn cans is discussed, the conventional drawing process is considered only, which is common for the manufacture of cans with a maximum diameter : height ratio of 1 : 1 - depending on number of draws -. The modern wall-ironing method is not suitable for chromium-plated materials today, because the CCO or CPT layer does not flow and, on the other hand, the "lubricating effect" of tin is still a decisive factor in the application of this method for tinplate.

3. TFS material in contact with products

(46) In the discussion of the performance of chromium-plated materials in contact with products we must consider that this material is regarded as a potential packaging material likewise for foods and non-foods and is even used for these purposes to some extent. The following basic deliberations apply to both product categories, the lack of tin being the essential factor.

(47) The tin which is available on tinplate is not only a prerequisite for soldering but is also a protection against corrosion. It is generally known that tin is a so-called amphotere element - it forms salts with acids and stannates with alkalis. In the use of tin-coated plate, this amphotere behaviour has pros and cons. No doubt, one advantage is the electrochemical element iron/tin, which developes according to product conditions and which, under the influence of potential polarization phenomena, permits the production of a technically safe package for most products under the aspects of corrosion performance.

(48) If tinfree steel is used, due consideration should be given to the non-presence of tin. As tin reacts with alkaline products to stannates, tin may, in case of damage to the inside can coating, be dissolved and the coating may delaminate. With highly aggressive, especially alkaline, but also acidic products, this results in extensive lacquer removal. This problem of lacquer removal by underfilm corrosion must not be expected with chromium-plated materials. As, firstly, the lacquer adhesion is outstanding and, secondly, no component exists between coating and substance which is undermined and may then cause lacquer removal, tinfree steel is clearly superior to tin-coated material, especially for alkaline products. This was the very reason why the first application of this material was in the field of detergents which are highly alkaline. With regard to a potential use of chromium-plated material for food products, the same considerations apply as for non-foods. The corrosion behaviour of the

container in contact with the produot may be different to that of tinplate containers. A negative phenomenon was sometimes observed with acidic products - evolution of hydrogen resulting in flippers. This may be explained as follows:

(49) As no tin is available, any attack by the acid in case of damage to the coating is directed onto the substrate, i.e. steel, so that the familiar metal-acid reaction takes place forming iron compounds and hydrogen. This problem might be excluded if poreless coatings could be produced. With a normal roller coating process, however, this cannot be warranted with 100 % safety, therefore the use of chromium-plated material for acidic products is extremely limited. Storage tests with low acid products (pH = 5 - 6) showed that TFS compared with tinplate cans tend to a higher release of iron. This problem must not be serious in any case, but it should be considered in packaging tests. Organoleptic and dis-coloration tests should be included.

(50) An outstanding feature is the excellent appearance of a TFS can, compared with a tinplate can, when emptied after extended storage, for example with fish preserves. Formation of black zones in connection with corrosion reactions does not occur with TFS cans.

3.1 The legal situation

(51) In the consideration of applications of chromium-plated materials for food packaging, relevant regulations under the food law naturally rank foremost. Layers of various chromium compounds are applied to the surface of the metal strip, so that, theoretically, there is a possibility that chromium compounds may migrate into the product. With regard to toxicity, however, chromium compounds are only mentioned where they are hexavalent, i.e. chromium in the hexavalent oxidation stage. The high toxicity originates from the very strong oxidation power of this ion. One should consider at first, therefore, which oxidation stages of chromium, either

chromium^{III} or chromium^{VI}, actually exist on the plate surface as a result of the production process. The metallic and trivalent chromium cannot be dissolved as hexavalent chromium under the conditions prevailing during preservation and sterilisation, because the oxidation potentials of practically all products are insufficient to induce this oxidation process. On the contrary, one may assume that potentially existing hexavalent chromium will in any case be reduced to trivalent chromium by the reducing components available in any food product. As a matter of fact, many food products originally contain traces of chromium in an order which may substantially exceed that which may be expected for a potential migration of chromium from the packaging container.

(52) Furthermore, the fact should be considered that a great number of containers are in daily use in households and industry which are manufactured of steel-chromium alloys and which serve for preparation and storage of foods. Up to now, problems of this kind have never occurred. Moxover, the coating, which is necessary for the container manufacture, virtually excludes any contact between container material and product.

(53) With respect to a potential migration of chromium into the product through possibly existing pores or scratches in the lacquer film, the packaging manufacturer will be responsible for proving the extent of potential chromium pick-up by the product. Storage tests have already provided ample results in this respect. The following table lists the most important test results for various products and storage periods:

Table 1

Product	Can specifications (all cans inside coated	Storage	Chromium pick-up in ppm at room temperature	at 37 °C (100 °F)
shrimps	3-piece, body: tinplate top & bottom end: TPS	1 year	0.01 - 0.02	0.02
	3-piece, all-tinplate can	1 year	0.02	0.02 - 0.03
herring in tomato sauce	2-piece can, drawn body and top end TPS	1 year	0.07 - 0.15	0.11 - 0.15
herring in horse-radish sauce	" "	"	0.09 - 0.14	0.10 - 0.16
herring in mushroom sauce	" "	"	0.10 - 0.15	0.13 - 0.17
mackerel in oil	3-piece, body: tinplate top & bottom end: TPS	1 1/2 years	0.02	0.02 - 0.03
mackerel in tomato sauce	" "	1 1/2 years	0.03	0.03 - 0.04
clams in oil	" "	1 1/2 years	0.12 - 0.15	0.12 - 0.16
liver paste	2-piece, drawn, all-TPS	2 years	0.15 - 0.24	-
mortadella	" "	"	0.23 - 0.27	-
blood sausage	" "	"	0.20	-
beef	" "	"	0.08 - 0.12	-
potted meat	" "	"	0.12 - 0.13	-
liver sausage	" "	"	0.16 - 0.20	-
peas	3-piece, body: tinplate top & bottom end: TPS	2 years	0.08 - 0.21	0.09 - 0.22
carrots	" "	"	0.06 - 0.18	0.08 - 0.24
dry beans	" "	"	0.11 - 0.22	0.10 - 0.26
green beans	" "	"	0.06 - 0.16	0.07 - 0.22
evaporated milk	3-piece, body: tinplate top & bottom end: TPS	1 year	0.25 - 0.30	0.28 - 0.35

3.2 Product performance

(54) It is common practice to make storage tests with new materials for packaging purposes in order to test their suitability for the products to be packed. Test packs were stored of much more different products than are actually introduced on the market. The great number of tested products provided a general survey of the product performance in these containers. One could anticipate for these storage tests that different main applications would develop in the various countries. In the first instance, those products were tested which were packed in containers which could easily and without much technical effort be made of TFS instead of electrolytic tinplate, for instance drawn cans for fish products. In the second place then, those containers were considered for which new manufacturing processes had to be developed for the application of TFS materials, so as to open up new markets for these materials, for instance beer and beverage cans.

(55) For a comparison with tinplate, the following considerations will be applicable in respect of the various products:

- (56) Use of tinplate coated on both sides:
  In this case, principally, TFS plate coated on both sides may be used, provided that compatibility tests have proven its suitability for the respective product.
  Examples: Drawn cans, top and bottom ends for cans, bottle closures.

- (57) Use of tinplate, inside coated, outside plain:
  In view of the problems involved in the conversion of this specification, an outside coating is recommended for TFS (sensitivity to surface scratches). In cases where a higher tin coating weight is specified for the outside in order to reduce outside corrosion, TFS coated on both sides may be used without economic loss.

- (58) Use of tinplate, inside plain, outside coated: Similar considerations as above apply. The manufacture of these components of TFS requires an inside coating as well. If no mechanical damage to the inside surface during manufacture were to be expected, inside plain TFS material might principally be used for packing of non-aggressive products, for instance oil, fat, dry products, etc. At any rate, care must be taken that the cans be stored before filling in an atmosphere which excludes atmospheric corrosion. Moreover, no residual humidity must remain in the closed can, a factor which should be born in mind in the choice of products to be packed. This requirement is established on account of the exposed weld seam, which is that portion of the container that is most liable to corrosion.

- (59) Use of tinplate, plain on either side: In this case, the plate should be coated on both sides, too, or at least on one side, as pointed out above. Whether the use of TFS material coated on either side will be economical, depends on the tin coating weight, as will be dealt with in detail later on in connection with economical problems. Calculations will have to be made in each individual case.

- (60) Use of untreated blackplate: Despite its higher price, the use of TFS materials will principally be recommended wherever storage conditions may cause extensive problems with regard to rusting of untreated blackplate. This applies in particular to those countries with humid climates and high temperatures which enhance rusting of blackplate. Tests with certain TFS materials showed that they may be stored over several months without rusting because of their stabilising surface finish.

(61) In this connection, reference should be made to new coating methods which are still in the development stage. For instance, they offer a possibility of coating untreated blackplate coils and of curing the lacquer by electron beams already in the rolling mill. This could mean that the present distinctive advantage of TFS might not predominate as much in the future as a result of the development of more economical coating procedures.

3.2.1 **Foods**

Meat products:

(62) Results on hand show that all-TFS cans (two-piece, drawn cans, coated on either side) are principally suitable for packing of meats and that no serious corrosion must be expected during storage. TFS is superior over tin-coated material inasmuch as the organic sulphur compounds developing during sterilization do not react with the surface to so-called "marbling stains", so that the lacquer adhesion is not jeopardized. Tests carried out so far include products like potted meat, various types of sausage, beef, hash, stew, etc. With spiced sausages, elimination of damaged coatings is of vital importance in order to avoid contact between product and iron.

Vegetables:

(63) These products, for instance beans, peas, carrots, are currently packed in 3-piece cans, therefore TFS will be considered for top and bottom ends only. If the plate is coated on both sides, normal storage periods without serious problems may be expected also in this case. With reference to the packing of mushrooms, asparagus and celery, no basic results are available for inside coated tinplate bodies. These three products are representative of a great number of products for which a light colour of the canned product is desirable. They are packed in plain tinplate cans today, because the tin has a reducing effect upon the respective colours, so that the product colour turns lighter.

(64) Under the food laws of various countries tin pick-up limits have been established, which are in force or will become effective shortly. The use of inside coated cans will be prerequisite under such regulations, and the appearance of the canned product will also play a part.

(65) When switching to inside coated cans, the possibility of undesirable black discoloration as a result of the reaction of, for instance, tannic acid compounds in asparagus with iron from the packaging material should not be overlooked. In any case, where TFS will be used as top and bottom end material for a fully inside coated can, storage tests and possibly also coating tests should be carried out.

Fruit products:

(66) Fruit products generally have a low pH. As indicated, TFS behaves quite different towards acidic products than tinplate because of its different electrochemical performance. With the present state of the art, TFS cannot safely be used for these products unless an adequate inside coating provides a reliable coverage of TFS against the product. The normal roller coating does not generally provide a film free from pores and scratches, however, therefore a subsequent spray-coating of top or bottom ends or of the entire can must be recommended. Storage tests were made for peaches, plums, pineapples, apples and apple sauce, oranges and gooseberries as well as dark coloured fruit like cherries, strawberries and currants. In all cases where corrosion occurred, damage of the coating from the conversion process was found to be the cause. It is important to note that - except for the dark coloured products, which are never packed in cans with plain bodies - the corrosion phenomena were contingent upon the use of either fully inside coated cans or cans with plain bodies. In the latter case, corrosion at the TFS top and bottom ends were not as serious as with plain cans.

Fish products:

(67) In this case, the product type is decisive. Two-piece cans are extensively used for fish products, therefore all-TFS cans are considered as an alternative to tinplate. No problems should be expected for all fish product types which are topped with oil, for instance, sardines, tuna fish, herring. These products are already packed in TFS cans to a large extent.

(68) Apart from these fish-in-oil products, there is still a great variety of formulae which is much more aggressive, for instance fish in tomato, mustard, horse-radish, beer sauce or the like. TFS was commercially adopted for these products during the past few years as well. The essential prerequisite is that the inside coating is adapted to the product to be packed and to the respective TFS material, in order to avoid the formation of pores and scratches in the coating film during drawing to the largest possible extent.

(69) The above products are sterilized goods. Semi-preserves which contain a very large portion of acetic acid, citric acid or salt and preservatives, are not yet packed in TFS cans because of the low resistance of TFS to high acid, corrosive products.

Soups:

(70) Soups are also packed in 3-pieces cans. A replacement of top and bottom ends by TFS is principally possible and has been affected for some products. TFS is commercially used as top and bottom end stock - in connection with a plain tinplate body - for mushroom and creme of tomato soup. Other soup recipes will certainly be changed to this can specification without causing serious problems.

Beer and beverages:

(71) This is the field where TFS - both CPT and CCO - made a true inroad during the past 2 - 3 years when the technological problems in can manufacture had been solved. One may say that

tin-coated material must still be used today where tin is required as a body soldering means on account of the production conditions. In all other cases where the cans are either welded or lap-glued, tin will not be required for the entire can any more. The bottom end is also made of TFS material. The respective top ends are generally made of aluminium which fulfils two functions:

1. The suitability of this material for the manufacture of easy-opening ends, i.e. ends which may be opened without any tool;
2. anodic protection offered by aluminium against potential iron pick-up of beer from the other can material.

(72) According to information circulated during the past few months, it is intended to replace CCO and CPT material - after the respective equipment for the manufacture of tinfree steel cans has become available - by a blackplate which is either "as rolled" or provided with a "passivation layer". At the present time, this process cannot be considered as finished and matured.

(73) Since iron pick-up plays an extremely important part with regard to canned beer quality, all cans are inside spray-coated in addition to the roller coating and the side striping. This procedure is not particularly necessary for TFS material, it was previously employed for tinplate cans as well. Thus it is possible to pack also comparatively acidic carbonated beverages with down to pH 3 in TFS cans. This is not contradictory to what was said before - that acidic products cannot be packed in TFS - for two reasons: the additional inside spray-coating covers practically all pores and thus eliminates the contact between product and metal and, second, the cans are not sterilised, so that potential corrosion reactions are eliminated, as these occur mainly with higher temperatures.

<u>Other foods:</u>

(74) A further application for TFS plate is the packing of dry products, for instance cans for coffee, biscuits, nuts, sweets, etc. It is principally suitable for all those containers which

were previously lock-and-lap-seamed or welded. Compatibility may be considered as warranted with adequate inside coating.

3.2.2 <u>Non-food packages</u>

(75) Where TFS is to be employed for non-food packages, the essential factors are the container manufacturing procedure and economics rather than the product to be packed. In general, one may say that TFS is suitable as an alternative to tinplate under technical aspects, if the respective package can be produced on existing equipment. This refers in particular to products of the chemical and technical industry, especially oils, lubricants, varnish, solvent-based paints and similar products. TFS may even be used in plain condition if the manufacturing process permits elimination of scratching. If cans or packages with welded bodies are required, the protective surface finish must be removed for welding and side-striping be applied afterwards in order to avoid corrosion by atmospheric influences on the outside and by the product on the inside. TFS is superior to tinplate for technical products such as water-based paints and varnishes. As these are highly alkaline in general, the undesired reaction with the tin surface of tinplate which may even result in lacquer removal over large areas is eliminated. TFS means technical progress for these products.

(76) The available test results for TFS may thus be summarised:

- Coated TFS: For water-based dispersion paints, offering advantages over coated tinplate.
- Plain TFS : For such products which contain so-called tin solvents, i.e., which cause early detinning. Furthermore, solvent-based paints and varnishes, alkaline soaps, detergents, solvent-based glues. No water-based products! The use of plain material, however, is based on the assumption that containers without surface damage are produced.

(77) TPS should not be used as a non-food package for acidic products, for instance paint remover, hardening agents for two-component systems consisting of anorganic and organic acids and similar products.

(78) TPS has found a wide field of application for battery shell manufacture, it is used on commercial scale here. Outside printing and coating will, however, depend on the surface structure. In cases where tin is used as a "silver colour" in decorations, TPS materials change the situation basically.

(79) TPS will gain importance shortly for the manufacture of aerosol cans, because some aerosol formulae still cause corrosion problems with tinplate cans. Highly alkaline products, such as oven cleaner, might take the lead here.

4. Economical considerations

(80) The economic factor is of decisive importance in using TPS in place of tinned material in the packaging industry. It is assumed that the basic material accounts for 50 - 80% of the sales price of the container, depending upon container specification. Therefore, the question of costs of the material used is of great significance. The material cost share in the sales price is, of course, higher for an unprinted, unlacquered container than for a container treated outside and inside, with multi-colour print and special lacquers, as this is the case for beer and beverage cans.

(81) It is not the object of this report to compare costs between the various types of material as these comparisons vary considerably in the various countries. Within the scope of this report it is, however, necessary to point out the basic economical points:

(82) TPS is produced on similar installations as electrolytic tinplate. The basic material for the production of electrolytic tinplate and for TPS is practically the same. It is a soft steel, low in carbon, in form of a blackplate coil, approx. 0.15 - 0.49 mm thick. This blackplate coil is fed into the

lines. An electrolytic process separates the metallic tin or, in case of TFS, the chromium compounds. The pre-treatments - de-greasing, cleaning and pickling of the coil - are essentially the same for both. The difference begins with the depositing process on the surface coating. In place of a tinning bath, baths of different composition are used, based on chromic acid or alkali chromates. A big cost factor is the current required for the separation process. As you know, the current efficiency for tinning is good; the current efficiency for chromium-plating, in particular of higher thickness, is considerably lower. In addition, the electrolytic tin separating process is followed by a flow-melting process. This brings about the shine, on one hand, and the formation of iron-tin-alloy layer on the other. This last process is not necessary in chromium-plating. Because of the low current efficiency in chromium-plating, it may be necessary to limit the maximum line speed accordingly.

(83) It is mainly the energy utilization and, possibly, the line speed which must be taken into consideration in a calculation. The essential advantage of chromium-plated material production is that one is independent of tin which is costly and subject to extreme price fluctuations.

(84) Roughly speaking, the calculation should, in any case, include the line costs, so that the general price structure of TFS is between untreated blackplate, and tinning of 5.6 g/m^2 (0.25 lbs./b.b.), which is the lowest tinning used. The end price of TFS between these two points is dependent upon several technical, economical and price-political factors.

5. **Prospects**

(85) On principle, TFS material will continue to make headway in the future, regardless whether tinned material is available or not, i.e. regardless whether the costs will swing in favour or in unfavour of the tinplate. As mentioned in this report, TFS has a number of true advantages, which must be utilised.

(86) In the foreseeable future, the use of TPS will extend in such areas in which individual components are produced, e.g. crown corks and other bottle closures. In addition, TPS will be used for two-piece cans, as these do not require the latest welding and gluing devices. Parallel to this, it is to be expected that top and bottom ends of three-piece cans will be made of TPS in case of product compatibility. All-TPS cans for sterilized food, require high-speed welding devices or the development of sterilization-proof glues. Both require great technical efforts and large investments, so that an expansion of TPS into this area is not foreseen in the near future.

(87) TPS, the new material, is in a very advanced state of development, but we have a long way to go until we can speak of a uniform material with optimum features with regard to economy in production and with regard to its use in the packaging industry. Practically all countries, which produce this material, are engaged in extremely intensive development work. As of this date, it is not possible to refer to a universal material. It is, for instance, possible to refer world-wide to tinplate of the specification 11.2 g/m^2 tin coating weight (0.50 lbs/b.b.) with corresponding passivation, as for instance No. 311, and we have a material, the product compatibility of which is known to large extent. We have a long way to go yet to reach this point with TPS.

(88) We must assume today that practically each rolling mill is working on its own development. If it is to referred to a universal material in the future - and this is to be endeavoured - it will be necessary to develop a quality which is universally usable and which need not to be tested individually for each product to be packed. As long as each product requires its particular TPS, there are certainly limits to the universal use of TPS in the future. This is particularly true for countries, which do not have their own production plants, and which have to fill their material demand by imports. These imports - which are very likely

to come from various countries - would be material of deviating specifications and would have to be tested individually with regard to the lacquers to be used and with regard to the products to be packed. It should be the definite aim of all parties concerned with the production and with the processing of this material to work out an ISO recommendation for this material, as has been done for tinplate, so that, one of these days, there are clear specifications and generally valid data on the performance of this material.

[redacted]

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