This invention relates to improvements in tin plate and treatment of tin plate containers. A co-pending application of William Clayson, filed July 2, 1936, Serial No. 88,689, describes the electrophoretic deposition of lacquer on tin plate in which an anodic film may be formed beneath the lacquer. I have now found that anodic protection is especially applicable to containers for foodstuffs with the object of preventing or reducing sulphide staining. I have discovered that by suitable electrolytic treatment, for example, in dilute ammonia, the tin plate forming the anode, films can be produced which, while being imperceptible, have the effect of rendering the tin plate resistant to sulphide staining by many foodstuffs which normally discolor tin, the containers appearing clean and bright after retorting.

According to the invention it is possible to pack suitable foodstuffs e.g. meat rolls, meat soups, peas, in anodically protected tin plate containers without any further protection by lacquer or otherwise. After washing the protected tin plate, drying is usually unnecessary before filling the cans with foodstuffs. The foodstuffs mentioned above are approximately neutral or only slightly acid in reaction, but in contact with strongly acid foodstuffs such as fruits, it is desirable to protect the anodically oxidised surface with a coating of lacquer, which may however be transparent. In some other cases it may be desirable to provide a layer of lacquer e.g. with foodstuffs which produce sulphur heavily such as canned shrimps. In this case prolonged anodic treatment may be followed by electropheresis of lacquer or by spraying or rolling lacquer, followed by stoving.

In applying this process on a commercial scale, a difficulty arises from the fact that often the tin plate used for making the containers comes from a number of different manufacturers. My investigations have shown that the surface of the ordinary tin plate of commerce is generally covered with a thin, almost imperceptible film probably consisting of oxide, organic matter, or both. The characteristics of this film, however, may vary considerably according to the source of the plate, and these differences are probably associated with variations in manufacturing procedure. As examples of the differences which are to be found between different brands of tin plate, I may quote the following:

1. The colour of the plate, when compared with a freshly de-filmed sample, appears distinctly yellow with some brands, while others show a scarcely perceptible difference; various degrees of coloration may be observed, according to the make or batch of plate.

2. If a sulphur-containing foodstuff is processed in unaliquerced cans, the intensity of sulphide staining under otherwise identical conditions depends considerably on the brand of plate, whereas with de-filmed tin plates the intensity is substantially the same in all cases.

3. On anodic treatment of the plate in an electrolyte such as dilute ammonia, at a current density such that a vigorous evolution of oxygen occurs, it is observed with some brands that the gas is evolved from the surface in fine bubbles, the surface itself exhibiting sequences of interference tints on continued electrolysis. With other brands, large bubbles are formed which leave the surface with difficulty, interference tints are not shown, and on withdrawing the sample the surface appears mottled, due to uneven thickening of the anodic film. On defilming, however, all samples behave similarly, giving fine bubbles and interference tints.

I have further found that this pre-existing film on the plate affects the anodic process, and owing to the above-mentioned differences, between the films on plates from different sources, it cannot be ensured that a given anodic treatment will produce the same result in all cases. This difficulty may be overcome by removing the pre-existing film by electrolytic means, before subjecting the plate to an anodic treatment for protection against sulphide staining.

I have now found that in many cases it is possible to remove pre-existing films by cathodic polarization, for example, in the same electrolyte as used for anodic treatment, but in practice I have found that this method is not always satisfactory. While reduction of pre-existing oxide appears to take place, cathodic treatment often fails to remove the film completely. This is shown by the facts that the tin plate surface still shows "water-break," i.e., is not completely wettable by water, and that the efficacy of the subsequent anodic treatment is less than when de-filming is achieved by the method to be described.

According to a further feature of the present invention, pre-existing films are removed and an anodic film formed on the tin plate surface by treatment in a single electrolyte, for example ammonia or ammonium carbonate, in which the tin plate functions alternately as anode and as cathode, the last function being as anode. For...
example, the tin plate may be made first anode, then cathode, then anode again. The complementary electrode is conveniently of nickel or stainless steel. In this example, the preliminary anodic and cathodic treatments are preferably effected at such current densities and for such times that vigorous gas evolution occurs, with the object of disrupting the pre-existing film, but the final anodic treatment is preferably carried out under such conditions of current density and time that substantial gas evolution is avoided. The conditions are not critical, and the following example is merely typical of many which have been found suitable.

First anodic treatment: 40–60 amps./sq. ft. for 2 secs.
Cathodic treatment: 40–60 amps./sq. ft. for 2 secs.
Final anodic treatment: 4 amps./sq. ft. for 2–6 secs.

I have found that the sequence of anodic and cathodic pre-treatments has the effect of removing the pre-existing film much more thoroughly than does simple cathodic treatment. Thus the plate after de-filming by the former method does not show "water-break," and effective protection against a given sulphur-containing foodstuff is obtained with a shorter final anodic treatment.

An important feature of the invention is that the whole of the operations may be effected in the same electrolyte, thus avoiding the need for intermediate washing between the various stages. Where the invention is applied to fabricated containers, the sequence of operations may be carried out with a single charge of electrolyte in each container, but where tin-plate sheets are treated it may be advantageous to pass the sheets through a separate bath of electrolyte for each stage, in order to avoid short-circuiting of the current between successive sheets undergoing different stages of treatment. Thus tin-plate cans may be treated on a conveyor or on a circular rotating platform, an electrode being automatically brought inside each can.

Although in the above examples the use of ammonia or ammonium carbonate as electrolyte has been mentioned, the invention is not restricted to such substances. These are, however, preferred, singly or in conjunction, on account of their complete volatility on drying by heat. Thus no deleterious residue need be left on the plate through insufficient rinsing after treatment. Alternatively, if the cans are rinsed but not dried, there is no possibility of harmful material entering the food. Many other solutions are suitable, not necessarily alkaline or oxidising, the essential requirement being that a compact film consisting of, or containing, tin oxide shall precipitate on the tin-plate anode as a result of electrolysis. Thus for example, sodium or potassium dihydrogen phosphate (acid), sodium or potassium mono-hydrogen phosphate (alkaline), or an equimolecular mixture of these (approximately neutral) are all suitable.

As an example of suitable strength, I may mention an electrolyte consisting of three parts of 0.880 ammonia and ninety-seven parts of distilled water.

Although a principal object of the invention is to enable sulphur-containing foodstuffs of a neutral character to be packed in tin-plate containers without the necessity for using lacquer, where this would otherwise be desirable, I have found that a valuable application of the invention is the pre-treatment of tin-plate sheets or cans which are to be lacquered. It is well known in the art that satisfactory lacquering of tin-plate requires the surface to be as free as possible from grease or other foreign matter, and any process, by removing pre-existing surface impurities and forming a clean film of tin oxide, provides an excellent basis for a lacquer film. This is not true of simple anodic treatment, since the pre-existing film is not then removed. The lacquer may be applied by roller, spray, or electrodoposition.

The invention includes the preparatory de-filming treatment whether followed by anodic protection, either in the same or in a different bath, or by application of lacquer. I have found, however, that when a lacquer of the usual resin/drying oil type is applied by either of the first two methods mentioned, the acidity of the lacquer may be sufficient for an oxide film on the tin-plate surface, whether already existing or formed according to the invention, to be dissolved in or disintegrated by the lacquer. In such a case tin-plate lacquered after treatment according to the invention so as to form an anodic oxide film does not show superior resistance to sulphur compounds, over plate lacquered without pretreatment, although the continuity of the lacquer film may be superior. This loss of resistance to sulphur compounds does not occur when the lacquer is sufficiently neutralized by emulsification in an alkaline medium, and applied by electrodoposition. In this method anodic protection of the tin-plate may be obtained concurrently with the deposition of lacquer, but since the two processes are interdependent the extent of anodic oxidation is a function of the lacquer deposition, and it may be advantageous to provide a preliminary anodic film by treatment according to the present invention, before electrodoposition of lacquer. Moreover, as has been mentioned, by this means an improved surface for reception of the lacquer may be obtained.

My experiments have further shown that even where the anodically oxidised tin-plate is lacquered by electrodoposition, the lacquered plate shows loss of resistance to sulphur compounds if the final anodic stage of the pre-treatment has been carried out at too high a current density or for too long a time. This does not happen if the final anodic stage of the pre-treatment is such that vigorous gassing does not occur, as already recommended.

I claim as my invention:

1. Process of treating tin-plate which consists in subjecting the tin-plate to anodic oxidation in an aqueous solution of an electrolyte capable of producing a compact film containing tin oxide, and then to cathodic treatment in a solution, the anodic and cathodic treatments being effected at such current densities and for such times that vigorous gas evolution occurs, and then coating with a thin film of tin oxide by a final anodic treatment carried out under such conditions of current density and time that substantial gas evolution is avoided.

2. Process of treating tin-plate which consists in subjecting the tin-plate to anodic oxidation in an aqueous solution of an electrolyte capable of producing a compact film containing tin oxide, and then to cathodic treatment in an aqueous solution, the anodic and cathodic treatments being...
effected at such current densities and for such times that vigorous gas evolution occurs, then to anodic oxidation under such conditions of current density and time that substantial gas evolution is avoided to form a coating of a thin film of tin oxide, and to coating with lacquer by electrodeposition.

3. Process of treating tin-plate which consists in subjecting tin-plate in an aqueous solution of an electrolyte to anodic oxidation and then to cathodic polarization, the anodic and cathodic treatments being effected at such current densities and for such times that vigorous gas evolution occurs, whereby a defilmed tin-plate is obtained, and finally in an aqueous solution of an electrolyte to anodic oxidation under such conditions of current density and time that substantial gas evolution is avoided to produce a tin-plate resistant to sulphide staining.

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