Modern Food Packaging Technologies: Regulatory Aspects and Global Trends
Prof Prem Prakash Srivastav
Department of Agricultural and Food Engineering
Indian Institute of Technology Kharagpur
Week – 06
Lecture – 30

Welcome to the NPTEL online certification course on Modern Food Packaging Technologies Regulatory Aspects and Global Trends. Dear friends in the last lecture we have seen the aluminum foils and aluminum collapsible tube containers. In this we will be seeing the corrosion of metal packaging. The topic which we will be discussing in this lecture is introduction electrochemical corrosion   factors affecting the rate of electrochemical corrosion which will include polarization of the electrodes, supply of oxygen, temperature, passivation and internal corrosion, stress   corrosion cracking, corrosion of tin plate, corrosion of plate, corrosion of plane tin plate canes, corrosion of enameled canes, corrosiveness of food stuffs. The metals are considered to be important materials for the packaging of foods, combining   properties of strength, toughness, ductility and impermeability. However, the structure of metals which gives them their valuable practical properties is also responsible for their main weakness or susceptibility to   corrosion.

Corrosion is the chemical reaction between a metal and its environment.   It is a universal process affecting all metals to a greater or lesser extent. All foods interact with the internal surface of the can in which they are packed. The most common form of this interaction   is   corrosion.

In plane tin plate containers this takes the form of itching or pitting corrosion. The staining of the surface may also occur, but internal lacquers are available which reduce this effect by providing a barrier between the food and the metal wall. It also allows the use of other forms of metal container like tin free steel or aluminium   which would otherwise be corroded very quickly. In the unlackered form only tin plate has some corrosion resistance to the acids found in foods. All the other metals must have to be lacquered.

Even tin plate must be lacquered where particularly aggressive products are packed such as tomato puree or where there is a danger of pitting corrosion or surface staining. The reaction of metals in aqueous solutions are under moist conditions which is also known as wet corrosion is electrochemical in nature including the transfer of electric charge across the boundary of metal surface and its environment. And electrolyte is a medium which conducts electricity by movement of ions the cations like Fe 2 plus and anions like

chloride moving in opposite directions. This picture depicts the action of corrosion how corrosion takes place what happens it is a two stage process. In the first stage the iron of the container will be lose two electrons and that is absorbed by the metals or the depolarizers like oxygen, acid and cations of more noble metals they will accept the electrons released by the iron present in that and by that way the corrosion starts.

When an electrode reaction takes place at a metal surface the electron flows in the metal corresponds to an ion flow in the electrolyte. When a metal corrodes atoms of the metal are lost from the surface as cations leaving behind the requisite number of electrons in the body of the metal. This dissolution of the metal is called an anodic reaction and takes place at an anode and anodic reaction always involves the release of electrons or electrochemical oxidation. Simultaneously, reagents in the electrolyte solution react with the metal surface to remove electrons left behind by the departing metals which has already been explained in the last figure. This removal of electron is termed as cathodic reaction and takes place at a cathode.

The cathodic reaction always involves consumption of electrons or electrochemical reduction. Since practically all metals are covered with an oxide film this must be removed before the metal can be exposed to an electrolyte. In the adjacent figure the another way of representing the start of the corrosion. The factors affecting the rate of electrochemical corrosion are polarization of the electrodes, supply of oxygen, temperature and passivation. The polarization of the electrodes when a current flows there is a change in the potential of an electrode that is known as polarization.

As the current begins to flow the potential of the cathode becomes increasingly negative and the anode increasingly positive. Consequently the potential difference between the anode and the cathode decreases until a steady state is reached when corrosion proceeds at a constant rate. Thus the corrosion current and therefore, the corrosion rate will be affected by anything which affects the polarization of the electrodes and the same has been depicted in the adjacent figure. The second important thing is supply of oxygen. The rate at which oxygen is supplied largely governs the rate of corrosion since corrosion by oxygen reduction requires the presence of oxygen for the cathodic reaction to proceed.

The rate of supply is proportional to the rate at which oxygen diffuses to the metal surface and this depends on the concentration of dissolved oxygen in solution. This is the justification for the practice of attempting to remove all the oxygen from canned foods prior to sieving on the canned end. The another factor is temperature. The rate of corrosion generally increases with the increase in temperature as more reactant molecules or ions are activated and are able to cross over the energy barrier. Also increasing the temperature have a tendency to increase the rate of diffusion of molecules

or ions in a solution although the solubility of oxygen in water decreases with increasing temperature.

Another factor is passivation. Passivation refers to a material becoming passive that is being less affected by environmental factors such as air and water. Passivation involves a shielding outer layer of corrosion which can be applied as a micro coating or which occurs spontaneously in nature. As a technique passivation is the use of a light coat of a passive protective material such as metal oxide to create a shell against corrosion. If the metal can be oxidized to an oxide that is stable in the electrolyte then the metal is called passivated.

Passivation usually requires strong oxidizing conditions.   Thus corrosion resistant metals and alloys can withstand an aggressive environment because of the presence of thin films of adherent oxides on their surfaces. The oxide layer will completely stop the anodic reaction which is the direct cause of corrosion. And if the film is insoluble in the electrolyte solution it will form an insulation barrier which will reduce the rate of cathodic reaction. For example, the stainless steel which is composed of iron carbon and chromium where the minimum chromium content is 10.5 percent the chromium content of the carbon that will come into the contact with the oxygen of the atmosphere and it will form a chromium oxide protective layer which does not corrode. The internal corrosion failure of cans may also be caused by internal corrosion as a result of mechanical damage to the cans or a manufacturing fault or an unusually aggressive reaction between the can and its contents. The mechanical damage to cans such as denting caused by poor handling can results in cracking of the internal lacquer. This will allow the product to gain access to the underlying metal and may result in quite rapid localized corrosion depending on the can and the product. The formation of beads in the can body or rings in the can ends can sometimes result in either cracking of the internal lacquer at these points or loss of adhesion between the lacquer and the metal.

Either may eventually result in local corrosion of the metal by the product. The cause of the problem often lies in insufficiently flexible lacquers caused either by an excessive lacquer thickness or incorrect stoving of the lacquer.   Similarly the formation of embossed cords on can ends may also result in cracking of the lacquer leading to local corrosion. Now, the stress corrosion cracking. Stress corrosion is the acceleration of corrosion in certain environments when metals are extremely stressed or contain internal tensile   stresses   due   to   cold   working.

Stress corrosion is one of the most important types of corrosion because it can occur in so many metals. Because the conditions that cause cracking in one metal may not cause cracking in another.   It is very difficult to predict where attack will occur.   Stress

corrosion cracking is sometimes seen in steel cans in the beaded area of the body where cracks occur in the metal and are preferentially corroded. The corrosion of the tin plate corrosion   of   enabled   cans   and   corrosiveness   of   the   food   stuffs.

  The corrosion of plain tin cans, the reversal of polarity. The tin plate surface consists of a large area of tin and tiny areas of exposed tin iron alloy and steel as a result of scratches in the tin coating. Hot dipping tin plate had a considerable tin iron alloy layer. Electrolytic tin plate has a much thinner layer which is electro positive to the base and tin thus acting as a chemically inert barrier to attack on the steel base. The effect of this barrier   is   to   prevent   a   significant   increase   in   the   steel   cathode   area.

  Thus the density or degree of continuity of the alloy layer has a material effect on the rate of corrosion. In the case of tin plate exposed to an aerated aqueous environment, tin is noble to iron   according to the electrochemical series.   Therefore all the anodic corrosion is concentrated on the minute areas of steel and the iron deserves that is rusts. In extreme cases perforation of the sheet may occur. This is the process which occurs on the   external   surface   of   tin   plate   containers.

  But inside the tin plate can the tin may be either anode or cathode depending on the nature of the food. In a dilute aerated acid medium the iron is the anode and it deserves liberating hydrogen.   In deaerated acidic foods iron is the anode initially, but later reversal of polarity occurs and the tin becomes the anode thus protecting the steel tin has been described in this situation as a sacrificial anode. This reversal occurs because certain constituents of the foods can combine chemically with tin 2 plus ions to form suitable tin complexes. As a consequence the activity of tin 2 plus ions with which the tin is in equilibrium is greatly lowered and the tin becomes less noble that is more electro positive   than   the   iron.

  Rate of tin dissolution the corrosion in deaerated acidic food cans comprises three stages. During the first stage the oil and tin oxide layers are removed from the can surface and the speed of tin dissolution is high. This stage continues for 4 to 15 days depending on the nature of the food. The mirror surfaces of the tin coating should change to one in which the shape of the individual tin crystals may be seen with the naked eyes. Rate of tin dissolution in the second stage the corrosion speed is slow and almost constant.

  The continued dissolution of the tin causes broadening of the existing pores and scratches uncovering the alloy layer and the steel. The unprotected steel provides sites for cathodic reaction and the developed hydrogen to taken up by the depolarizers in the food. The area of exposed steel dictates the rate of hydrogen evolution and as the ratio

between the area of tin and steel decreases that is as more steel is exposed polarization decreases. This stage is slow and can last for over 2 years. The third stage is shown by a high rate of tin and iron dissolution.

A large area of tin is exposed hydrogen produced at a faster rate and accumulates in the tin causing swelling. Once the internal pressure in the can causes the ends of the can to bulge the product is no longer sellable since consumers cannot distinguish between a swollen can caused by microbial spoilage or hydrogen evolution. Also the metal content of the food may have reached an unacceptable level by this stage. Therefore this third stage is of little importance since by then the food will have reached the end of its acceptable shelf life. The possible tin iron coupled situations the four possible scenarios are possible in plain tin plate can depending on the nature of the food and the presence of depolarizers.

For example, normal detaining, rapid detaining, partial detaining and pitting, pitting corrosion and their normal detaining. Normal detaining is an essential process in plain cans of most foods. It has already been described earlier as the second stage and leads initially to itching and later detaining of the can. Food products characteristics of this type of corrosion include low pH products such as citrus, pineapple, peach and apricot packed in plain tin plate cans. Rapid detaining, rapid detaining is caused by the use of tin plate with a tin coating mass that is too light or by a product that is intrinsically too corrosive or contains corrosion accelerators such as dissolved oxygen or anthocyanins which are chemically reduced.

Food products characteristics of this type of corrosion include tomato and aggressive citrus fruits such as lemon juice as well as berry fruits. Partial detaining and pitting with partial detaining and pitting the tin is anodic to iron, but protection is limited because local anodes on the latter are more anodic than the tin. Early failure occurs because of hydrogen swelling or perforation as a result of the exposed steel continuing to corrode. This type of behavior is associated with products such as prunes or pier nectar or with steel of inferior quality. Pitting corrosion it is a reversal of the normal situation with iron being anodic to tin thus the tin does not corrode, but pitting corrosion of the base steel occurs.

In rare cases pitting corrosion will also occur when the tin is in fact, corroding, but at too slow rate to provide sufficient electrochemical protection to the exposed steel. Pitting corrosion used to be rare appearing in highly corrosive products such as pickles and carbonated beverages formulated with phosphoric acid. However, it is becoming more common and it is the major cause of failure in can piers and pier products. Corrosion of enameled cans food cans with enamel coatings are used to protect against

excessive dissolution of tin, sulphide staining, local itching and change in color of pigmented products such as berry fruits. However, the use of enamels will not guarantee the prevention of corrosion and in some cases may actually accelerate it.

Therefore, careful consideration must be given before selecting an enamel for a particular can food. The general pattern of corrosion in enameled can is very difficult from that in plain cans and is generally more complex. The only exposure of metal is an enameled can is at pores and scratches in the enamel coating and the cracks at the side seams. Some of these decontinuities in the enamel coating may coincide with pores in the tin coating thus resulting in exposure of the steel. Even if defects in the enamel film expose only the tin coating the availability of all the corrosion promoters in the can for attack on the limited areas of tin ensures that steel is soon exposed to them.

Thus it is easily possible for the use of an enamel to actually reduce the shelf life of the can product. The most important corrosion accelerators in foods include oxygen, anthocyanin, nitrates, sulfur compounds and trimethyl amines. From a corrosiveness point of view it is convenient to divide foods into five classes. Mildly corrosive such as apple and grape juices, berries, cherries, prunes, pickles and sauerkraut. Moderately corrosive such as apples, peaches, pears, citrus fruits and tomato juice.

Mildly corrosive such as peas, corn, meat and fish. Strong detinners such as green beans, spinach, asparagus and tomato products. Beverages are conveniently considered as a fifth class. The various factors that can influence the corrosiveness of food products and beverage are acid, pH, sulfur compounds, nitrates, plant pigments, synthetic colorings. Acids it has been well established that the tendency of an acid to form a complex with the dissolved tin has an important bearing on the relative polarity of the tin and steel and hence the degree of corrosion.

The type of organic acid is more important than its concentration and the addition of nitrate increased pitting severity in all acid solutions. pH, the pH of the system also determines the relative cathodic protection given to steel. In some cases tin is cathodic to steel over a certain pH range. In the case of acetic acid the range of pH is from 2 to 4.5 while in others it offers protection up to pH 4 above that level it may accelerate erosion.

Sulfur compounds, sulfur and sulfur compounds may be introduced into the can in a number of ways for example, as spray residues from agricultural chemicals as residues from sulfur containing preservatives and as components in sulfur containing compounds such as proteins in meat, fish and certain vegetables. There are two types of sulfite staining iron sulfide staining also called sulfite black and the other involves tin sulfides. Iron sulfide stains are characteristically black and usually occur at isolated points on the

can like head space during or immediately after heat processing. Iron sulfide is not formed at pH values below about 6. So, that it is uncommon to find it in the portion of the can in contact with the contents.

The problem may be overcome by using enameled cans or plain cans with enameled ends. Tin sulfide staining is usually widespread throughout the can and is blue black or sometimes brown. Two stages are believed to be involved in oxidation of the tin followed by deposition of an insoluble tin sulfide precipitate on the surface. It occurs during or soon after heat processing and shows little or no increase in intensity during storage. It may be reduced by using sulfur resistant enamels into which quantities of zinc oxide or carbonate are added before being applied to the plate surface.

These reacts with sulfur bearing gases to form almost invisible white zinc sulfide, nitrates, plant pigments, synthetic colorings, copper. The nitrates are very efficient cathode depolarizers. Since they are capable of being reduced all the way to ammonia, they have been responsible for serious economic and toxicological problems in some canned foods notably tomato products. Although nitrates and nitrites are also present as intentional additives in processed meats, they present no problem. This is because meat products are above the critical pH range that is 5.5 for detaining to occur via the nitrate tin reduction system. Plant pigments, anthocyanin and related pigments are among the most important potential corrosion accelerators since they are easily reduced. Anthocyanin pigments can also act as anodic depolarizers through their ability to form complexes with cations particularly those of iron and tin salts. The nature of the anthocyanin pigment is also important. For example, raspberries contains cyanidine glucosides which have ortho dihydroxy groups in their structures.

It is these groups which are involved in the formation of blue tinted complexes with metals such as tin. Synthetic colorings, the canned products which most commonly contain synthetic colorings are soft drinks which consist basically of sugar based syrups and carbonated water containing flavors, acidulants and colors. The behavior of soft drinks depends to the considerable extent on the presence of azo dyes and the amount of residual oxygen in the filled can. Both of these components are capable of acting as corrosion accelerators and are potentially active corrosive agent. Iron dissolution may adversely affect the color of some products and iron dissolution may lead to perforation and flavor defects thus fully enameled cans are essential. That is all for today. Thank you very much.