DOI: 10.24425/amm.2021.134769

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STEEL PACKAGING PRODUCTION PROCESS AND A REVIEW OF NEW TRENDS

Packaging steels are thin gauge flat carbon steels coated with tin or chrome on both sides. They are very important raw materials for the production of steel packaging, which allow food to be stored safely and with an extended shelf life. The publication focuses on the production process of ETP and ECCS steel, as well as the problem of corrosion of steel packaging.

The topic of legislative changes that require the elimination of chromium (VI) compounds from the steel passivation process was also discussed. The packaging steel industry is currently facing the need to develop a new passivation technology. Leading packaging steel manufacturers in cooperation with varnish and paint suppliers have developed chromium (VI) free technologies by implementing chromium (III) compounds and titanium oxide technology.

Authors focus also on new trends and potential development directions for the packaging steel industry.

Keywords: packaging steel, corrosion, ETP, ECCS, TCCT, CFPA

1. Introduction

Packaging steels are usually thin gauge flat carbon steels coated on both sides with tin (ETP) or chromium (TFS or ECCS). In some cases, the packaging steel can be coated with organic coatings, e.g. varnishes or polymer laminates (PET, PE or PP films). Thanks to the coatings used, the steel receives appropriate performance properties desired during its processing, including strength, stiffness, formability, lacquer ability and printability, weldability, aesthetic appearance as well as corrosion resistance. These properties provide adequate protection during transport and storage, as well as the safe storage of food and beverages, and other necessary functions required for packaging materials [1-3,23].

The mass production of tinplate began in 1810 when Nicolas Appert published a book about food preservation sterilization techniques, and in the same year, Peter Durand patented the use of metal cans for storing foodstuffs. Since then, the steel production process and the steel itself have been constantly improved to meet the requirements of the food packaging market [1-3].

The total European packaging steel production is estimated at 4.6 million tonnes per year. Annual turnover of EUR 3 trillion, with direct and indirect employment of over 15,000 people. This represents one-third of the estimated packaging steel production worldwide [12].

Packaging steel is used in many applications. Examples include various types of containers for food, personal hygiene, home, and automotive care, industrial products, and paints, gifts, or promotional products, as well as closures and aerosols. The figure 1 presents the division of packaging steel in Europe divided into product segments [12].

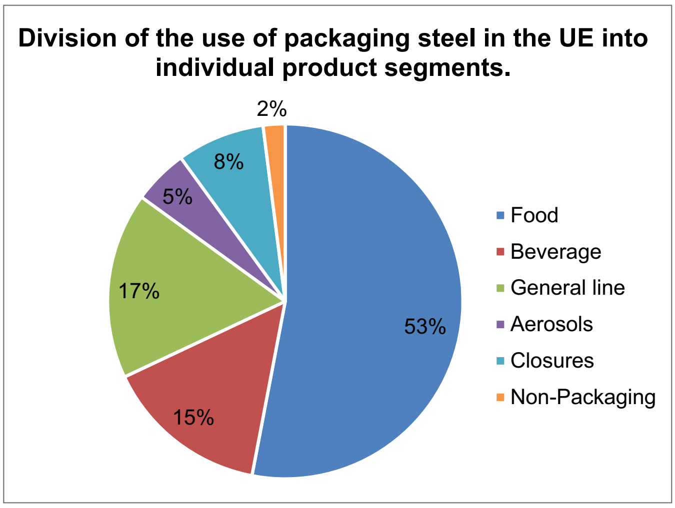

Fig. 1. The division of packaging steel in Europe divided into product segments

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2. Steel packaging production process overview

The tinplate steel production process (ETP) is complex and multistage. The first stage is to determine the so-called "Hot and cold phase". The pig iron is produced from iron ore and coal coke (1) in large quantities. Currently, the blast furnace accounts for around 70% of global steel production. Pig iron is transformed into low-carbon steel with an appropriate chemical composition in an oxygen converter (2). In the next stage the continuous casting of liquid steel in solid slabs of typical thickness 235 mm takes place (3). The slabs are hot rolled in the temperature range of 900-1200°C in order to be transformed into hot coils (4) with a thickness in the range of 1.5 to 3.8 mm and a typical width of 800-1300 mm. The coils weigh from 8 to 28 tons or more. Hot coils are the raw material for the production of packaging steel [2,5].

Hot coils get into a pickling process (5) to remove the scale from the surface from the hot rolling process. The process is continuous and takes place in a 20% sulfuric acid solution at a temperature of about 98°C. The steel strip is finally oiled to protect itself against corrosion and then coiled [2].

In the next step, the so-called cold metallurgical process can be presented. It is divided into 3 steps. The first is cold rolling to reduce the thickness of the steel strip to a required final gauge (6). Typical reduction values range from 85% to 95%. For example, it can be from 2 mm to 0.2 mm thick [2].

The second stage is continuous (CA) or batch (BA) annealing. This is a necessary treatment at a temperature of about 600-800°C to recrystallize the steel strip, restore its ductility and forming capability (7). In the case of batch annealing, the coils are placed in a furnace for a few hours in a protective atmosphere, e.g. nitrogen, to prevent oxidation of the steel surface. In the case of continuous annealing, the steel strip is constantly passed through the furnace, where the temperature is elevated and the protective atmosphere is also present. Continuous annealing is more popular due to obtaining material with higher yield strength and more homogeneous properties. An example of obtaining packaging steel from a continuous annealing process is TH500, while the batch is TS550 [2-3].

Despite the restored crystal structure in the annealing process, further rolling of steel is necessary. The temper rolling takes place without lubricants (8). It prevents the occurrence of so-called Lauders' bands during material formation. In addition, the steel strip thickness is reduced between 0.4 and 2.0% in this process, and the surface roughness is obtained. The higher steel strip thickness reduction ratio, the harder steel grade is obtained. According to ASTM, there are two reduction ranges: single (SR) and double (DR). The SR grade ratio corresponds to a reduction factor of less than 5%, whereas for DR grade ratio is more than 5%. DR grades are generally more durable and less embossing than SR. After this process, the black steel is obtained. It can be sold in coils or sheets or further processed [2-3]. Typical hardness values for black steel and ETP are shown in Table 1.

The tinning process of black steel takes place in an electrolyte bath (9). The tin anode is electrolytically dissolved in the solution and tin deposited on the steel strip. The process diagram is presented in Figure 5. The level of tin can be different on both sides of the strip, depending on the needs. Currently, the most common tin coating is from 1.0 g/m^2 to 11.0 g/m^2. Table 2 presents the ETP grades available in most countries together with the nominal tin mass [3,6].

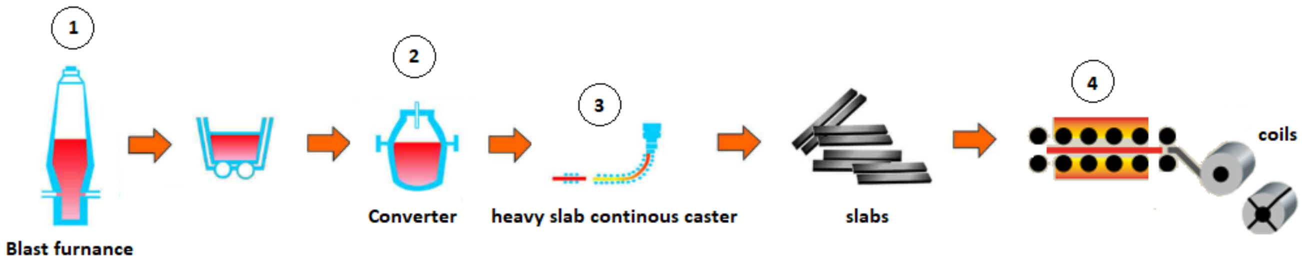

Fig. 2. Packaging steel production process scheme part 1/3 [33]

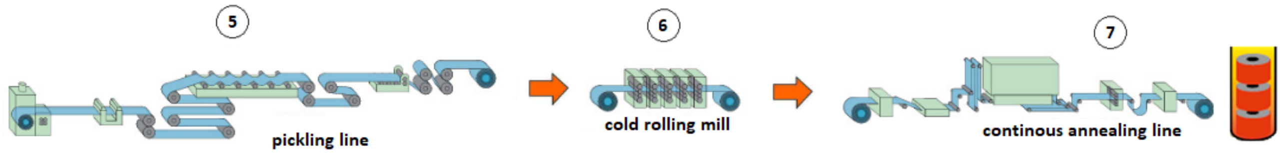

Fig. 3. Packaging steel production process scheme part 2/3 [33]

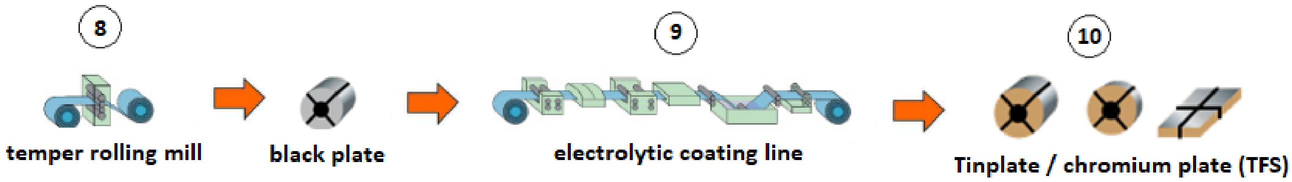

Fig. 4. Packaging steel production process scheme part 3/3 [33]

TABLE 1

Typical values for black steel and ETP [6]

Temper			Rockwell Hardness 30 T Scale	Formability	Applications
TS230	T50	T1	46-52	Soft for extra-deep drawing	Nozzles, spouts and closures;
TS245	T52	T2	50-56	Moderate deep drawing	Rings and plugs, dome tops, closures and shallow-drawn cans
TS275	T57	T3	54-63	Shallow drawing and general purpose	Can ends and bodies, large diameter closures and crown caps
TH415	T61	T4	58-64	General purpose where increased stiffness required	Crown caps, can ends and bodies for noncorrosive products
TH435	T65	T5	62-68	Increased stiffness to resist buckling	Can ends and bodies
—	T70	T6	67-73	Very stiff	—
TH550	DR550	DR8	70-76	High strength and stiffness	Small diameter round can bodies and ends
TH620	DR620	DR9	73-79	High strength and stiffness	Large diameter round can bodies and ends
—	DR660	DR9M	74-80	High strength and stiffness	Beer and carbonated beverage ends and DRD cans
—	DR690	DR10	77-83	Maximum strength and stiffness	Ends

TABLE 2

Standard Grades and Nominal Masses of ETP [6]

Code		Nominal Coating Mass per Surface	
Euronorms (145-156)	ASTM (624-626)	(gsm)	(Ib/Base Box)
	No. 10	1.1/1.1	0.05/0.05
E.2.8/2.8	No. 25	2.8/2.8	0.125/0.125
E.5.6/5.6	No. 50	5.6/5.6	0.25/0.25
E.8.4/8.4	No. 75	8.4/8.4	0.375/0.375
E.11.2/11.2	No. 100	11.2/11.2	0.50/0.50
D.2.8/0	—	2.8/0	0.125/0
D.5.6/2.8	No. 50/25	5.6/2.8	0.25/0.125
D.8.4/2.8	No. 75/25	8.4/2.8	0.375/0.125
D.11.2/2.8	No. 100/25	11.2/2.8	0.50/0.125
—	No. 135/25	15.1/2.8	0.675/0.125
D.8.4/5.6	No. 75/50	8.4/5.6	0.375/0.24
D.11.2/5.6	No. 100/50	11.2/5.6	0.50/0.25
D.15.1/5.6	—	15.1/5.6	0.675/0.25

E – equal coatings on each Surface; D – differential coatings on each surface.

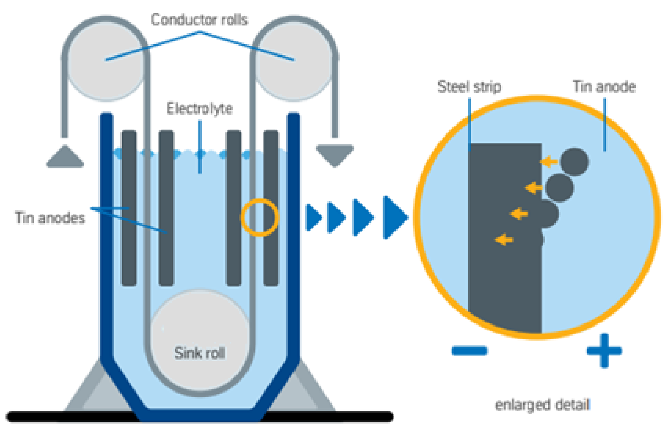

Fig. 5. Tinning tank [3]

The glossy of tin steel is obtained by heating the steel strip above the melting point of tin, i.e. 232°C, followed by temper in water. High tin surface adhesion and corrosion resistance can be obtained through a process called passivation. The most common is 311 passivation in a sodium dichromate bath for the electrolytic deposition of metallic chromium and chromium oxide on a tin surface. Details on this passivation are provided in Table 3.

TABLE 3

Chromium passivation types [2]

	Passivation code	Chromium coating [mg/m^2] per side
Dipping passivation	300	1-3
Electrolytic passivation	310	3.5-7
Electrolytic passivation	311	3.5-9
Electrolytic passivation	314	>5

If good varnish adhesion properties to the steel surface are required, 310 passivation is recommended. For 300 dipping passivation, only metallic chromium is deposited on the tin surface. This passivation is not recommended for a long period of steel storage (over several months). The last step is oiling the surface to improve processing, to protect against scratches and reduce friction. Dioctyl sebacate (DOS), butyl stearate (BSO) and acetyl tributyl citrate (ATBC) are most commonly used [2,3,17].

The chromium coating was developed primarily as a cheaper alternative to the tin coating. This process is similar to the electrolytic deposition of tin on black steel. Metallic chromium and chromium oxide are deposited on the black steel in the chromium acid electrolyte bath. This coverage is usually in the range of 0.05 g/m^2 to 0.14 g/m^2. The nominal chromium coating is shown in Table 4. The name of the steel obtained is „electrolytic chromium coated steel" (ECCS) or „tin free steel" (TFS). The appearance of ECCS is less attractive than ETP in terms of surface brightness. Chromium steel has very good adhesive properties for varnishes, however, it is not suitable for welding and storing acidic food due to its low corrosion resistance. As in the previous case, the last stage is oiling [2-3].

TABLE 4

Nominal chromium coating regarding to z UNI EN 10202:2004 [9]

Nominal chromium coating per both sides	Min quantity (g/m^2)	Max quantity (g/m^2)
Cr total	0,05	0,14
Cr oxide	0,007	0,035

2.1. ETP and ECCS as packaging material

As mentioned earlier, steel with tin (ETP) or chromium (ECCS) coatings is used to make steel packaging. The chemical composition of these two steels is presented in Table 5. The differences between the ETP and ECCS steel are shown at Figure 6 [1-3].

TABLE 5

Chemical composition of ETP and ECCS [4]

	Chemical composition						
	C (wt.%)	Mn (wt.%)	P (wt.%)	S (wt.%)	Si (wt.%)	Al (wt.%)	N (ppm)
ETP	0.052	0.256	0.010	0.011	0.005	0.037	55
ECCS	0.074	0.260	0.021	0.016	0.012	0.032	45

When comparing the properties of ETP steel and ECCS it should be mentioned that the main advantage of ETP steel is the possibility of welding. This property is useful in the production of three-piece cans, where welding occurs. ETP (even uncoated) is ideal for storing light, acidic foods because it prevents the food from darkening and changing its taste due to oxidation. Carbonated drinks are also more often packed in ETP steel [1].

ECCS steel has much better adhesion properties for varnishes and coatings compared to ETP. It is more accepted for the application of printing inks, enamels and varnishes than ETP due to the lack of a tin layer with a low melting point (232°C). Varnishes apply to ECCS can be dry at a high temperature, which reduces the drying time of ECCS and thus costs. No dust is generated during processing, which is observed in the case of ETP steel. In combination with foods rich in protein or containing organic sulphur (e.g. meat, fish, peas, corn), the tin in ETP steel can cause tin oxide stains. For this reason, products of this type are packed in ECCS [1].

In addition to the above technical criteria for choosing between ETP and ECCS, market availability and price are also important factors. There are definitely more ETP steel producers than ECCS. Unpainted ECCS steel is cheaper than passivated tin steel, due to the lower cost of metallic chromium than tin, and also because of the lower chromium coverage than tin per square meter (Table 6) [1].

TABLE 6

The cost of ETP vs ECCS [1]

	ETP		ECCS	
	Thickness [g/m^2]	Cost [cent €/m^2]	Thickness [g/m^2]	Cost [cent €/m^2]
Tin layer	1-11.2	1.62-18.11	0	0
Chromium layer	0.005-0.010	0.0075-0.015	0.114-0.35	0.717-0.525
Total cost		1.62-18.12		0.171-0.0525

However, ECCS steel is always coated with organic coatings, which is not required for ETP. Even if the ETP is covered with an organic coating, one layer is sufficient, where ECCS requires a minimum of two. When we consider the coating process, it may turn out that ETP is cheaper. It is also worth mentioning that the tin sources are slowly running out, which may change into greater demand for ECCS steel in the future. Table 7 compares the properties of the two steels: ETP and ECCS [1].

3. Corrosion of packaging steel

Steel is a very important packaging material. However, the chemical structure that gives it the appropriate properties is not resistant to corrosion. Corrosion is a surface oxidation. In the case of packaging steel, the metal inside the package, dis-

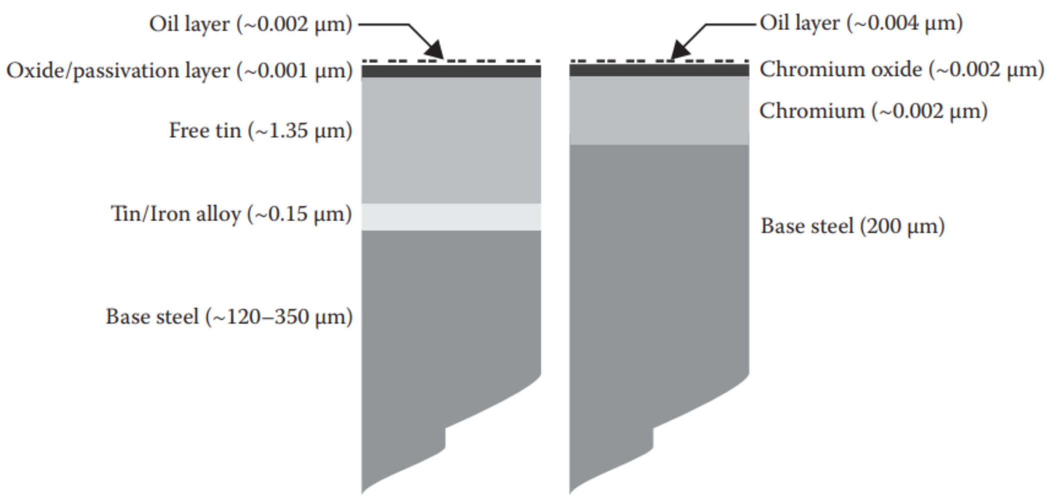

Fig. 6. ETP and ECCS – the difference and main functional layers (not to scale) [6]

TABLE 7

Comparison of ETP and ECCS properties

Properties	ETP	ECCS
Welding possible	√	x
Adhesion for varnishes and coatings	poor	good
Storage of food rich in protein and organic sulphur	x	√
Storage of acidic foods	√	x
Storage of carbonated drinks	√	x
Possibility of drying at high temperatures (above 232°C)	x	√
Market availability	big	average
Price*	higher than ECCS	lower than ETP

* Depending on the application of the organic coating.

solves, e.g. iron or tin. This is due to the reaction between the food and the package surface. The ability to corrosion control is extremely important for food packaging manufacturers, as well as for consumers. The goal is to keep the quality of packaging food as high as possible.

3.1. Internal corrosion of packaging steel

Food products in metal packaging are products with different pH, buffer power, and chemical composition. These factors can affect corrosion in different ways – some slow it down, others accelerate it. However, the main factor affecting corrosion is the type of steel from which the packaging was made: ETP or ECCS. Another factor is the type of galvanic coating, as well as several others: packaging characteristics, food composition, filling process, and storage conditions. When examining corrosion mechanisms, it should be taken into account that the metal packaging is a closed system, without any exchange with the external environment [7-10].

3.2. ETP corrosion

Corrosion of tin steel is a complex process. It can be considered as the result of the concurrence of several cathodic and anodic processes. The surface of tin steel due to several different layers is a very heterogeneous electrode. The variety of layers is due to different production conditions. Two corrosion schemes are considered for ETP steel. The first is electrochemical Sn and Fe coupling: galvanic cell (Fig. 7). Exchanged currents between different anodic and cathodic areas can affect the extensive surface of the electrolytic conductor. For this reason, the conductivity of the electrolytic environment, as well as the geometric surface, have a very big impact [7].

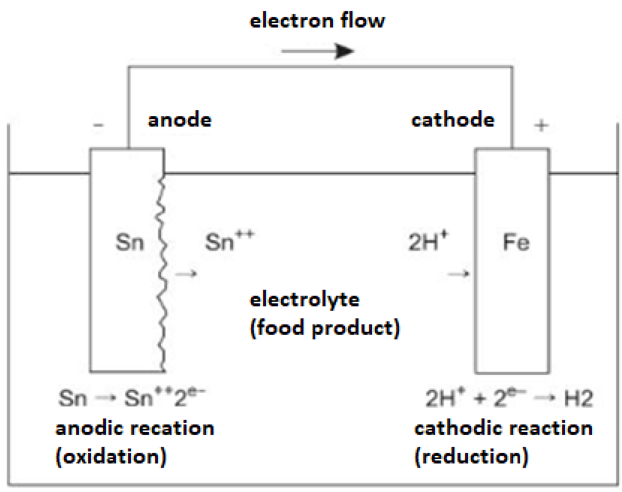

Fig. 7. Electrochemical coupling of tin and iron [7]

The second scheme is direct contact of iron and tin. In this case, anode reactions occur on the tin. Several corrosion mechanisms are possible here. Examples are shown in Figure 8. In the case of the scheme (a), tin is an anode, while in the case of the scheme (b) steel has this role. Scheme (c) shows lacquering

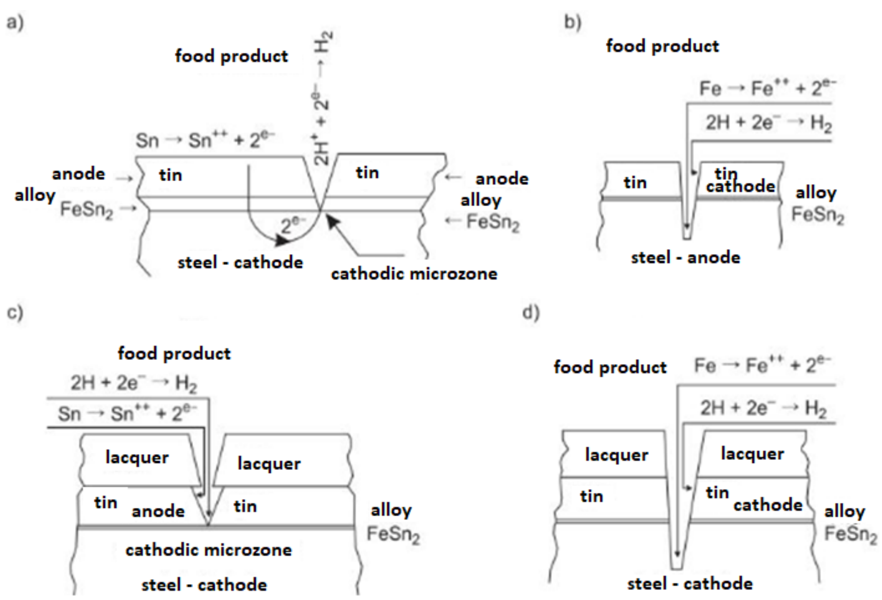

Fig. 8. The schemes of various types of corrosion mechanisms on ETP steel [7]

tinplate and tin as an anode, while in the scheme (d) lacquering tinplate and steel as an anode. In order to limit the interaction between the packaging batch environment and steel, the internal surface undergoing a varnishing process. In most cases, these varnishes contain a sulphur compound and also have a high acid reagent. The varnishing process is also desirable for aesthetic reasons [7,11].

It should be noted that chemical composition has an extremely important role in the steel corrosion process. In particular, an important role has steel structure dependent on cold and heat metallurgical processes. In the case of non-metallic Al_2O_3 inclusions, steel may be susceptible to perforation. Surface conditions as well as the presence of metalloids and metals are another important factor. Optimization of structure and surface allows obtaining steel with good coating uniformity and surface quality, which affects corrosion resistance. However, some metalloids such as sulphur, phosphorus and metals as copper have an adverse effect on corrosion resistance under specified conditions. An important factor affecting corrosion inside the packaging are the conditions under which the food is packaged. It is important that air and oxygen levels are kept to a minimum during this process. To this end, various packaging techniques are used, e.g. “hot filling” “steam jet”, pre-filling system or the use of a modified atmosphere [7,29].

Before the food arrives at the final recipient, the packaging is undergoing complex logistics and distribution. Also, these processes can affect the increase of corrosion. The main factors are packaging collisions and various types of transport-related vibrations. Storage temperature and humidity also have a significant impact, which promotes the increase of corrosion outside the packaging. Mechanical damage and transport vibrations under load can accelerate the phenomenon of corrosion, both by modifying surface relations and by creating conditions for the activation of the localized stress corrosion process [7].

3.3. ECCS corrosion

Chromium steel (ECCS) cannot be used without the varnishing process due to low corrosion resistance. During the process of forming ECCS steel, iron is exposed and acts as a corrosion initiation site. For this reason, this material must be used in combination with an organic coating (varnish or laminate). In addition, the ECCS steel surface is very hard and causes high consumption of processing tools in case of the absence of coating. The most important two corrosion mechanisms for this type of steel are wet corrosion, which occurs when the steel contacts the package contents, as well as atmospheric corrosion on the outer surface of the package [11,27].

It should also be noted that various annealing and rolling modes have a large impact on the surface morphology and grain size of ECCS products, and consequently on corrosion resistance [27].

4. New challenges in the steel industry – legislative changes

The packaging industry is facing changes due to new legislation. REACH legislation require the withdrawal of the use of chromium (VI) compounds that are used in the passivation process of steel. Chromium (VI) compounds are highly oxidizing substances and are easily reduced to chromium (III) compounds. If released into the environment, they may be in soil or water, which can lead to human exposure, e.g. through drinking water or contact with soil. People who have continuous contact with chromium (VI) compounds are at increased risk of lung, nasal cavity, and sinus cancer. The latency period is up to 20 years. Chromium (VI) compounds belong to the group of carcinogens for humans [18,19].

Therefore, chromium trioxide and acids produced on its basis were attached to Annex XIV of the REACH Regulation of April 21, 2013 (EU Regulation No. 348/2013). On this basis, the use of chromium (VI) compounds was allowed until 21 September 2017. After this date, appropriate authorization for their use is necessary. Seven applicants submitted a joint CTA Sub application that covers all their downstream users for six specific CrO_3 applications. These applications include: (1) formulation of mixtures, (2) functional chrome plating, (3) functional chrome plating with decorative character incl. etching of plastics, (4) surface treatment for applications in the aeronautic and aerospace industries, unrelated to functional chrome plating or functional plating with decorative character, (5) surface treatment for application in various industry sectors such as architectural, automotive, metal manufacturing and finishing and

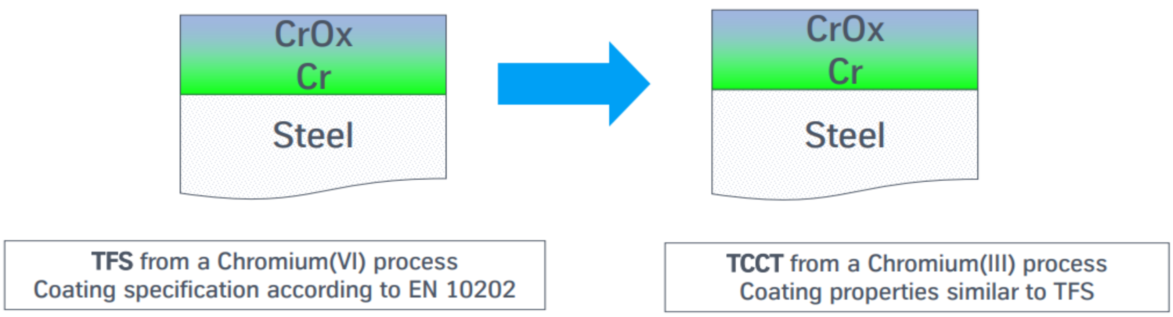

Fig. 9. TFS (ECCS) vs TCCT [24]

general engineering (6) passivation of tinplate steel (ETP). The application was submitted before the final date, which means that all users have been covered by transitional arrangements from 21 September 2017 [20,21].

For REACH to issue a positive decision authorizing the continued use of CrO_3 for appropriate use, appropriate alternatives must be provided. An extension is expected until 2024. Therefore, steel producers are required to develop new methods of steel surface passivation. Researches in recent decades have focused on developing trivalent chromium electrolytes, as chromium (III) compounds are not toxic or carcinogenic. TATA Steel has developed and patented the innovative technology "Trivalent Chrome-Coated Technology" (TCCT), where chromium (III) salts are used in the process in combination with formic acid. This technology will replace current ECCS steel production. Consequently, the surface structure of the passivation layer is practically the same as when using chromium (VI) compounds – Figure 9 [13-16,21,22].

Chromium (VI) compounds are also used in the tin steel (ETP) passivation process. The APEAL association unites European producers of packaging steel. Its members have actively worked in recent years to develop an alternative to chromium (VI) compounds. The newly developed technology is "Chromium-free Passivation Alternative (CFPA), where ETP steel is passivated on both sides with titanium oxide with a coverage of 1 ± 0.2 mg/m^2. The structure is shown in figure 10. CFPA passivation ensures balanced control of the growth of tin oxide during storage, ensuring adequate product functionality. CFPA is fully compliant with EU and FDA regulations and is approved for both coated and uncoated tinned food contact materials. The European standard EN 10202 is currently being updated to include CFPA as a new European passivation standard [14,25,26,30].

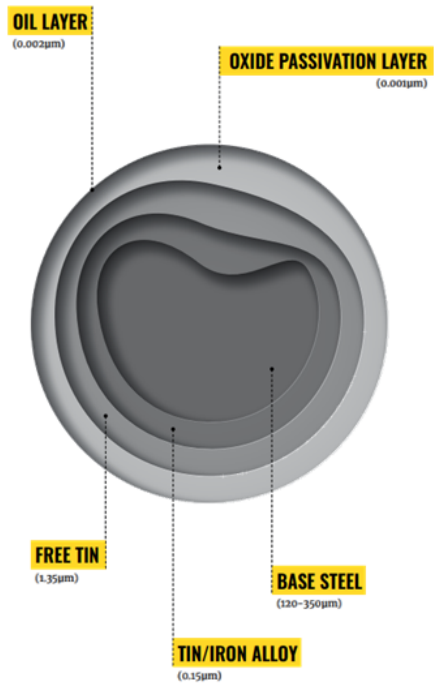

Fig. 10. Schematic structure (not to scale) of tinplate showing the main functional layers [25]

5. New development directions in the steel packaging industry

The sustainable development and trend of environmentally friendly packaging are constantly growing. The use of smaller amounts of raw materials for the production of packaging steel, i.e. the design of new packaging made of thin steel, is an extremely important trend for ecology. Producers of packaging steel together with packaging producers are facing the requirement to develop packaging from increasingly thinner steels while maintaining the same processing and quality requirements for the final product.

Europe has shown leadership in the world through a key and visionary European Green Agreement plan to combat climate change and make the EU climate neutral by 2050. An ambitious new action plan for the circular economy (CEAP 2.0) is necessary to impose difficult waste and recycling targets [30]. Recycling of steel packaging in Europe achieves a record average level of 82.5%, according to data published by APEAL (Fig. 11).

This new record indicator, which represents data from 2018, confirms steel as the most recyclable packaging material in Europe and means that more than 8 out of 10 steel products placed on the EU market this year have been processed into new steel products. Steel is by far the best of all packaging materials to achieve the goals of the new circular economy action plan (CEAP 2.0). The industry must continue to improve the collection and recycling of steel packaging throughout the EU.

Intelligent packaging is another important development direction in the steel packaging industry. The term 'intelligent packaging' covers many different technologies, including QR codes, artificial intelligence, virtual reality, and short-range communication. These technologies encourage interaction between the product and the customer. Currently, virtual reality is still not easily accessible to the client. More and more packaging manufacturers are turning to offer intelligent packaging technology, but this area is still in need of development.

Packaging manufacturers are becoming increasingly aware of the chemicals used during the production process and their impact on the product and the final consumer. Among other things, it has been proven that many chemicals have adverse effects after prolonged exposure. The safety and well-being of people have always been a top priority, which is why manufacturers reduce the chemicals used in production and find more efficient ways to create packaging that is safe for consumers, especially for food packaging. Examples include new passivation technologies without chromium (VI) compounds as well as water-based paints.

The common problem of packaging steel corrosion is also an important development direction. The development of new, intelligent anti-corrosion coatings can have a significant impact on the steel packaging industry. The results of corrosion tests of new electrolytic coatings based on titanium oxide and chromium (III) compounds also show that these solutions should be improved because of insufficient corrosion resistance and adhesion to paint coatings. The laminating of PE or PET film also requires

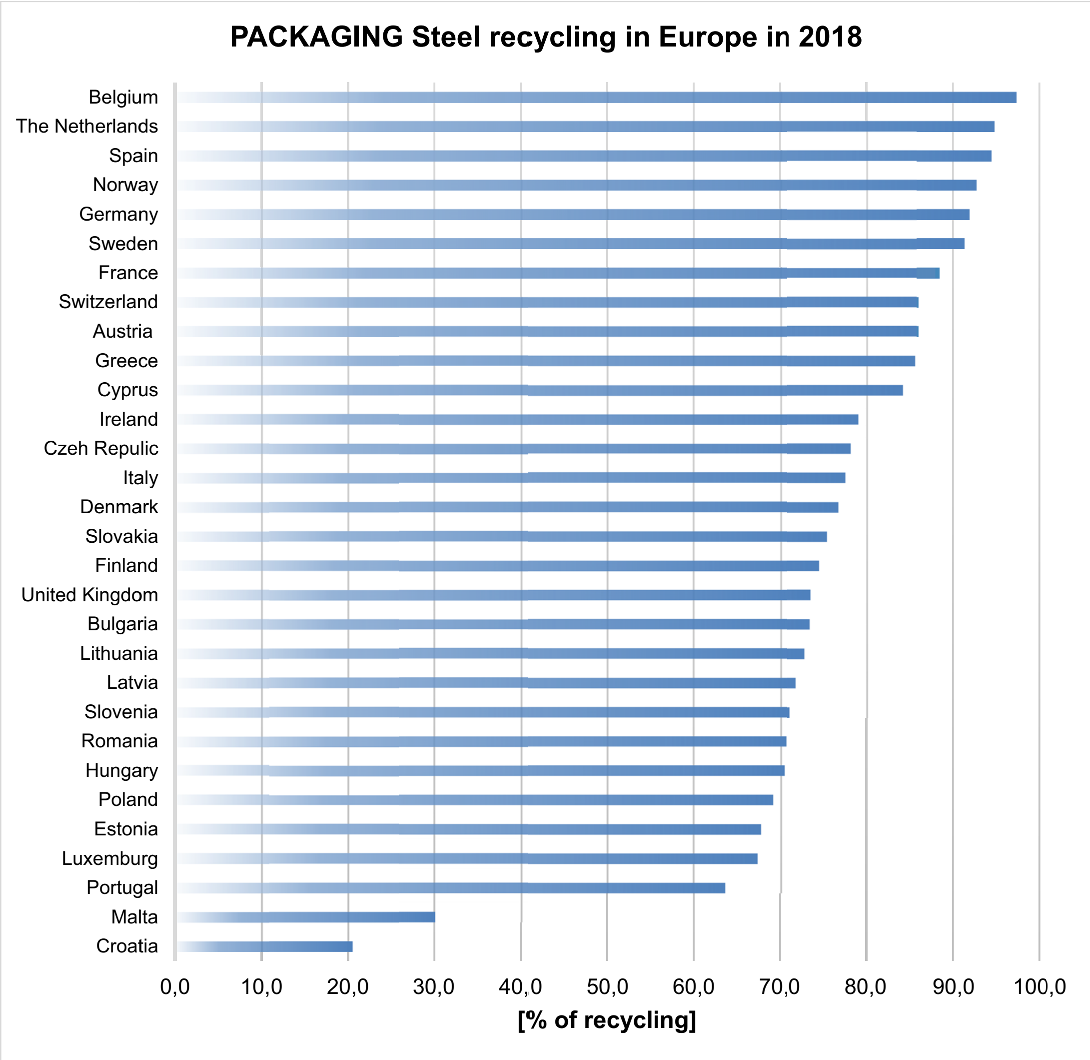

Fig. 11. Recycling of steel packaging in Europe in 2018

refinement. In the case of PE, the problem is to low temperature resistance in processes requiring thermal treatment (e.g. pasteurization). In case of PET film, there may occur problems during the embossing process, where it can remain visible PET fibers on the end product, which affects the negative reception of the final customer. In the case of crown seal manufacturers, there is a problem with the seal application, i.e. the lack of adhesion between the foil and the applied compound.

6. Summary

The basic material for the production of metal packaging is thin gauge flat carbon steels with a reduction factor of SR or DR. In the case of a three-piece can, mainly tin (ETP) steels are used, which can be welding processing and also have better corrosion resistance for acid food batches. For foods with a high organic and sulphur content, chromium steel (ECCS) is a better choice, as it also has better adhesive properties for paint coatings.

The problem of metal packaging is its common corrosion. Depending on the stored food, the level of corrosion can vary, so it is extremely important to choose steel: ETP or ECCS. Filling processes, storage conditions and transport are also important corrosion factors.

The packaging industry is currently facing legislative changes. For the passivation process of steel surfaces, chromium (VI) compounds are necessary, which are carcinogenic to people working in their environment. For this reason, REACH legislation provides a total ban on the use of chromium (VI) compounds. Packaging steel producers in recent years worked intensively on creating new passivation technologies for both ECCS and ETP steel. The result are two technologies whose planned commercial availability is 2021. TCCT technology based on chromium (III) compounds has been developed for the production of ECCS steel. However, CFPA technology was developed for ETP steel, which is based on titanium oxide.

New development directions in the packaging steel industry are very important. Directions of sustainable development in packaging, an increasingly higher level of steel recycling, intelligent packaging and coatings are the directions on which the packaging business should focus in the coming years.

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