Functional Surface Coating Technologies of Steel Industry

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Technical issues of steel industry change along with other industrial progresses. Traditionally, steel protection from corrosion environment was the major issue and galvanic metal coatings were mainly used to extend the lifetime of steel products. Nowadays, requirements for steel have become more diversified. More various surface and material properties are required from different field of applications. Naturally, functional surface coating has become one of the most studied areas in steel industry. For functional surface coating, various process technologies and coating products are investigated. In this article, recent trends of functional coating technologies and products are introduced with brief technical descriptions of representative coating products.

Keywords *: protection, corrosion, coating, steel*

1. Introduction

Steel is applied in industry very broadly. Technical development goes along with other industrial progresses. Traditionally, the biggest issue in steel industry was corrosion protection to extend the lifetime of steel. As the technical development is proliferated, requirement on steel products becomes more varied. Lighter, thinner, more flexible, stronger steel sheets with lots of functional surface properties have been required from different field of applications. The roles of functional coatings are highlighted to expand application areas or to satisfy customers' requirements.

The history of functional surface coating on steel surface is not very long. It was 1980s that functional coatings were introduced to extend the lifetime of steel products.[1)] Cr-free coating was adopted to replace environmentally hazardous chromate coating. Since then, it was realized that more functions could be incorporated to surface coatings and a lot of novel concept coatings have been developed. Nowadays, functional surface coating plays a crucial role to expand application areas and to design advanced surface coating steel sheet products. Fig. 1 shows the number of international patents published for various areas in steel industry from Korea between Sep. 2008 and Sep. 2009. Functional surface coating has the second largest number of patent publications next to steel making area, which demonstrates that functional surface coating is currently one of the most studied areas in steel industry.

Application of functional surface coatings on steel sheets are generally achieved by coating wet solution onto steel sheet coils followed by drying and curing process. Roll coating is the most widely used method for continuous application. In order to obtain maximum productivity, coating speed needs to be as high as possible, which brings surface defects together. Various approaches are possible to increase coating speed while minimizing surface defects. Thermal convection is the most common drying and curing technology, which heats up the temperature of air and steel strip by electric resistance. Recently,

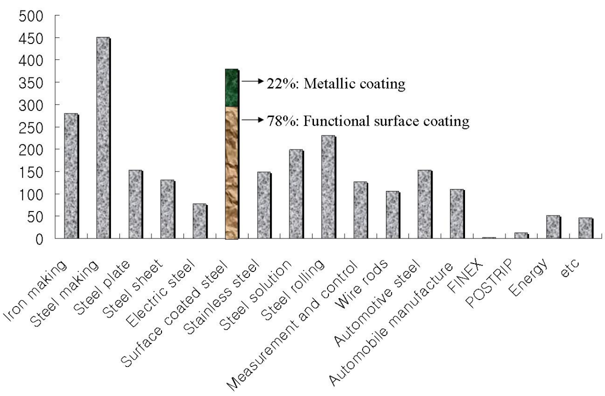

Fig. 1. The number of international patents published from different areas in steel industry from Korea between Sep. 2008 and Sep. 2009.

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more energy efficient and environment-friendly approaches are studied. Induction heating and several photo radiations are included. In this article, the trends of process technologies for functional coatings and a few examples of surface coating steel sheet products are discussed with brief technical details.

2. Process technologies for functional coatings

Several process technologies are involved to produce functional surface coating steel sheets. Solution coating and curing technologies are mainly studied process technologies. Solution coating technologies are used to apply wet chemicals onto steel strip continuously and they are dried and cured by subsequent drying and curing process. Technical descriptions and trends for these techniques are introduced in this section.

2.1 Coating technologies

Roll coating is the most widely used to apply chemical solutions onto steel sheet coils. Rolls revolve to pick up and transfer solutions to steel surface. Steel coil continuously passes for surface coating. Coating thickness and surface state are controlled by various process variables including nip force, relative roll speed, direction of roll revolution, etc. In order to obtain maximum productivity, coating speed needs to be maximized. However, faster coating process has more chances of surface defects like ripples, ribbings, etc. Coating solutions have various rheological properties i.e. solid content, viscosity, etc. Process variables of roll coating must be carefully controlled to minimize defects while increasing coating speed for various solutions. However, it is sometimes difficult to increase coating speed with simple roll coating no matter how the process variables are optimized.

A few different approaches are investigated. One of them includes patterned roll coating. Patterned roll coating utilizes an engraved roll to pick up solution from solution reservoir (Fig. 2). Flat pick-up roll in normal roll coating system causes surface defects due to inconsistent amount of coating solution. Engraving on a pick-up roll delivers rather consistent amount of solution and reduces surface defects while increasing coating speed. Not only surface defects are reduced but also the uniformity of coating thickness is greatly improved. In spite of the high quality coating, major drawback of patterned roll coating, expensive roll price and maintenance fees, makes it difficult for line application.

Another modern concept of coating technology is touchless coating, where the application of wet solution onto steel strip is carried out without mechanical contact between coating equipment and steel strip. A lot of different approaches are possible for touchless coating and schematics of a few examples are illustrated in Fig. 3, which includes slide coating (a), slot coating (b), and curtain coating (c). Touchless coating reduces maintenance fees of coating equipment significantly due to its different coating mechanism. However, rather expensive installation and difficulty to obtain thin coating thickness need to overcome for line application.

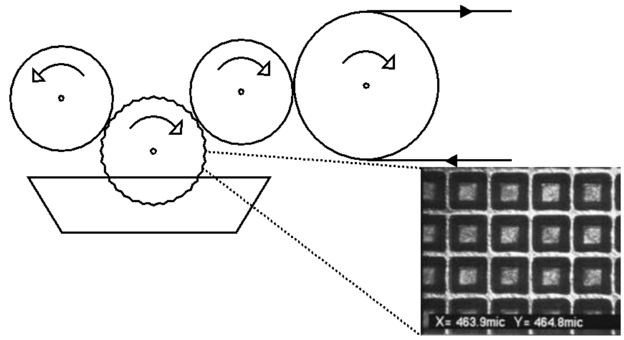
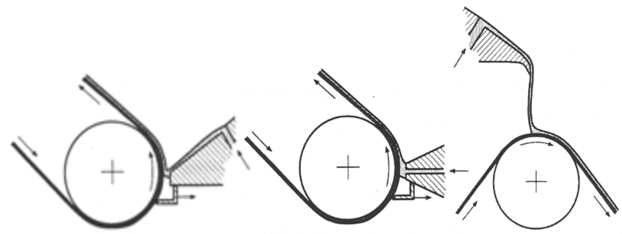


Fig. 2. Schematic of patterned roll coating and the surface image of an engraved roll.



(a) (b) (c)

Fig. 3. Schematics of touchless coating methods. (a) slide coating; (b) slot coating; (c) curtain coating.

2.2 Drying and curing technologies

Drying and curing process change liquid phase of solution to solid phase. It not only dries wet coating but also causes polymeric network structure to form. Polymer is a macro molecule with repeating structural units connected by covalent bonds and cross-link connects linear polymeric chain to form physically different materials.

Traditionally the most common curing method is heat treatments such as thermal convection. Steel strip with wet chemical solution passes through a heated zone where energy is transferred from air to coating solution and cause curing. Thermal convection curing is very effective to produce high quality coating surfaces. However, it is quickly being replaced from production line due to a couple of main disadvantages. One is its inefficiency of energy consumption. Thermal convection requires high electrical energy to reach the temperature that is necessary to start curing. This is due to the indirect heating mechanism of thermal convection. Electrical resistance of coil inside oven generates heat that is transferred to the air next to it. Heated air is circulated inside oven and transfers heat to coated solution on steel strip. The other is its requirement of long production line for complete curing. Heat transmission from the heated air to steel strip takes a long time which requires long curing line. Long production line is a huge disadvantage in industry.

Several principles and approaches are possible to replace thermal convection oven. One of them is induction heating. Induction heating is a direct heating technique for electrically conductive materials (mainly metals). Major components of induction heater consist of AC power supply, induction coil, and a workpiece to be heated. AC power supply sends alternating current that passes through induction coil, which generates electromagnetic field. When a workpiece is placed inside the coil, eddy current is induced and heat is generated due to the workpiece's electrical resistance (Joule effect, Fig. 4). Frequency of AC current needs to be carefully selected for the size of target product. The induced current is concentrated at the surface of specimen and decayed exponentially. The depth at which the current density drops to a value of 37% is called skin depth or penetration depth, δ, and all of the current value is considered to be held within this depth. The skin depth is a function of frequency following the equation

$$\delta = \sqrt{\frac{\rho}{\pi f \mu}} = \frac{0.0252}{\sqrt{f}} \qquad (1)$$

where ρ is electrical resistivity of strip [Ωm], μ is magnetical permeability of strip [H m^{-1}], and f is frequency of AC current [Hz]. The Eq. 1 shows the relationship between skin depth and frequency, which means the skin depth depends on frequency control. Therefore, frequency needs to be considered when selecting heater specification. Replacing thermal convection with induction curing can reduce line length by 50 % or so. Further technical details are available from commercial suppliers and articles.[2,3]

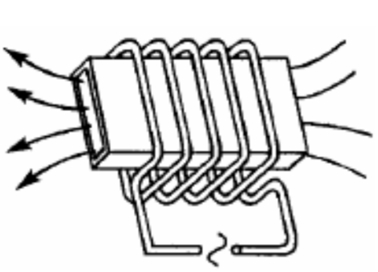


Fig. 4. Concept of strip induction heating.

More advanced curing techniques involve photo radiation. Near infrared (NIR) radiation curing is one of them and utilizes light with wavelength of 780~1400 nm as a thermal source. NIR radiation increases temperature of surface coating and metal substrates. It has several advantages over conventional thermal curing method. It takes only 0.2~3.0 sec for complete drying and curing compared to 1~3 sec of induction heating and about 30 sec of convection oven. Temperature profile generated by NIR is very uniform over strip regardless of surface irregularities. Energy density of NIR can reach up to 1500 kW/m^2, which is much higher than convection oven having less than 1 kW/m^2. Energy efficiency is more than 85%. Curing temperature using NIR is normally lower than induction heater by 5~10 % or so. Further readings are available.[4,5]

Ultra-violet (UV) light curing is another photo radiation method using light with wavelength of 200~400 nm. Mechanism of UV curing is different from NIR. In principle, UV curing utilizes light induced chemical chain reaction or polymerization while NIR is thermal curing. UV light has a higher energy than NIR by having lower wavelength and higher frequency. Radiation of UV light on some chemical materials generates radicals which are thermodynamically very unstable. Unstable radicals react with other molecules generating other radicals, which causes continuous chemical reactions. These chain reactions connect molecules and tighten molecular network, which is cross-linking. The initiation of chain reactions requires a special photoinitiator in coating solution that absorbs UV light and produces reactive radicals. Oligomers, monomers, and additives are included in UV coating solution as main components. UV coating has many advantages over conventional curing methods. The biggest advantage is extremely small floorspace requirement. Only a quarter of line length compared with convection oven is enough for UV curing. Another big advantage is zero emission of volatile organic compound (VOC). Conventional thermal curing systems require coating solution to involve macromolecules suspended in a solvent or emulsified in water. Thermal treatment dries solvent and forms intermolecular networks which produce solid surface layer. In UV coating system, solution can be made up of 100 % reactive components without using solvent and hence no solvent is evaporated (no VOC). VOC-free process also removes facilities for waste and emission treatment. In addition, no cooling line is needed for UV curing since it is not thermal curing and curing temperature is low, which is why UV curing is called cold curing. Cold curing not only removes cooling line but also provides another advantage like possibility to coat heat-sensitive substrates i.e. bake hardening (BH) steel. The penetration depth of light into coating solution is deeper than NIR. More information is available from the webpage of the association for UV & EB technology.[6]

The state-of-the-art of curing technology is electron beam (EB) curing. It has not been known to be applied in line production so far. EB curing equipment generates accelerated electron that strikes metal surface. Electron beam has high energy and triggers polymerization or curing when it collides with coating solution. EB curing has a lot of advantages i.e. high energy efficiency, no VOC emission, no requirement of photo initiator, etc. Penetration depth of EB is even much higher than NIR curing. One disadvantage of EB curing is the generation of hazardous X-ray. X-ray is generated when electron beam hits metal surface and hence X-ray shield is required to protect line workers. Further readings are available.[6,7,8,9]

3. Functional coating technology and products

Steel has a number of products and modern technology advancement requires more various products with different surface as well as material properties. Surface coating on steel plays a crucial role for product diversification. In this section, a few examples of chemical coating steel products from POSCO are introduced with their technical descriptions.

3.1 Cr-free coated steel

Steel is double protected from corrosive environment by galvanic and chromate coating. Zinc coating prevents steel corrosion by sacrificial or cathodic protection. Electric potential of zinc oxidation is lower than that of steel, which means zinc corrodes before steel does when they are in contact. Steel is protected from corrosion until zinc is depleted. Exact mechanism of protection by chromate coating is not proven yet. However, two effects are generally known to function as corrosion protection mechanisms. One of them is known as barrier effect. Chromate coating has a network structure through which corrosive elements can hardly pass. This tight molecular structure works as a barrier and protects zinc and steel. The other mechanism is known as self-healing effect. Chromate coating consists of Cr^{3+} combined with hydroxide ions to form $Cr(OH)_3$. Cr^{6+} ions move around chromate coating surface and fill in cavities to recover tight molecular structure and corrosion resistance (Fig. 5).

The combination of galvanic coating or zinc coating and chromate layer system is very efficient for protecting steel sheets from corrosion and for coating another layer on top with high adhesiveness. However, Cr^{6+} has been revealed as a carcinogen and prohibited to use by EU restriction of hazardous substances directive (RoHS) effective since July 1st 2007. Various substances have been studied to replace chromate coating layer, including metal phosphate,[10,11,12,13] silicates and titanates,[14,15,16] lanthanide,[16,17,18,19,20] permanganate,[10,11,21] and other metal oxides i.e. yittrium[18,20] and molybdenium.[22] These are normally called Cr-free coatings and their main ideas to obtain chromate coating properties are to imitate molecular structure of chromate layer. None of Cr-free coatings has been known to have better performance than chromate layer and only a few of them are commercially available.

POSCO has developed various Cr-free products based on different substrates like galvanized iron (GI), hot galvanized iron (HGI), electrolytic galvanized coil (EG), etc. EG based Cr-free products have a commercial name of POS E-GREEN. POS E-GREEN has mainly two types of coating layer, namely 1coat-1bake and 2coat-2bake. Cr-free coating is generally required to have particular functions like anti-fingerprint property. 2coat-2bake type POS E-GREEN products contains functional properties and Cr-free characteristics in two separate layers while 1coat-1bake type products require only one layer. 1coat-1bake system is advantageous in process since it requires only one coating and curing process. 2coat-2bake system is simpler in coating solution design but lowers productivity. Therefore, 1coat-1bake system is considered for most applications. 1coat-1bake Cr-free coating normally

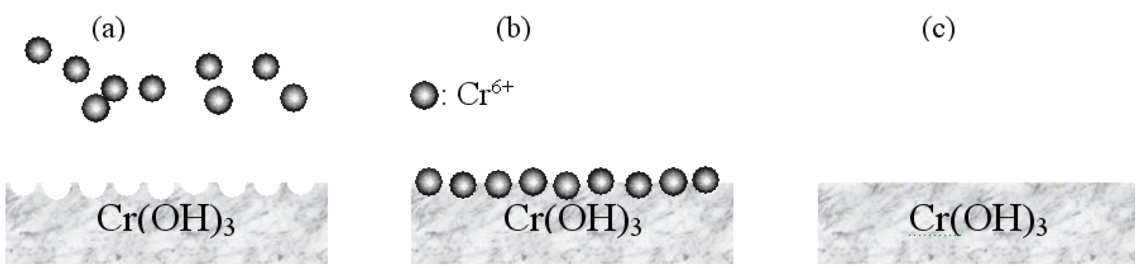


Fig. 5. Illustrtion of self healing effect by chromate coating. (a)mobile Cr^{6+} ions move around chromate layer; (b) Cr^{6+} ions adheres to the defect surface of chromate layer; (c) surface defects are healed.

has double layer structure, where the bottom layer is for maximum adhesion between metal substrate and Cr-free coating while the top layer embraces functional properties. Further products properties are available from our website.[23]

3.2 Black resin coated steel

Electronic industry commonly uses black panels for display rear cover materials. Conventionally, plastic or pre-coated metal (PCM) is used for electronic display rear cover. Recently, black resin coated steel has been developed having rather thinner coating thickness. As a rear cover material, plastic, PCM, and black resin coated steel has several advantages and disadvantages over the others.

Plastic has several benefits including light weight, complex formability, and higher bending stiffness. Plastic is normally lighter than steel panels. More complex formation is possible for plastic since injection molding can be used for plastic while steel panels are press formed. When the panels are thin, low bending stiffness of steel panel is a disadvantage for handling while plastic has higher bending stiffness. On the other hand, plastic is normally more expensive than steel panel and productivity is quite low. Conventional PCM has quite thick coating layer of 20 ~ 25 ㎛, which is the main reason of expensive price. Black resin coated steel has several advantages over plastic and PCM. It has thinner coating of 10 ~ 12 ㎛ and Cr-free coating is applied, which is environmentally-friendly. The speed of part formation is faster than plastic which means higher productivity. Although it is heavier than plastic and has lower bending stiffness, major advantage of low production cost would make black resin coated steel sheet a major rear cover material for electronic display in near future.

Thin coating layer of black resin coated steel with equivalent or better surface property is obtained by forming self-gradient layer of black coating. Wet coating of black resin contains hard components like silica and they are lifted up to the top during the drying and curing process. This self gradient layer formation enables the thin black coating to show maximum performance. Silica-rich top layer is beneficial for formability and silica-deficient bottom layer is soft and good for adhesion to Cr-free bottom coat.

The performance of black resin coated steel is competitive to PCM. The required properties of panel as display rear cover include electromagnetic interference (EMI) shielding, formability, chemical resistance, corrosion resistance, hardness, appearance, etc. Fig. 6 shows the performance comparison between PCM and black resin coated steel sheet. Quite recently, the quality of black resin coated steel from POSCO has been certified by a few electronics companies.

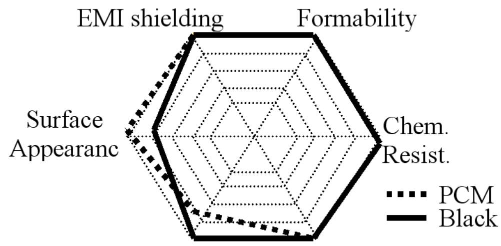


Fig. 6. Performance comparison between PCM and black resin coated steel.

3.3 Self cleaning steel

A lot of novel concepts of functional coatings are reported and self cleaning surface is one of the most highlighted coatings. Surface contamination on steel provides shelter for corrosion elements. It has been found that some surfaces from nature i.e. lotus leaf surface are preserved very clean without manual cleaning. More detailed investigation on its surface revealed the surface has lots of micro bumps that make the surface super hydrophobic. Super hydrophobic surface makes the contact angle of water drop very high and flow away easily along with surface dirt and potential corrosion factors. Further study discovered that two approaches are possible for obtaining self cleaning property. One is super hydrophobic and the other is super hydrophilic surface. Both approaches make water drop on the surface flow easily carrying away dirt particles.

POSCO adopted light sensitive super hydrophilic surface to manufacture self cleaning steel. Light sensitive hydrophilic surface become super hydrophilic by UV radiation. Contact angle of water drop is about 12° compared with conventional PCM surface showing 68° (Fig. 7). In order to check the self cleaning capability, mist was sprayed for the same time on both conventional PCM and self cleaning steel surface, where the self cleaning surface shows excellent self cleaning performance (Fig. 8).

4. Summary

Steel products are applied in industry very broadly and their technical trends follow other industrial fashion. Nowadays, the most significant trends are environmental protection and energy saving. In addition, steel industry is required to keep pace with other industrial advancement. Fast changing business environment demands more various steel products having upgraded material and surface characteristics. Functional surface coating plays a crucial role to diversify and enhance product qualities. Solution coating and curing technologies are essential process tech-

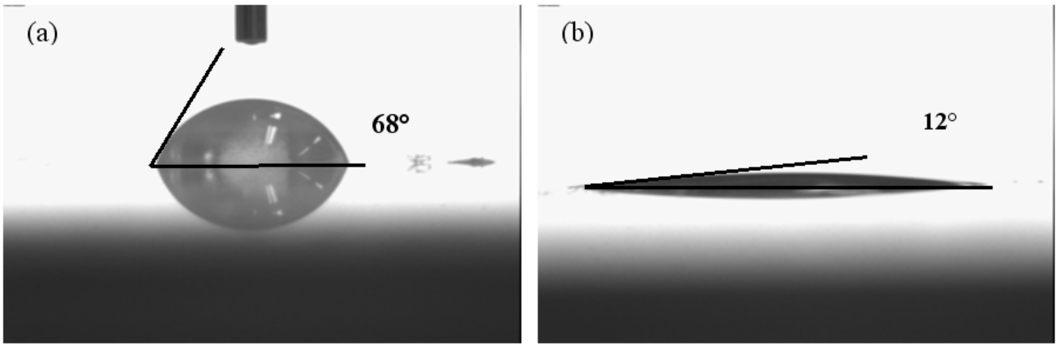


Fig. 7. Contact angle difference of water drop on the surface of conventional PCM (a) and self cleaning surface (b).

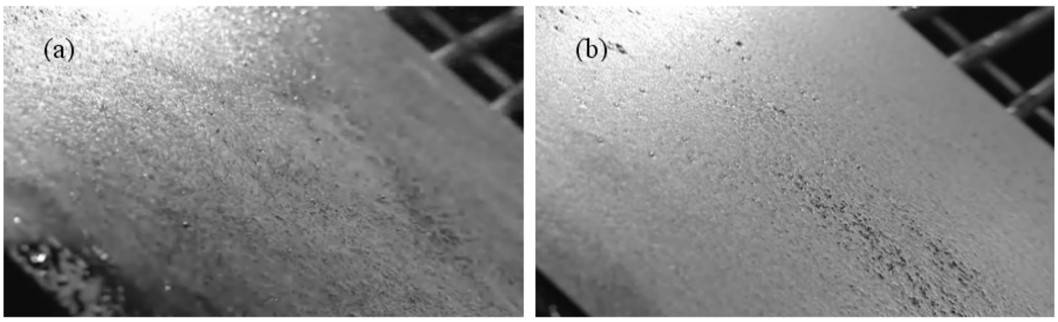


Fig. 8. Comparison of dirty steel surface after spraying water. Self cleaning surface (a) becomes much cleaner than conventional PCM surface (a).

niques in order to produce high quality functional coating steel sheets. They are investigated to increase productivity and surface quality and to reduce energy consumption and line length.

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