JPMTR-2118
DOI 10.14622/JPMTR-2118
UDC 655-028.25:686.4

Review paper | 158
Received: 2021-12-17
Accepted: 2022-02-15

Printing methods used in the label and package printing industry for the production of metallic embellishments with a focus on metal effect pigments

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Abstract

In the label and package printing industry, many methods are used for the application of a metallization on a substrate for graphical purposes. By applying metals like aluminum and copper-zinc on a substrate, outstanding visual effects can be achieved. It is shortly discussed why metallic surfaces appear different compared to non-metallic surfaces and what kind of terms can be used to describe a metallic appearance. Further, different printing methods for metallization are categorized according to the form of the initial metallic material used for the given printing method. It is distinguished between methods using metallic pigments with and without printing ink and metallic foils. Special attention is paid to the printing methods using aluminum pigments in printing ink. The appearance influencing properties of aluminum pigments are listed and different methods of their production are described. The influence of the different ink systems on aluminum pigments and printing methods using these inks are outlined. Furthermore, printing methods using metal effect pigments not incorporated in an ink such as bronzing and the EcoLeaf technology are shortly explained as well as different metallization methods using foil directly involved in the printing process like foil fusing, foil transfer and foil stamping methods.

Keywords: metallic pigments, metallization, metallic effects, print

1. Introduction

Over the past 30 years, the use of metallic pigments on printed products has increased, and today printed products on which at least partial metallic effects can be found are everywhere. For instance, they can be found on chocolate boxes, high quality greeting cards, perfume wrappings, gift wrap papers and labels of cosmetic products or alcoholic beverages, on the packaging of tobacco products or book covers (Freeman, Chapman and Rimmer, 2008; Kehren, 2013; Pfaff, et al., 2021). By applying special effects such as metallic effects on printed products, the noteworthiness and aesthetic value can be greatly improved, compared to reference samples without special effects (Bertholdt and Müller, 2014; Laine, Leppänen and Nurmi, 2009). Hence, by applying metallic effects on packaging, a product can stand out from the mass of the offer and can influence a customer at the point of sale (Silvennoinen, Peiponen, and Myller, 2008; Wißling, 2013). Research has shown that purchase decisions are strongly influenced by the attractiveness of a product and by how much it stands out. The more the packaging of products draws the attention of a customer, the more likely it is purchased (Clement, 2007; Hartmann and Haupt, 2019).

Already thousands of years ago, the attracting effect that is caused by metallic effects on products was realized. Early civilizations, for instance the Egyptians, worked gold into thin sheets and applied it on wood, bones or other materials (Wheeler, 1999; Pfaff, 2017). One religion that early used special effects for books extensively, among others also the application of gold, was the Manichaeism, which spread widely starting in the 3rd century AD not mainly because of its ideas but mostly because of the attractive visual appearance of its books (Monro, 2014). According to MAN Roland Druckmaschinen (2002), in Germany, the first ones who used metallic embellishments in no relation to religious usages were brewers and winemakers in the

19th century who produced bottle labels with golden, silver, and bronze effects. In the label and package printing industry real gold is not applied due to its high cost. Today, the material used to create metallic effects in all kinds of colors is mainly aluminum while copper-zinc pigments are only used to some extent (Wicks, et al., 2007; Pfaff, et al. 2021). Aluminum can relatively easy be processed to foils or pigments and its application can result in a metallic effect (Wheeler, 1999). According to Krietsch (2021), in the label and package printing industry, the proportion of aluminum pigments to copper-zinc pigments is about 70 % to 30 %. Copper-zinc pigments provide for a shiny gold effect. Aluminum pigments provide for a metallic appearance without hue and can be overprinted with any color to obtain a colorful metallic effect.

1.1 Classification of printing methods for producing metallic embellishments

In a general sense, printing is the replication of originals. In 2D graphic printing, the focus is on the correct reproduction of color information as well as textual and pictorial information on a substrate (Meyer, 1999; Hupp, 2008, p. 3). In a wider sense, graphical printing does not only regard the reproduction of color information but moreover, the reproduction of appearance information, which besides color also includes texture, translucency and gloss. In this review, not only printing methods using conventional printing processes i.e. printing processes with a printing plate such as offset, flexo, gravure and screen printing but also inkjet printing, electrophotography, bronzing and the EcoLeaf technology are reviewed as well as those involving foil in the printing process. In this paper, the word "film" is used to describe thin polymer films. The word "foil" is used to describe a thin metal surface that is applied on film and can be removed from it or transferred to a substrate.

The methods used for the metallization of a substrate in the label and package printing industry can be divided into two general categories. First, those methods that use metal effect pigments which are either dispersed in printing ink or not dispersed in printing ink. Second, methods that use some sort of foil, which is directly involved in the printing process. A schematic for the classification of the different methods can be seen in Figure 1. Which method is best suited for a specific product is dependent on the subject to be printed, the number of copies, substrate, available machines and material and further processing steps (Morlok and Beckmann, 2009).

Depending on the printing method, parameters within the process and the material used, the appearance of the metallization can differ greatly. Figure 2 shows this on the basis of eight samples. They have been metalized by foil fusing, cold foil stamping, gravure printing, flexo printing and offset printing.

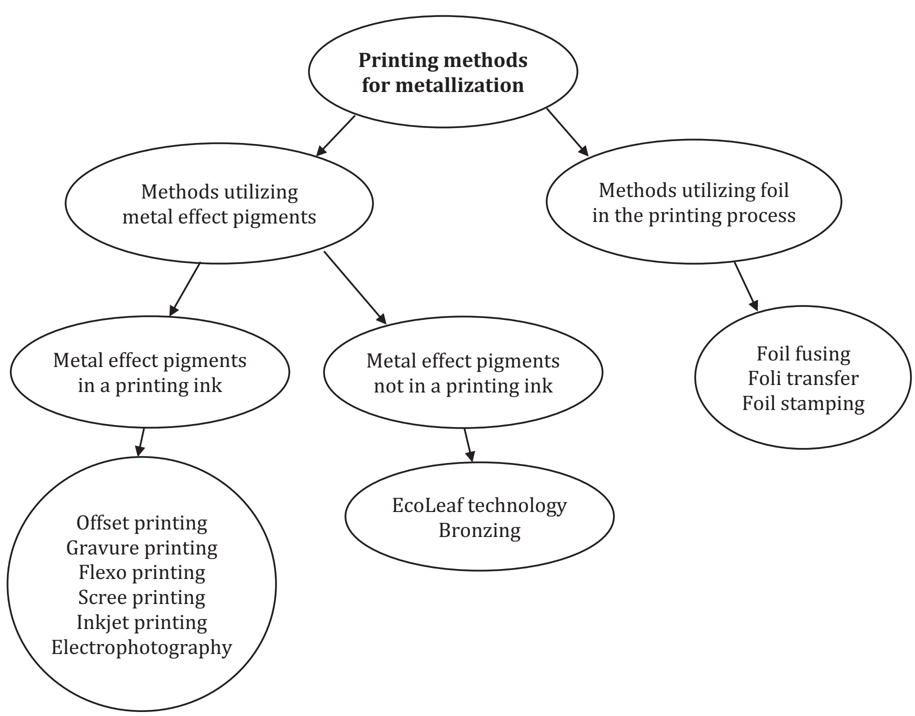

Figure 1: Classification of methods used for the production of metallic embellishments in the label and package printing industry

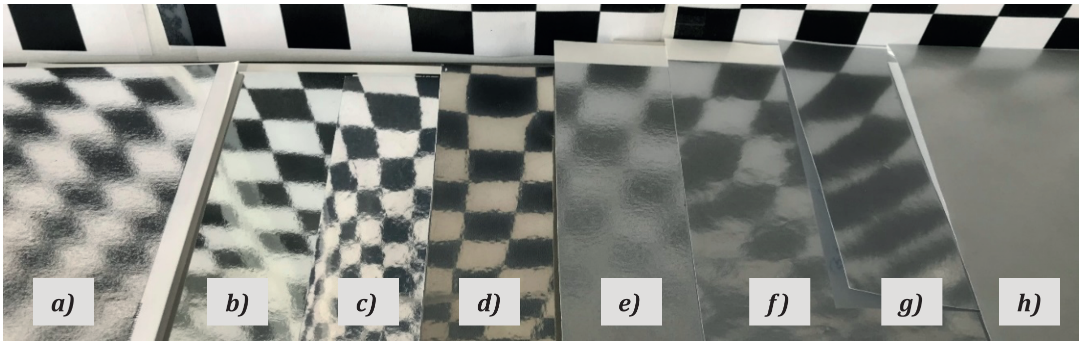

Figure 2: Printed metallic gloss samples made by foil fusing (a), cold foil stamping (b, c), gravure printing (d), flexo printing (e to g) and offset printing (h); the samples were photographed in front of a checkerboard pattern (Weber, Spiehl and Dörsam, 2021a)

2. Appearance of metallic surfaces

Metallic surfaces look different from e.g. paper or plastic surfaces due to the specific peculiarities of metal on the atomic level. Commonly used terms to describe the metallic appearance are briefly explained.

2.1 Peculiarities of metal on the atomic level with effects on the appearance

According to Nassau (2001), the metallic effect that is perceived due to the high reflectivity of a metallic surface has its origin in the interactions between the metallic atoms in the material. The root of the shiny metallic appearance with its high reflectivity is the delocalized nature of the valence electrons with their ability to move freely through a piece of metal. When dealing with an insulating material, the percent reflectivity R for a beam of light falling onto the material at normal incidence is given by Equation [1] as stated by Nassau (2001, p. 165).

$$R = 100\ \% \ \frac{(n-1)^2}{(n+1)^2} \qquad [1]$$

The refractive index of the material is n which is defined as the ratio of the phase velocity of light in vacuum to the phase velocity of light in the goven material (Hass and Hadley, 1972). Typical glass has a refractive index of about $n = 1.5$, which results in a reflectivity of about $R = 4\ \%$. Hence, most of the light is transmitted into the glass and absorbed and only a small part is reflected (Nassau, 2001, p. 165). As mentioned by Nassau (2001, pp. 162–166), metal behaves different to that. If light falls on a metallic surface it is so intensely absorbed that it can only penetrate it into a depth of a few hundred atoms, typically less than a single wavelength. The absorbed light, which is an electromagnetic wave, induces alternating electrical currents on the metal surface. These currents cause the immediate remittance of light out of the metal, which leads to a strong reflection. For the refractive index for metals, N, a complex component is added which results in Equation [2] as stated by Nassau (2001, p. 165).

$$N = n + ik \qquad [2]$$

where k is the coefficient of the absorption that is related to the exponential decay of an electromagnetic wave as it passes through the regarding material (Hass and Hadley, 1972). According to Nassau (2001, p. 165), the percent reflectivity with k now becomes

$$R = 100\ \% \ \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \qquad [3]$$

For an aluminum sample, under sodium illuminant (sodium D lines, which denotes light at a wavelength at around 589 nm), the values $n = 1.2$ and $k = 7.1$ result in a reflectivity of $R = 91\ \%$.

2.2 Terms to describe the appearance of a metallization

The optical impression one gets from metallic surfaces is due to a combination of directional reflection and scattering of light (Wißling, 2013). Terms that can be used to communicate a “metallic” appearance are introduced in the following.

Gloss: Metallized surfaces are often described to appear glossier than non-metallic surfaces. Beneath color, texture and translucency, gloss is a visual perception attribute that describes the perceived appearance of an object. It can be subdivided into various different aspects such as specular gloss, haze or distinctness of image. Weber, Spiehl and Dörsam (2021b) describes aspects of gloss that can be measured with commercial gloss meters in greater depth. Contrast gloss is described by Hunter and Harold (1987) as the contrast between specularly reflecting areas and non-specularly reflecting area of one material. Leloup, Audenaert and Hanselaer (2019) introduce a gloss meter that enables for the measurement of contrast gloss.

Luster: Pfaff, et al. (2021) points out that "the term 'luster pigments' is also often used for effect pigments because almost all effect pigments provide lustrous effects in their applications". Often, metallic surfaces are described to have "a rich luster." However, it is not well defined how luster differs from flop or contrast gloss of metallic surfaces and which surfaces can be described with the term. According to Hunter and Harold (1987, p. 79), luster is usually used in the textile industry to describe the contrast between areas of one material that are in the specular angle of light reflection and areas that are not in the specular angle and thus only reflect diffuse light to an observer. According to McCamy (1996), the term luster is also appropriate for metals due to the similarity of metallic paint on a cylinder compared to satin wrapped around a cylinder. In ASTM E284 – 17 (American Society for Testing and Materials, 2017) it is noted that the term luster is not used for surfaces that are as glossy as to form clear mirror images.

Lightness: Lightness is an attribute of color perception by which the color of a non-self-luminous body is judged equivalent to a series of neutral ranging from black to white in terms of reflected light (American Society for Testing and Materials, 2017; Berns, 2019). It is communicated using the L^* value of the CIELAB system.

Brilliance: The term brilliance is used in some publications on metallization, such as Wißling (2013), to describe a metallic appearance. However, according to Kirchner, et al. (2007), the term brilliance is not well defined and it is unclear how it is different to other phenomena such as gloss or sparkle.

Flop: The change of appearance of e.g. gloss or color with the viewing angle of a metallic surface is called flop (Wheeler, 1999; American Society for Testing and Materials, 2017; Nanetti, 2016). McCamy (1996) describes the measurement and calculation of flop in detail. In some scientific publications flop is used to characterize the appearance of a coating containing metal effect pigments. However, Bertholdt and Müller (2014) and Rich, et al. (2017) state that flop does not track the visual assessments of printed metallic ink well.

Visual texture: Kirchner, et al. (2007) defined two texture parameters that describe the visual texture under two different illumination conditions, which are directional lighting and diffuse lighting. Those two parameters are glint impression and diffuse coarseness. Visual texture refers to the perceived small-scale non-uniformity of an effect coating when viewed from a distance of a meter or less.

Glint impression: According to Kirchner, et al. (2007), glint impression is the impression of tiny light spots (glints) that are much brighter than the surrounding. These glints turn on and off as the observation or illumination geometry using unidirectional light is changed.

Diffuse coarseness: According to Kirchner, et al. (2007), diffuse coarseness describes the perceived contrast in the irregular light/dark pattern that can be exhibited by metallic effect coatings under diffuse illumination conditions.

Sparkle: The appearance of small bright points that appear to be much brighter than their surrounding and that is especially apparent if the observer, specimen or the light source are moved is called sparkle (American Society for Testing and Materials, 2017). While sparkle refers to small highlights widely separated from each other, the term glitter that is also used in some publications described a "grainy finish" (Kirchner, et al., 2007). Ferrero and Bayón (2015) and Ferrero, et al. (2021) describe the measurement of sparkle in detail.

Opacity/hiding power: The covering capacity of an ink is described as hiding power and opacity. It is "the property of an ink film that enables it to prevent the passage of light and thereby to hide the substrate on which it has been applied" (Schaeffer, 2012). According to Wißling (2013), this term is especially important for inks containing metallic pigments as the opacity of those depends on the pigment size distribution. The more fine-grained the pigments the better the hiding power.

2.3 Remarks on the communication of metallic appearance in the printing industry

Although a lot of research has been conducted in the field of the characterization of metallic appearance (Rich, et al., 2017; Rosenberg, 2000; Bertholdt and Müller, 2014; American Society for Testing and Materials, 1968) there are still no standardized methods widely applied in the printing industry to communicate the appearance of metallic embellishments. Most print shops rely on the subjective appraisal of experienced staff or the measurement of specular gloss in the 60° angle to judge and compare metallic embellishments. However, these two methods of judgement can lead to problems. The subjective appraisal can fluctuate from day to day, and depends on a specific person. Furthermore, it is still hard to communicate a subjective appraisal. Also, for metallized samples the measurement of the specular gloss fails to capture the perceived gloss precisely and cannot be used well for the comparison of samples that have been metallized using different printing methods. A further problem that arises when using gloss meters for the measurement of metallized print products is the lack of defined fields for measurement on the print control strip. This can make the measurement of gloss of the metallized parts of the print product impossible, as these are often smaller than the measuring field of the instrument.

3. Metal effect pigments

Reasons why methods using pigments could be chosen for metallization instead of using foils is their high flexibility that allows spot-wise application and could prove as cost saving in the case of spot-wise application compared to using foils. The application of inks containing metal effect pigments could also be chosen, if no foil application module is available in the machines used by the printer.

3.1 Categorizing metal effect pigments

As stated by Buxbaum and Pfaff (2005), the historic meaning of the word “pigment” which has its origin in the Latin language (pigmentum) is “color”. The modern meaning of the word originates from the 20th century.

According to DIN 55943-1993-11, which got withdrawn due to reasons unknown to the authors (Deutsches Institut für Normung, 1993; 2019), a pigment is a substance consisting of particles that are insoluble in the application medium and that are used as a colorant, for its corrosion-inhibiting or magnetic properties. Pigments can be divided into organic and inorganic pigments. Metal effect pigments belong to the inorganic effect pigments (Brock, Groteklaes and Mischke, 2000; Deutsches Institut für Normung, 2011; Kipphan, 2000; Pfaff, 2017). Their optical effect is based on the directional reflection from predominantly flat and aligned metallic pigment particles.

The main differences between metal pigments and organic pigments are particle size, specific gravity and particle geometry (Wheeler, 1999). While conventional light-absorbing pigments are spherical particles with diameters below 1 µm, metal effect pigments are 100 to 1000 times larger and are shaped like thin flakes with diameters of up to 200 µm (Benzing, et al., 1992; Wheeler, 1999; Brock, Groteklaes and Mischke, 2000; Maile, Pfaff and Reynders, 2005; Pfaff, et al., 2007). The shape factor of the metallic pigments that describes the ratio of thickness to diameter is between 1 : 50 and 1 : 500 (Brock, Groteklaes and Mischke, 2000).

3.2 Appearance influencing properties of metal effect pigments in a printed layer

The key characteristics that directly affect the optical properties of a printed metallization using metal effect pigments are the size, shape, surface roughness, spatial orientation, concentration and size distribution of the flakes as well as their distribution after printing (Eckart, n.d.; Sung, et al., 2002; Wißling, 2013). These properties can influence all the appearance characteristics mentioned in section 2.2. The different properties influence the appearance as follows.

Pigment size: The larger the size of the pigments used, the greater the reflective share of every pigment which leads to an increased lightness and flop. Additionally, for the reason that the edges of the pigments contribute highly to the scattering of light (edge effect), the reflection is clearer if the ratio of the surface area to the amount of edges of the pigments becomes greater (Sung, et al., 2002; Wißling, 2013). Furthermore, the smaller the pigment size the more opaque the ink layer (Kipfmüller, 2013). If the d_{50} size of the pigments is below 1 µm, they are too small to act as a mirror and light is scattered (Prölß, Trummer and Kröll, 2007). As described by Wißling (2013), d_{XX} is a measure for the average particle size distribution. Therefore, d_{10} means that 10 % of all particles are smaller than the value specified and 90 % are bigger. The d_{50} means that 50 % of the measured particles are bigger and 50 % are smaller than the given value.

Pigment shape: As described by Wißling (2013), the shape of the pigments also influences the ratio of the surface area to the amount of edges. In case of coarse pigments, there is a higher amount of edges and the light gets more scattered. In the case of round pigments, the edge amount of every pigment is at its minimum and the light gets scattered less. Additionally, the thickness is an important shape factor. The thinner the pigments the better their parallel orientation. However, the thicker the pigments the greater their hiding power (Brock, Groteklaes and Mischke, 2000).

Pigment surface roughness: The greater the roughness of the pigment surface, the more light is scattered and the lower the gloss and clarity of the reflection (Wißling, 2013).

Pigment size distribution: As described by Wißling (2013) and Wheeler (1999), a tight size distribution of the pigments leads to a brighter visual effect than a wide span value with pigments of the same median size. This is because there are less larger flakes that disrupt the smooth orientation and fewer small particles that lead to a darker appearance though they are contributing to the hiding power. McCamy (1998) states that a high concentration of small pigments leads to a more uniform look and to no noticeable sparkle even if the illumination is highly directional. Pigments with a large surface area lead to sparkle.

Orientation of the pigments: According to Sung, et al. (2002) and Wißling (1999), the orientation of the metal effect pigments is a very important aspect. The better the flat orientation of metal effect pigments after their application on a substrate, the higher the measured gloss values of a surface. Bertholdt and Müller (2014) state that platelet shaped metallic pigments can experience a tilt in the printing direction. In this case, the visual impression of the metallic effect is different in the printing direction from against the printing direction.

Leafing und non-leafing properties of metal effect pigments: As described by Becker, et al. (2018), Rich, et al. (2017) and Wißling (2013), pigments used in printing inks can have leafing and non-leafing properties. As described by Pfaff, et al. (2021) this is linked to the wetting behavior of the pigments. Leafing pigments float up to the surface of an ink layer while there is still a thin layer of polymeric coating on top of the pigments. Thus, they are not exposed to air. Non-leafing pigments with favorable wetting behaviors are equally distributed in the ink film. Inks with non-leafing pigments can more easily be overprinted with color inks. While leafing pigments tend to lead to a brighter and higher gloss, the non-leafing pigments are more scratch resistant. The wetting behavior of the pigments is determined by the additives used in the production process and by the additives used to prevent chemical reactions of the pigments in the ink. The distribution of leafing and non-leafing pigments in an ink layer is shown in Figure 3.

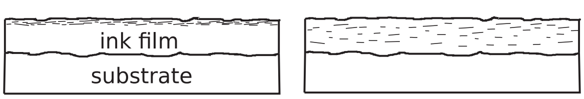

Figure 3: Distribution of leafing (a) and non-leafing (b) aluminum pigments in ink

Pigment dispersion: As reported by Eckart (n.d.) and Pfaff (2017), the dispersion of the pigments in an ink and the even distribution of these is a further influencing factor. If the pigments are not well dispersed, they tend to aggregate in the ink, which finally results in lower gloss of the printed product as well as in a "salt and pepper effect". The pigment aggregation also leads to an increased need of ink to obtain the desired hiding power. Hence, proper dispersion equipment is needed prior to the printing process while considering the flaky shape of the pigments that does not allow for high shear forces. Krietsch (2021) and Wyss (1989) recommend cone shaped stirrers for the preparation of an ink prior to printing as shown in Figure 4. By using these sorts of stirrers it is possible to achieve homogenous stirring without strong turbulences and shear forces and hence not damaging sensitive substances like the thin metallic pigments.

Figure 4: Cone shaped stirrer

Protective layer on pigments: Wißling (2013) explains that in many applications metal effect pigments have to be protected from corrosion or other chemical reactions between the pigments their surrounding have to be inhibited. For the reason that light is scattered on the protective layer, the visual appearance is influenced as the gloss decreases with the application of a protective layer. As described by Wißling (2013) and Schlenk (2008) the pigments can be stabilized by treating them using organic phosphorus compounds or by coating them with silica. Organic phosphorus compounds are more in use in the printing industry because the scattering of light is relatively small. Silica layers are mainly used in the car industry because they can make pigments weather-resistant.

3.3 Production methods and different types of aluminum pigments

According to Smalley (1924, cited in Edwards, 1927, p. 9), the inventor Sir Henry Bessemer was the first to invent an industrial process in the 19th century for the production of bronze powder in order to obtain a gold-colorant. If the pigments are mainly made of aluminum, high purity aluminum (min. 99.5 %) is used because the purer the aluminum the more stable it becomes in its chemical form (Kokot and Kleeberg, 2013; Wheeler, 1999; Wißling, 2013).

Today, there are two common methods for producing different types of aluminum pigments with different properties. One of the methods is the wet milling process. In this process ball mills are used to produce "cornflake" and "silverdollar" pigments. Using the physical vapor deposition process, vacuum metallized pigments (VMPs) can be produced.

3.3.1 Conventional production method by wet milling

The conventional production method of aluminum flakes is the wet milling process. Wheeler (1999) and Wißling (2013) describe it. Here, first aluminum granulate is produced by atomizing melted aluminum. Afterwards, the aluminum cools down immediately. This aluminum grit is given to the ball mill, which is partly filled with steel grinding media. Then a lubricant, in this case a long chain fatty acid, typically oleic acid or stearic acid or white spirit, is added to prevent cold fusion and to achieve the desired leafing or non-leafing properties. When adding stearic acid, leafing flakes are produced while the adding of oleic acid leads to the production of non-leafing flakes. Additionally, a high boiling aliphatic hydrocarbon blend is added to form a mobile slurry. During milling, the particles become so thin that they begin to break up. The median particle size of the thin metallic flakes produced is typically thinner than 1 µm (Maile, Pfaff and Reynders, 2005; Wheeler, 1999; Wißling, 2013). Brock, Groteklaes and Mischke (2000) states that the grinding time and the type and quantity of grinding aids already adjust the pigments for their subsequent properties and area of application. According to Wheeler (1999) and Wißling (2013), the flakes produced through the wet milling process are called cornflake pigments due to their irregular shape and their resemblance to breakfast cereals. By using special, very fine aluminum grit and a gentler, time-consuming milling process that involves smaller, more expensive grinding media, silverdollar pigments can be produced. Due to their extremely narrow particle size distribution their application leads to better optical effects, compared to cornflake pigments. They are the brightest and most brilliant metal effect pigments that can be produced by a milling process but their covering power is only moderately. Due to the strong mechanical forces on the cornflake and silverdollar pigments during production their surface is rougher than compared to pigments produced in the physical vapor deposition process (Pfaff, et al., 2021).

3.3.2 Physical vapor deposition process

Vacuum metallized pigments (VMPs) achieve the highest gloss of all metal effect pigments. According to Eckart (n.d.), using the right print application it is possible to obtain similar gloss effects compared to using foil printing methods. Levine, et al. (1982), Wheeler (1999) and Krietsch (2021) describe that for the production of VMPs, first a thin polymer film is coated with a release layer by gravure printing. Afterwards, a layer of 40–60 nm of aluminum from the gas phase is applied onto the release layer. This process of metallization takes place under very high vacuum while several layers of release layer and aluminum can be applied on one film to obtain a higher yield. Hereafter, the aluminum layers are released from the film in a solvent bath under ambient pressure. In a further process, the released aluminum is reduced to small flakes until they reach the desired size distribution. The process of reducing and treating of the VMPs can take several days.

As stated by Wißling (2013) and Wheeler (1999), the aluminum layer applied on the film has nearly the same smoothness as the film itself and therefore, the surface of the resulting pigments also has a very smooth surface, which reduces the scattering of light. Additionally, due to their small thickness, the pigments do not hinder each other so much in their alignment to the coating surface after printing when comparing them to the thicker cornflake and silverdollar pigments. Hence, in terms of gloss and mirror-like appearance, VMPs are far superior over cornflake and silverdollar pigments. The costs of the VMPs are very high compared to cornflake and silverdollar pigments due to the very high vacuum provided for the process, the vaporizing of aluminum and the long time needed for the treatment of the pigments.

If VMPs are used in UV-curable inks, they necessarily become leafing pigments due to the treatment with organic phosphorus compounds that makes them float. In solvent-based inks (e.g. ethyl acetate ink systems) the same pigments can be used as non-leafing pigments because they do not need a protective layer in this case (Krietsch, 2021).

4. Printing methods for application of metal effect pigments in printing ink

Substrates can be metallized using metal pigments incorporated in printing ink. The printing methods mentioned in this section can be used to apply these inks onto the substrate.

4.1 Composition of printing inks and the influence on the appearance

According to Kipphan (2000) and Teschner (2017), printing inks are made up of colorants (pigments or dyes), binders, additives, and solvents. The ink transfer mechanism and the type of drying/fixing of the ink on the substrate determine the structure and the components of a printing ink and hence influence the metal effect pigments used. The commonly used drying and curing systems to produce metallic embellishments by applying ink with metal effect pigments to a substrate are solvent-based inks, water-based inks, UV-curable inks and oil-based inks. The system used influences the resulting appearance. As stated in Eckart (n.d.), when comparing solvent-based, UV-curable and water-based systems, solvent-based systems lead to the highest gloss and brightness, followed by the UV-curable inks, while water-based systems represent the greatest challenge. Oil-based inks normally also do not lead to results with a high gloss.

4.1.1 Solvent-based inks

Solvent-based inks contain a large amount of solvent that evaporates after printing, leading to a shrink of the ink layer of up to 70 %. Additives and one or more binders are also part of the ink. Small amounts of binder in solvent-based inks result in high brilliance and hiding power (Eckart, n.d.).

As described by Karlsson, et al. (2008) and Wißling (2013), out of the ink systems used for printing inks, the stability of the aluminum pigments is best in solvent-based inks. This also means that there is not necessarily a need for protecting the pigments with a protective layer against corrosion, which would reduce their optical properties. Additionally, pigments in solvent-based systems align very well to the substrate surface because they are pressed against it as the solvent vaporizes and the wet film shrinks. The lower the viscosity of the coating film, i.e. generally the higher the proportion of solvent in the coating, the better the alignment. Hence, metallic gloss is easier to achieve with low concentrated inks than with high concentrated ones. For environmental and legal requirements, solvent-based inks are less and less used while it is desirable to develop water-based inks.

4.1.2 Water-based inks

In general, the mechanism for orientation of the pigments is the same as for solvent-based inks: the water-based media evaporates and due to the shrinking of the film, the pigments are aligned along the substrate surface. However, as described by Eckart (n.d.), water-based inks are microscopically inhomogeneous due to organic binder suspended in water. During drying, the film does not shrink as much as compared to solvent-based systems. The change of viscosity during drying does not favor the pigment orientation and the dried ink layer is thicker than that of solvent-based systems. The binder particles do not always flow into each other to create an optimal film, which creates light scattering points, which leads to less gloss.

Additionally, water-based media present great challenges for the application of aluminum, as well as gold bronze pigments because they are prone to react with water what can result in a grey, non-glossy appearance of the final print product. According to Wißling (2013), the reaction of "gassing" that takes place with unprotected aluminum pigments in water is as shown in Equation [4].

$$2\,Al + 6\,H_2O \rightarrow 2\,Al(OH)_3 + 3\,H_2 \qquad [4]$$

Additionally, to the out-greying of the pigments, the hydrogen can cause pressure in the ink containers that can even cause punching of the container and explosions (Eckart, n.d.; Karlsson, et al., 2008; Li, et al., 2008; Wheeler, 1999; Wißling, 2013). Hence, a highly requested demand for aluminum pigments is a good resistance against "gassing" in water-based media (Wißling, 1999). This protection is achieved by treating the pigments with a layer of organic phosphorus compounds or by coating the surface with silica.

4.1.3 UV-curable inks

According to Eckart (n.d.) and Kipfmüller (2013), UV-curable inks are also called 100 % systems, which means that the full layer is cured and nearly no evaporation takes place. Metallic UV-curable inks need to have a higher reactivity than conventional pigmented UV-curable inks because the metallic platelets act as small mirrors that prevent the UV-rays from penetrating deep into the ink layer. Hence, the amount of pigments, binder and photo initiators has to be matching, otherwise the ink is not cured optimally.

In UV-curable inks, silicate and polymer-coated aluminum and bronze pigments are used. Uncoated aluminum and bronze pigments catalytically induce polymerization of the binder components (Eckart n.d.; Wißling, 2013). This in return means that residual chamber material from the printing machine is not recommended to be mixed with fresh ink because the damage on the stabilization of the flakes that can occur during the printing process leads to a chain reaction and therefore to pre-polymerization of the ink (Eckart, n.d.). The coating of the pigments can result in a lower gloss of the print result but it is not regarded as significant as for the coating of metallic pigments in water-based systems. As mentioned by Bertholdt and Müller (2014) and Eckart (n.d.), when using UV-curable inks it is recommended to place the curing unit well behind the printing unit to optimize the metallic effect. The reason for this is that the ink needs time to flatten and leafing pigments need enough time to float up. To further optimize the result, heat can be induced into the ink layer to reduce its viscosity, which leads to a faster and better-aligned orientation of the pigments (Kurreck, 2021). However, when printing on film, due to the effect of heat on the printing material, register deviations may occur (Kokot, 2007, p. 239).

4.1.4 Oil-based inks

There are also oil-based printing inks with metal effect pigments as described in Wißling (2013) and by Becker, et al. (2018). They are commonly used for offset printing machines. According to Krietsch (2021), the orientation of pigments is somewhat different in offset oil-based inks compared to UV-curable inks, however, to the authors' knowledge, these differences have not been characterized yet.

4.2 Classic printing methods and their peculiarities

The method used for printing metallic embellishments decides about the size of pigments that can be used, the thickness of the printed layer, the ink system used, as well as the viscosity of the ink used in the print process. While for offset printing ink containing platelet shaped pigments the viscosity is typically in the range of 20–80 Pa·s, which is highly viscous (Becker, et al., 2018), the viscosity of typical flexo printing inks and of gravure printing inks is at about 0.05–0.5 Pa·s (Kipphan, 2000, p. 139). The inkjet printing inks typically have a low viscosity in the region of just a few mPa·s, which is highly watery (Becker, et al., 2018).

4.2.1 Offset printing

As explained by Kipphan (2000) and Teschner (2017), offset printing technology is an indirect printing technology. The printing and non-printing elements of the printing plate are in one plane while the printing elements are hydrophobic and the non-printing elements are hydrophilic. The ink adheres to the hydrophobic areas but does not adhere to the hydrophilic ones, which are wetted by a fountain solution. From the printing plate, the ink is further transferred to a rubber blanket that transfers it to the substrate. The task of the inking unit is to supply the printing plate continuously, streak-free and evenly with ink. For roller inking units, the ink is transferred from an ink metering system via rollers to the printing plate. These roller-type inking units consist of 10 to 15 alternating stiff and flexible rollers. For the most inking systems the stiff rollers (hard surface) generally perform an oscillatory movement in a transverse direction (they are also referred to as "distributor rollers") to smoothen the ink profile on the roller surface and the scores/lines in the ink which appear in the travel direction of the sheets.

As pointed out by Krietsch (2021), due to the reciprocating movements of the distribution rollers, high shear forces are applied on the metallic pigments and they can be destroyed in printing process. Thinner pigments are better suited for being transferred through the inking units because more ink is around these pigments, resulting in a better protection of these pigments in the printing process. With a decreasing size of the features to be printed and a subsequently small ink reception of the substrate, the printing ink also remains longer in the ink distribution system of the printing machine. This can affect the pigments as well as the viscosity of the printing ink due to the fountain solution that can accumulate in the ink.

For the reason that offset printing machines use these kind of roller-type inking units, the metallic pigments used in offset printing must be comparatively smaller to be carried from one roller to the other. Hence, the d_{50} size of gold bronze pigments commonly used for offset printing is only 2–4.5 µm and the d_{50} size of aluminum pigments is 4–9 µm (Wißling, 2013). Inks containing metal effect pigments used in offset printing are commonly either oil-based inks or UV-curable inks.

4.2.2 Gravure printing

As described by Kipphan (2000) and Teschner (2017), the distinctive feature of gravure printing is that the printing elements are engraved into the printing cylinder in the form of cells, while the non-printing areas are at a constant original level. During the process, the entire printing cylinder is flooded with ink in an ink fountain and the surplus ink is removed from the non-printing areas by a doctor blade. The remaining ink in the image elements (the cells) is directly transferred to the substrate from the gravure cylinder. The simplicity of the printing principle contrasts with a more complex and expensive production of the engraved printing cylinder and the relatively long delivery times of the printing cylinders. For this reason, as well as for the high printing speeds of about 15 m/s that are achievable and the wear resistance of the printing cylinder, gravure printing is mostly used for large print-runs. However, by laser engraving of the cylinders, the printing method becomes more economically efficient.

In case of using metal effect pigments the size of the pigments and the dimension of the cells of the printing elements have to fit to each other what allows the pigments to be transferred without problems. Different sources make differing statements about the size of platelet shaped pigments that can be used in gravure printing. Wißling (2013) states that commonly bronze pigments in gravure printing have a maximum size of 10 µm while the maximum size for aluminum pigments is 18 µm. Wheeler (1999, p. 132) mentions that "in gravure […] particles with any dimension larger than about 25 µm will block the cells of the print cylinder […]." However, according to statements of Krietsch (2021) and Kurreck (2021), pigments with a size of up to 200 µm can be used in gravure printing. In this case, the cells of the cylinder have a depth of about 150 µm and the cylinder has 20 lines engraved per centimeter. Literature states that the brilliance that can be reached using gravure printing is superior in comparison to offset and flexo printing because the used ink systems and flake sizes allow an optimal orientation of the pigments (Wißling, 2013).

For the inks used in gravure printing, the highly volatile solvents with fast drying properties are fundamental for their successful performance. However, also UV-curable inks and water-based inks find their use in gravure printing (Leach and Pierce, 1993; Wißling, 2013; Kurreck, 2021).

4.2.3 Flexo printing

In flexo printing, the images stand up in a relief, which serves a direct transfer of the ink to the substrate. Mostly, an anilox roller that takes up a specific amount of ink from an ink fountain doses the ink. A doctor blade, that can be chambered, removes surplus ink that is not in the cells of the anilox roller. From the anilox roller the ink is given further to the printing cylinder that transfers it to the substrate (Kipphan, 2000; Leach and Pierce, 1993). In contrast to gravure printing, flexo printing requires additional ink splitting and pigment transfer, which places increased demands on the mobility and transfer properties of the pigments. According to Wißling (2013), for this reason, flexo printing usually uses finer-particle pigments than gravure printing. However, according to Krietsch (2021), it is also possible to use pigments up until a size of 200 μm in flexo printing if a high sparkle effect is desired.

Using flexo printing, the achieveable gloss is higher than that of offset printing. However, compared to gravure printing, flexo printing comes in second place in terms of gloss that can be reached.

4.2.4 Screen printing

Screen printing is a process in which ink is forced through open stencils of a screen onto the substrate. The screen consists of a fabric that serves as mechanical support and the stencil material for the image generation (Kipphan, 2000). Wheeler (1999) and Wißling (2013) state that the screen printing process has the smallest demands upon the metallic pigments and pigment sizes of 50–100 μm can be used given an appropriate choice of screen mesh size what leads to a very intense sparkling result. In screen printing solvent and water-based as well as UV-curable inks can be used.

4.2.5 Inkjet printing

Inkjet printing belongs to the non-impact printing technologies and does not require an intermediate carrier for the image information and the ink can be transferred directly to the substrate (Kipphan, 2000). This offers the advantage that the printed subject can be personalized and that print jobs with short runs can be printed economically. The aluminum pigments used in inkjet printing are stated to have a small size with an average size distribution curve from 1 μm to 15 μm. If the pigments are greater than 15 μm they might not pass through the printing system such as tubes, channels, filters, and nozzles (Prölß, Trummer and Kröll, 2007).

4.2.6 Electrophotography

Different methods for the application of metal effect pigments on a substrate by electrophotography are offered by several companies as for instance Xerox providing dry toner with integrated metal effect pigments that are applied by dry electrophotography (DEP), also called xerography, or HP Indigo that provides so called ElectroInk Silver that is applied by liquid electrophotography (LEP).

The process of DEP can be divided into five steps, which are explained by Kipphan (2000). First, the print image is imaged on the photoconductive surface of a roller by initially homogenously charging and then discharging the non-imaging parts of the surface of the roller. Second, special ink particles with a size of about 8 μm, which is powder toner and contains the pigments, is transferred to the roller. The toner particles are charged so that they stick to the imaging areas of the roller. Third, the actual printing takes place and the toner, containing the pigments is transferred onto the paper by generating electrostatic forces between the roller and the substrate. In this case there is no contact between the roller and the substrate. Fourth, the toner is melted and fixed on the substrate by applying heat and pressure onto the toner particles on the substrate. Last, residual toner particles on the drum are cleaned up to prepare the drum for the next turn. The LEP technology is described by HP Indigo (2020). Essentially, at the beginning the process of LEP is similar to DEP. The surface of an imaging cylinder is charged on the areas where the inking is performed. After inking, the ink is not directly transferred onto the substrate but transferred to an offset cylinder where heating takes place to melt the ink particles together. Last, the ink film is transferred from the offset cylinder to the substrate while there is direct contact between the offset cylinder and the substrate.

Both DEP and LEP require different solutions to integrate metal effect pigments into the ink. As described by Jan (2017), for DEP the toner components, which are latex or wax particles are partially coated with aluminum using a sputter coater or electron-beam vapor deposition to form a hybrid metallic component that consists of a chargeable part needed for the application in DEP and the aluminum pigment to achieve the desired metallic effect. The solution for

LEP is described by Chun (2016) and by HP Indigo (2020). Here, aluminum pigments are encapsulated in a special resin and hence form chargeable particles. These are dispersed in the carrier liquid that is used in the printing process.

4.3 Influence of shear forces during the printing process

According to Eckart (n.d.), Pfaff (2017) and Wißling (2013), before the printing process starts, the metallic ink has to be stirred using a special low-shear stirrer at low rotation speed in order to obtain a good pigment dispersion, which is important as explained in section 4.2. One should be cautious when stirring the ink, otherwise, pigments could be damaged. The highest shear forces emerge from the doctor blade if a printing process is chosen that uses one. The printing speed, the angle of the doctor blade, the pressure between doctor blade and cylinder as well as the lubrication of the cylinder and blade that should always be sufficient, all influence the shear forces on the pigments.

However, there are also common features in conventional printing processes. In all of these printing processes, doctor blades are used to meter the ink. In offset printing, this is on the ink fountain roller, in gravure printing on the printing plate, and in flexographic printing in the chambered doctor blade. Due to the doctor blade the ink is strongly sheared in the printing process. The doctoring process itself is a complex process and is not yet fully understood scientifically (Bitsch, 2021). Therefore, it is also not clear what influence the doctoring processes have on the metallic effect in the various printing processes.

4.4 Influence of the substrate

According to Eckart (n.d.), Wißling (2013) and Stahl and Dörsam (2013), choosing the right substrate and preparing it before the application of metallic ink is as crucial as choosing the right ink and printing process to obtain the desired appearance. Since the applied ink follows the surface structure of the substrate, only smooth substrates with a low level of roughness lead to results of high gloss. Applying primer on the base paper helps smoothing the surface and enhancing the substrate. Coated paper and calendered paper sorts are best suited to achieve high gloss and bright effects. It is also important to check the pH-value of the used paper. Acidic paper and board can affect the metal effect pigments in a negative way (Wißling, 2013).

As stated by Kurreck (2021), when applying primer to smoothen the surface it should be considered that water-based primer intrudes more easily into the base paper and hence, does not have a smoothing effect as high as UV primer has. Furthermore, the right amount of primer for the specific substrate used has to be chosen. If a quite rough base paper is used, more primer has to be applied to smoothen the surface. If the base paper is already smooth, less primer should be applied. Otherwise, the excess primer can lead to an orange peel effect. Eckart (n.d.) adds that the benefit of applying primer is also the reduced water absorptivity of the base paper. A high absorptivity leads to a separation of binder and pigments of the metallic ink. Due to the changed binder to pigment ratio, a poor rub resistance, poor adhesion and a limited over-printability can be the result.

5. Other printing processes for the production of metallic embellishments

In the following section, technologies are presented that also can be used for producing metallic embellishments. First, the bronzing technology is presented, which is a relatively old technology that is nowadays only used by a few print shops. With the bronzing technology, mostly bottle labels of e.g. wines are embellished. The EcoLeaf technology on the other hand is a very new technology that until today only finds its application at pilot customers. Next, embellishment methods are presented that utilize foils in the printing process.

5.1 Printing methods for application of metal effect pigments without ink

5.1.1 Bronzing

In the printing industry, the term “bronzing” refers to two different meanings. The first is the printing method for the metallization of print products. The second meaning refers to an effect that is responsible for the colored metal-like shine that sometimes appears at the surface of ink layers in the specular direction, that is also called gloss differential (Hébert, et al., 2015). Here, bronzing refers to the method for the production of metallic embellishments. Usually, bronzing is used for the application of gold effects on elaborate labels for beverages (Rosenberg, 2000). Because of the great size of the flakes that are usually made out of copper and zinc, a particularly eye-catching sparkle effect can be reached. As stated by Kirwan (2013) and Rosenberg (2000), in the process of applying the metallic flakes, an adhesive base is printed on the substrate on the areas to be bronzed. Hereafter, in the bronzing application system, special dusting devices apply the bronzing powder all over the sheet but the flakes only adhere to the areas with adhesive. Afterwards, the sheet is cleaned to remove the excess powder. Mainly for the reason that the bronzing process is relatively slow and expensive it is not commonly used.

5.1.2 EcoLeaf technology

The EcoLeaf technology is intended to provide an alternative for foil-based processes for metallization. The technology is quite new and first companies have just finished test programs (Labels & Labeling, 2021). As stated by Lohmann (2020) the technology was presented to the public for the first time in 2016. It is presented to be more economic- and environment-friendly than foil-based processes. Web presses and further processing machines can be retrofitted with this technology.

As described by Landa, et al. (2016a; 2016b; 2016c; 2016d), and Lohmann (2020), the EcoLeaf technology uses aluminum pigments that are applied as a monolayer on a substrate, which means that the height of the metallization is only the thickness of one pigment. In order to apply the pigments on the substrate, first a "trigger image" is printed onto a substrate that makes the metallic pigments stick on the surface. Print processes used for the trigger image can be screen, flexo, and inkjet printing. Using screen printing, haptic metal effects can be created. Using flexo printing, fine metallization with a high resolution can be achieved and inkjet printing enables a metallization that is variable within the running process. Afterwards, the metallization is applied onto the trigger image inside a metallization unit. Inside the metallization unit, aluminum pigments suspended in a fluid are applied onto a donor roller. The pigments adhere to the surface regions of the donor roller that are not preoccupied with pigments. Surplus pigments as well as the fluid are extracted. In the next step, which is the metallization of the substrate, the surface regions of the donor roller that has just been completely covered with pigments that lay planar on the surface of the donor roll come into contact with the substrate. If there is contact between the donor roller and a part of the substrate that has been primed with the sticky trigger image, the pigments adhere on the trigger image because the adhesion between trigger image and pigments is stronger than the adhesion between donor roll and pigments. In the next step, a new monolayer of pigments is applied on the parts of the donor roller that released pigments to the trigger image.

5.2 Printing methods using foil in the printing process

Generally, it can be said that using foils it is much easier to obtain high gloss than compared to aluminum pigments because they provide for a closed layer of thin metal without interruption of pigment edges. Compared to pigments in printing ink there is also no additional ink layer that scatters light and reduces the gloss. In Figure 5, samples metallized by four different foil technologies can be seen.

Figure 5: Samples metallized by foil fusing, cold foil transfer, hot foil stamping and digital hot foil stamping (sample from Konica Minolta) from left to right and up to down

5.2.1 Foil fusing

For foil fusing, a substrate which is mostly paper or board is joined with a metallized film. For the reason that the film stays on the printed matter, it becomes tear resistant.

The lamination is only possible over the entire surface of a sheet (Morlok and Beckmann, 2009). Erdmann (2018a) explains that parts of the surface that should not exhibit the metallic gloss of the foil have to be overprinted with opaque white, which makes the method uneconomical if only spot effect of individual highlights should be achieved. According to HTWK Leipzig (2020) and Morlok and Beckmann (2009), the lamination film has a thickness of 12–30 µm and is made of polypropylene, polyester, acetate, or polyamides. It can be applied by wet-lamination or thermo-lamination. While for wet-lamination a wet glue is applied on the sheet before lamination, for thermo-lamination a dry glue is applied that is activated by heat. Thermo-lamination has the benefit that the glue is not soaked up by paper with a high water absorptivity.

5.2.2 Cold foil transfer

When metallizing a substrate using cold foil transfer from a metallized film, the thin aluminum layer is transferred onto the substrate, but not the film. For instance, using metallized films from the company Leonard Kurz, Germany, only a layer with a thickness of 0.2 µm of aluminum is transferred onto the substrate. The polyester film for the transfer has a thickness of 12 µm (Niemela, 2020). According to Heidelberger Druckmaschinen (n.d.) and Castleton (2000), one unique characteristic of cold foil transfer compared to film lamination and hot foil stamping is that the process of metallization can happen in-line in an offset printing machine at full printing speed of 16 000 sheets per hour, while the speed of the transfer has little effect on the quality of the finished product. Normally, an adhesive pattern is applied in the first offset unit of a printing machine using an offset plate with register accuracy, which results in the fact that very fine lines of 0.05 mm (0.002 inches) can be reproduced. In the foil transfer unit, which comes next, the foil is pressed against the substrate between two cylinders, while the adhesive is activated (e.g. by exposure to UV light). Hence, the metallization adheres to the areas where the adhesive pattern is printed but not anywhere else. The film from which the metallization is transferred can then be spooled up. For the reason that the pressure cylinders only exert minimal pressure, the film can be removed from the substrate easily while a distortion of the substrate is prevented. In the following, at least four offset printing units are needed to overprint the substrate together with the metallized parts with CMYK colors and to obtain a colorful metallization. For the application of cold foil, generally smooth surfaces are required that do not completely absorb the adhesive and the thinner the foil the better the metallization because that enables the foil to adhere better on the substrate.

5.2.3 Hot foil stamping

Different to foil fusing and cold foil transfer, hot foil stamping, as the name of this method implies, needs an extra heat supply and an extra die that has to be made (Erdmann 2018b). According to Morlok and Beckmann (2009), the foil consists of the film with a layer that enables a transfer layer to detach easily when heated and the transfer layer that consists of an adhesive, the metallization, a color pigmented layer if a colored metallization is to be directly applied, and a protective layer. As described by Castleton (2000), the application of hot foil on a substrate is normally done offline after color printing. In the process of foil application a shaped and heated die presses the foil on the substrate, which activates the adhesive on the transfer layer of the foil. Hence, the part of the metallization corresponding to the shape of the die stays on the substrate. According to Heidelberger Druckmaschinen (n.d.), in contrast to cold foil transfer, motifs and text in hot foil are only possible from a line thickness of approximately 1 mm (0.039 inches). For the reason that the foil transfer is limited by the time taken for the heat to transfer through the foil, only throughputs of 6 000 to 8 000 sheets an hour can be reached. Additionally, there is a greater outlay in time and costs for manufacturing embossing dies compared to offset plates. However, using hot foils it is possible to produce metallizations with a high artistic value that is not flat and also can create a 3D effect due to the deformation of the paper that cannot be produced in line with cold foil. Furthermore, also rough substrates can be metallized because of the ironing effect of the die. Metallizations with hot foil are overprintable, however, another process step in a different machine is needed for overprinting. Hence, often foils that already have the right color are used.

As stated by Bühler, Schlaich and Sinner (2018, p. 52) there are also digital hot foil stamping methods, although these are no real stamping methods because no embossing takes place. One example is the digital hot foil by Konica Minolta, described by Yamamuro (2020). This invention solves the issue that foils applied on adhesive printed with digital printing methods do not resemble the visual effects of hot foil stamped methods because of the missing 3D effect. Using this method, visual effects normally known from hot foil stamping can be created without the use of a specially made die and without heat what speeds up the progress. In this method, toner or ink layers are printed on a substrate to form areas with large and small thickness. Then a foil with a high adhesiveness to the ink is pressed against the thickened layer on which the metallization is peeled from the film and is transferred to the substrate with the texture of the foundation layers.

6. Conclusion

This review paper provides an explanation of different printing methods used in the label and package printing industry to produce metallic embellishments and summarizes the most relevant literature on the topic. One major outcome is the classification of the printing methods according to the input material used for the metallization process of a substrate. Furthermore, important terms used for the communication of metallic appearance are listed and explained. Further developments in the area of printing methods for the metallization will aim for three different goals. The first is the enhancement of the print quality and gloss achievable with the respective methods. For instance, manufacturers of pigments and inks will search for solutions to achieve gloss results with their products that are comparable with methods employing foil. Manufacturers of foils will find solutions to produce thinner and thinner foils to gain better qualities and reduce consumption of resources. Second, manufacturers will strive to reduce the costs of their products, especially providers of digital printing methods such as electrophotography, and inkjet printing as the inks used for these methods are very expensive and as more and more customers favor digital printing and require solutions for short runs and individualized packaging and labels. The third development regards environmental matters as an increasing number of governments enact laws to reduce greenhouse gas emissions and other environmental pollution and as more and more customers include the environmental impact of products into their purchase decisions. This will probably have impact on the production methods or the energy sources for the production of raw materials that are energy consuming but also on the respective printing processes. Further, in the field of printing inks, water-based inks will be further developed to achieve higher qualities comparable to UV-curable inks or solvent-based inks as the use of UV-curable inks induces problems in paper deinking and as it is to be prevented to use solvent-based inks releasing volatile organic compounds.

Acknowledgments

The authors would like to express their gratitude for the financial support by the Heidelberger Druckmaschinen AG as well as for the provision of metallized printing samples and the exchange of knowledge about various printing processes. Furthermore, we kindly acknowledge Schlenk AG, Roth (Germany), especially Mr. Burkhard Krietsch, for sharing information about metal effect pigments, and the application of metallic inks in printing processes. Besides, we kindly acknowledge H. C. Moog, Rüdesheim (Germany), for supplying gravure printed metallic samples and especially Mr. Achim Kurreck for providing information on ways of printing metallic embellishments. Eckart GmbH, Hartenstein (Germany) is to be thanked for sharing information about metal effect pigments and printing inks. We also thank Multi-Color Bingen Germany GmbH for discussions about bronzing and supplying samples.

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