Toner Technology and Security Solutions+

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From desktop printing at home and small offices to high speed commercial printing, toners applications and its uses can be found in everyday life. Toner based electrophotography is the underlying print engine technology that drives the entire laser printer and toner industries. The entire electrophotographic process can be broken down to essentially six primary steps, which are described and explained. Although all toner particles have to perform well in the electrophotographic system, the major requirements for toners are ultimately dictated by the end use application of the imaged substrate they help create. Hence, toner composition is often uniquely tailored to provide that function. Toner particles are predominately manufactured by conventional melt pulverized process but the use of chemical toner is continues to increase in printers. Chemically prepared toner offer an easier way to produce smaller toner particles and allows control of toner shape to help simplify the printer design. For fixing a toner image to a substrate, heat is typically applied to fuse it to the paper or other substrate. There are many different methods of fusing or fixing used in the industry, but a nip forming roller system is most predominantly used in printers.

Many different types of security features can be incorporated in toners to generate prints with the desired level of security. These features could be either covert or overt. Some of these security features that are currently employed in electrophotographic toners are discussed.

Introduction

Toners play an important role in our daily lives today. Their utilization is no longer limited to producing multiple copies of text documents. These days, the impact of toners can be felt in other applications such as printing photos, faxing, packaging, marketing collateral etc. Image quality has improved to such a high degree that almost all customized photo books are now created using some type of toner. The advent of digital age has created an abundance of opportunities for printing and toner development has kept pace with these ever increasing requirements. With increase in documents generated on computers and the overall digitization in communication, toner based digital printing has led the growth of on-demand printing, variable data printing, and distributive printing with quick turnaround. As the digital printing applications have grown, additional capabilities, such as security, are also being fulfilled by toners.

Despite the growth in the array of digital devices and computers that are available now, the production of the toner still continues to increase. A steady growth in the world-wide production of toner is being realized despite other avenues now possible to read and send digital documents and pictures. The worldwide production of all toner is expected surpass 250,000 metric ton soon as shown in Figure 1 [1]. Although, the use of toner in office documents and books may be slowing, it is enjoying growth in other applications such as packaging, photobooks, marketing collaterals etc. Electrophotographic toner has positioned itself as a viable alternative to commercial off-set printing inks.

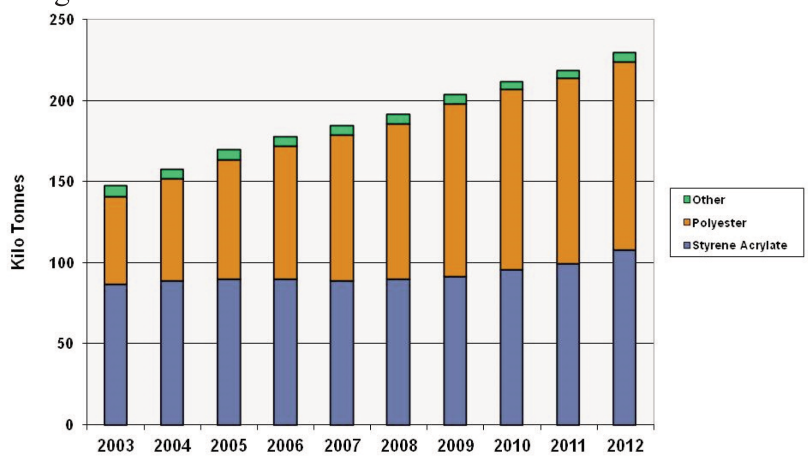

Figure 1: *World-wide toner production volume for all types of binder polymers*

Toner particles play a very important role in electrophotography because they come in intimate contact with almost every sub-system in electrophotography. It can either negatively affect the life of a sub-system or permit its simplification by virtue of its properties and composition. The primary function of a toner is to provide visual information on the substrate onto which it has been deposited. The electrophotographic process was developed by Chester Carlson which now provides the ability to instantly produce an exact replica of a document on a substrate. Before the advent of copiers and printers, the only common way to reproduce a complex document was to either produce a new original, or produce a silver halide based photograph of the original. Today, all copiers and digital printers still operate under the fundamental principles developed by Carlson which is collectively referred to as electrophotography.

In electrophotography, charged toner particles are used to develop or "make visible" a latent image on a surface that represents the desired image [2]. The entire electrophotographic process can be broken down into six individual steps as shown in Figure 2.

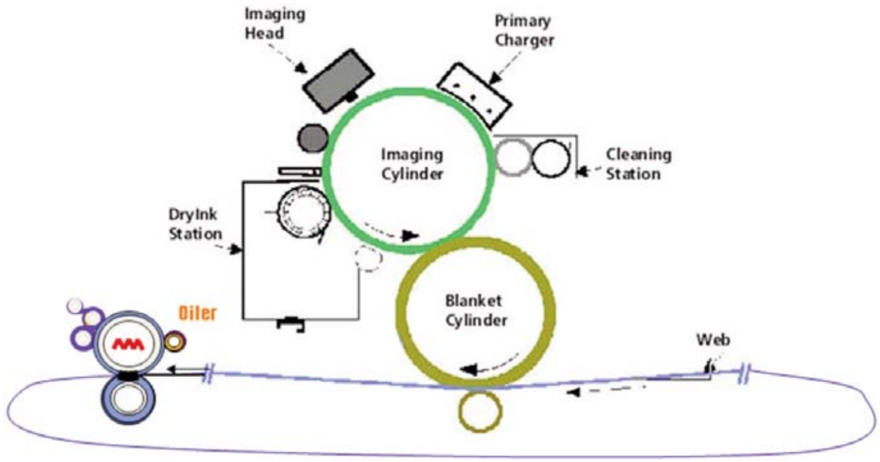

Figure 2: *Electrophotographic Process*

These six steps were defined by Carlson in 1938 and though the technologies within each step may have evolved over time, the basic process has remained essentially unchanged [3]. These six steps are:

1. Charge.
   The dielectric surface of a photoconductor is uniformly charged using a corona wire or roller. The polarity of the charge could be negative or positive depending on the type of charge on the toner and the development method.

2. Expose
   Previously, in copiers a flash bulb was used to discharge the photoconductor image wise. With printers, the latent images are produced using LEDs or laser writers

3. Develop
   The latent image on the photoconductor is developed using the charged toner particle. Development is carried out by either mono-component or dual component methods. In mono-component process, the toner is charged via a corona wire or roller. Most high speed printers use a dual component process where a coated magnetic particles, referred to as carriers, are used to both charge the toner particles with the right polarity and also to bring the toners in the vicinity of the development nap using a magnetic rollers which hold the carrier particles back. The development can be either CAD where the charge area on the photoconductor is developed using toners with the opposite polarity toners. Almost all the printers use DAD techniques wherein the discharged area is developed using the same polarity toner as the charge polarity on the photoconductor [4].

4. Transfer
   The developed toner image is then transferred directly to final receiver such as paper or first transferred to an intermediate surface before being transferred to the final substrate receiver.

5. Fuse
   Developed image is then fixed to the paper typically by applying pressure and heat to the toner image by passing them through a nip formed by two heated rollers.

6. Clean
   All residual toner particles left behind on the photoconductor after the transfer step are typically discharged and removed from the photoconductor surface by either a rotating fur brush or a blade cleaner. After the cleaning step the cycle is repeated for the next image.

Toner Composition

Primary function of a toner particle is to enable visualization of printed information. But beyond this simple function, there are many restrictions that are imposed on the toner particle and the subsequent final image. In order to meet these requirements, the toner composition is optimized to deliver the desired performance.

A toner particle comprises essentially of a thermoplastic polymer which forms the resin matrix for the other toner ingredients. Whether dry or liquid, a toner is a finely divided pigmented powder to help develop the latent electrostatic image formed on the photoconductor [5]. A typical non-magnetic toner composition would have the following ingredients as shown in Table I:

An inadequate dispersion of toner components listed above can either result in poor charging behavior or inadequate color properties. An optical micrograph of a toner in Figure 3 shows how the pigment particles are uniformly dispersed throughout the toner particles. When wax or release additives are required in the toner formulation, it is extremely difficult to achieve good wax dispersion' On the other hand, very small domains of the wax or release additives may not be as effective in providing the optimum release performance from heated fuser rollers. In Figure 4, a Transmission Electron Micrograph of cross-section of a toner is shown.

Ingredient	Amount (wt. %)
Polymer Binder	85-95
Pigment or Dye	3-10
Charge Control Agent (CCA)	1-3
Wax/Release additive	3-10
External Additives	0.1 to 5

Table I: *Toner Composition*

In this micrograph, the crystalline structure of the pigment can be clearly seen inside the toner particles. The surface of the toner shows the presence of an external additive. It can be seen in the micrograph that the external agents are present in an aggregated form and not distributed on the surface as primary particles.

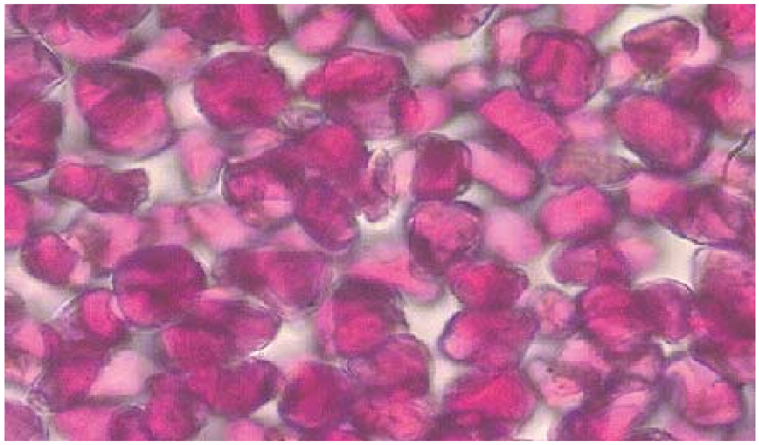

Figure 3: *Optical micrograph of a conventional ground toner.*

Most toner binders are thermoplastic polymers which bind the toner ingredients together and allow the toner to soften and melt flow at elevated temperatures to facilitate fusing or fixing to the substrate. The polymer binder accounts for the largest amount of a toner composition. Hence, it stands to reason that toner properties are highly influenced by the choice of the properties of polymer selected as the toner binder. There are many different, and often conflicting, requirements of a toner binder. Moreover, these binders requirements are also influenced by the toner manufacturing technique used, e.g. melt pulverized or the type of chemical method selected [6].

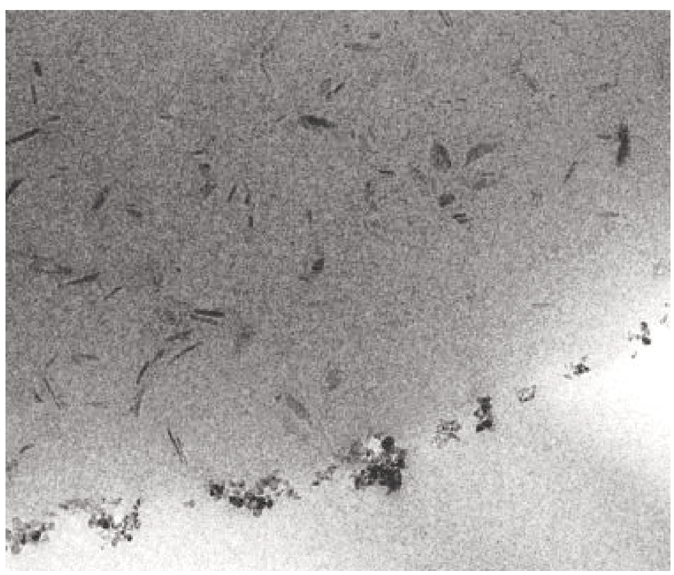

Figure 4: *TEM x-section of a toner particle.*

Toner Manufacturing

Toner manufacturing can be classified in two major categories. One method of toner manufacturing is by the conventional melt pulverized toner (MPT) while the other method is the chemically prepared toner (CPT). During the early days, all toners were produced by pulverizing process. In 1980's Nippon Shokubai and Nippon Zeon started to produce toners via the suspension polymerization methods. Even though the MPT is still the most predominant method for toner manufacturing, the toners produced by CPT processes continue to grow.

Melt Pulverized Toner (MPT)

In the early days of electrophotography, toners were prepared by this method only. A typical flow diagram is charted in Figure 5 showing major steps that take place during the toner manufacturing using this method [6]. In this process, all the toner components are fed into a twin screw extruder at a temperature above the softening temperature of the binder polymer. With the shear action and melt flow caused by the heat, the toner ingredients are either melt dispersed or the aggregates are broken down and uniformly dispersed in the polymer matrix. Once a desired dispersion of toner ingredients has been achieved, the toner melt is cooled and is pelletized to the final toner size.

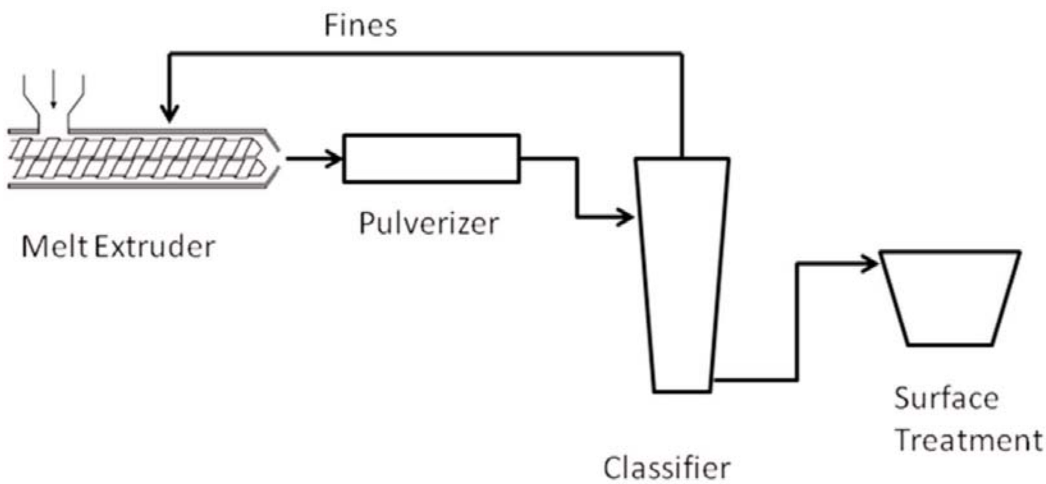

Figure 5: *A process flow diagram of MPT toner manufacturing process*

One of the foremost difficulties with conventional melt pulverized toner is the increase in the energy required to produce for smaller toner particles. The primary reason for this increase in power requirements is the increase in the surface area that needs to be created when preparing smaller toner particle size. In addition to the increase grinding energy, the small toner particles are also more difficult to classify. This all leads to lower productivity and increased cost of manufacturing small toners by this method [7].

Chemically Prepared Toners (CPT)

As mentioned previously, the chemically prepared toners were first produced by the suspension polymerization process, as an alternate toner manufacturing technology. The first chemically prepared toners were polymerized by addition/suspension polymerization, in which the monomer suspensions were chemically combined in the presence of an initiator etc. As a result, the term "CPT" used to describe such toners. However, since that time other methods of producing toners have also emerged. Even though many of these new methods of producing toners do not have involve any chemical reaction, all these new methods have been placed under the same CPT category.

There are many driving forces that have lead to the rapid acceptance of the CPT processes. One principle advantage with CPT processes is their ability to prepare smaller toner particles size. Since the CPT grows sub-microns particles to the final desired size, it is possible to stop the growth at any point and produce smaller toner size. Initial CPTs were spherical shape particles that were more difficult to clean from the photoconductor surface using the blade cleaner. But it is now possible to control the shape of the toner particles with the more recent advances in the CPT processes.

As mentioned previously, there are several different type of CPT processes that are being practiced now. The main CPT processes that are producing commercial toners are [8]:

1. Suspension Polymerization
2. Emulsion Aggregation (EA) Process
3. Solvent Dispersion
4. Chemical Milling

Suspension Polymerization

In this process, the polymer monomers are dispersed in an aqueous phase using the some combination of stabilizer and dispersants. Typically the size of the toner particle is controlled by the amount of shearing of the oil/water mixture and the amount of stabilizers/dispersants in the aqueous phase. Other toner ingredients, such as, pigments, charge agents and other additives are also added to the monomer mixture prior to the polymerization step. The monomer mixture also contains the initiators that start the polymerization process when the temperature is raised to start polymer chain propagation. Sometimes a chain transfer agent or a cross-linking agent can also be added to the monomer mixture to control the molecular weight of the polymer resin. This helps control its melt viscosity and other thermal-mechanical properties. Once the polymerization has been completed, the mixture is cooled down and the toner particles isolated and dried.

Emulsion Aggregation

In the emulsion aggregation process, sub-micron emulsions of polymers are allowed to aggregate by altering the physical properties of the dispersion medium via the pH control of the solution and/or by the addition of salts. Typical emulsions are several hundred nanometers in size. Other toner additives are also dispersed in the aqueous phase along with the polymer emulsions. The rate of addition of emulsion can be used to control the final size as well as the structure of the toner particle. For example, a core could be formed first and then a shell of different polymer could be created outside the core to protect the core and to control its other properties and thereby creating a toner with core-shell structure. These agglomerates still comprise many loosely attached small emulsion particles and need to be further attached to each other. Once the emulsion aggregation is complete, the aqueous dispersion of agglomerates is heated together above the softening temperature of the polymer resin. By controlling the temperature and the hold time at the elevated temperature, the shape of the final toner particle can be controlled.

Solvent Dispersion

In this method of toner manufacturing, a pre-formed polymer resin is dissolved in a solvent to form an organic phase. This organic phase is mechanically dispersed in an aqueous phase. The particle size in this method depends on the degree of homogenization and the amount of stabilizer in the aqueous phase. Once the desired particle size has been achieved, the solvent is removed and recovered for next batch. The aqueous phase also contains some solvent and is also recycled to ensure that the loss of any solvent is almost eliminated. The control of shape is readily possible in this approach because of the loss of volume due to solvent removal step and the accompanying shrinkage of the surface.

Chemical Milling

The chemical milling method involves the steps of first dissolving a pre-formed polymer in a solvent/plasticizer to form a high viscosity solution. The organic mix is then mechanically sheared in a dispersion media which contains some surfactants to form the desired toner particles. The high temperature of the dispersion phase initiates the evaporation of the solvent/plasticizer. When all the solvent/plasticizer is removed, the final toner particles can be isolated. Toners formed by this approach are essentially spherical in shape.

The types of toner produced by each CPT manufacturing technology are quite different and thus results in wide variety of toner properties. The suspension or emulsion aggregation methods can only produce vinyl polymer based toners.

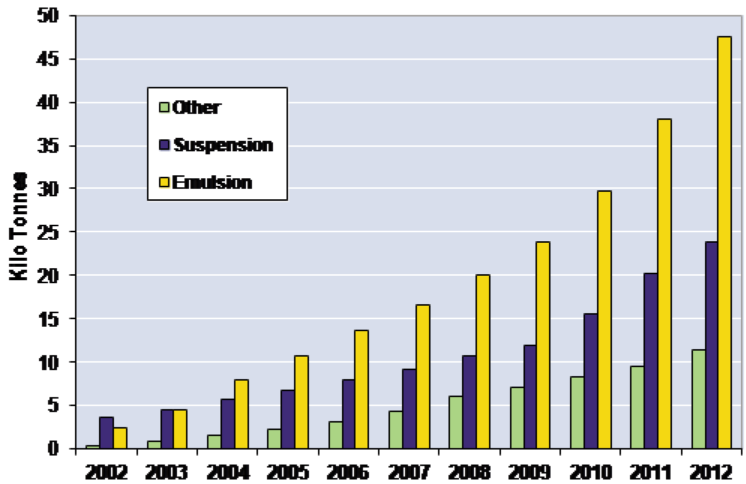

Figure 6: *Worldwide production of Chemically Prepared Toner*

Among the various CPT proccesses that are being used commercially today, the suspension and emulsion aggregation process are are the most prevalent as shown in Figure 6. Even though there are many advantages with the CPT processes, there are some issues that have not been addressed yet. Unlike the MPT process, where almost all the fines can be recycled and thus avoid waste, the CPT processes are not typically conducive to recycling process. Many of the CPT processes use surfactants which have to washed evenly otherwise toner properties can be impacted. Most of CPT manufacturing processes are batch processes which use a large amount of water phase to be heated and eventually discarded.

Fusing

Once the toner particles have been transferred and deposited on the final substrate, they need to be fixed in order to permit handling of the prints and to provide the desired appearance to the print. Another major benefit of fixing is to improve the physical properties of the prints, so that they are not easily damaged by mechanical abrasion and rub. The preferred degree of fixing is achieved by fusing the toner to the substrate or paper with assist from heat and pressure. By applying heat, the toner particles are softened and allowed to flow. Unlike offset and inkjet inks, the toner melt does not penetrate into the paper fibers.

The fusing step is the most demanding and most critical step in the electrophotographic process because the finial image appearance and its uses are directly influenced by degree of fixing. The physics of fusing includes a complex understanding various different disciplines which includes paper handing, toner rheology, colorimetry, mechanical design, high performance elastomers design, heat transfer and temperature control.

There are many different ways that a toner based images can be fused and fixed to the substrate. Most optimum fusing schemes are normally selected based on the type of paper or image substrate that is being utilized. Webs fed based continuous paper based printers typically lend themselves to fusing techniques that are more difficult to adopt with cut-sheet paper based printers. Among the variety of different fusing techniques that are being practiced today, the more common methods are [7]:

- Nip forming 2-roll systems
- Radiant fusing
- Flash fusing
- Solvent
- Extended Dwell
- Transfuse
- Dual stage Fusing

Nip forming fusing are the most common technique used in fixing a toner based image. In most cases, the internally or externally heated fuser roller forms a nip with a heated pressure roller. A very important term that is used to define conditions in a 2-roll fusing is the nip time or dwell time. In general, the nip time or dwell time, is defined by the amount of time portion of an image spends in the nip formed by the two rollers. The nip time can range from 5 to 50 milliseconds.

Security Printing

With continuing growth in digital printing, there are increasingly different types of documents and images that are being printed with electrophotography. Many of these documents require that some type of a security feature be included in the print. Security features are necessary against counterfeits and forgery of printed materials such as documents, photos, packaging materials, checks, financial documents, ID cards, bank notes, travel documents, tickets etc. In addition to the brand protection, security features are usually incorporated to guard against counterfeit and forgery in order to reduce revenue loss and to keep corporation profits up. Owing to the high image quality that can be achieved today with electrophotography, it is becoming increasingly simpler for counterfeiters to make a high quality forged document using a toner based printer. It is now possible to incorporate a security feature within such a document, which not only provides various levels of security without compromising the image quality. All this can be achieved by using clear toner in addition to the standard CYMK toners by using a printer that has the capability of using more than four toners.

Security features that are typically applied to a document can be both overt and covert. Various levels of security features that can be implemented in a document along with their authentication technique are as follows [9]:

- First Level
  -allows inspection of document with human senses alone
- Second level
  -hidden security features authenticated using simple devices as UV, IR, magnetic readers etc.
- Third Level
  -requires very special equipments in a forensic laboratory to authenticate the document

When security features are added to a document, the goal is to make the forgery as difficult a possible. At the same time, the authentication process needs to be simple to use and .easily accessible. Since these authentication requirements are normally at odds with each other, it is a common practice to incorporate more than one type of overt and covert security features in a document.

Most electrophotographic printers consist of four development modules to generate images based on CYMK process colors. Often a printer hardware design can accommodate more than the standard four development modules. In such cases, extra modules can be used to provide additional features to the resulting image. If a clear toner is used in one of these additional modules, wide variety of image enrichments can be integrated in the final image. The most common application for the clear toners is to provide a protective barrier to physical abrasion to the image as well as to impart uniform image gloss. It is possible to incorporate security features in the clear toner or any of the color toners used in the digital printer. There are several types of security features that can be enabled with the use of clear toners. Clear toner can be judiciously placed in or around the image to provide either positive or a negative watermark to the image. Another security feature that can be enabled with clear toner is raised letter printing to provide a tactile appearance similar to thermography. Not only are these features difficult to copy, they also provide an easy detection capability.

By utilizing a special clear toner, many different types of overt and covert security features can be incorporated in the document. Some of the security features can be implemented with the use of clear toners are [10]:

- Digital Watermarking
- Raised Letter Printing
- TRACELESS Printing
- UV Fluorescent Printing

Digital Watermarking
It is often desirable to protect a document just against copying. This could be done in a manner that part of the content can be readily observed by a human reader but not by a copier or scanner. An image that is printed using clear toner or ink, creating

a difference between reflected light and diffused light that can be distinguished by a human reader who views the paper at an angle other than 90°, but cannot be detected by a copier or scanner that is restricted to reading at right angles to the page [11]. Clear or white toners can be used for producing clear watermarks, low-density watermarks, and high-density watermarks [12]. This digital watermark technology controls the differential gloss of an image using the steps selecting a first halftone image having a first anisotropic structure, selecting a second halftone image having a second structure different from that of the first halftone, applying the first halftone to at least some portion of the halftone image, and applying the second halftone to another portion of the halftone image [13]. The second structure may be anisotropic as well.

Raised Letter Printing

In certain classes of printing, a tactile feel to the print is considered to be highly desirable and security feature. Specifically, ultra-high quality printing such as for stationary headers, business cards, or greeting cards and invitations, utilize raised letter printing to give a tactile feel to the resultant print output. This is currently carried out in the off-set industry via thermography in an off-line process. The raised letter printing is also well suited for security authentication. As the first level, the tactile feel can be easily detected by sight as well as it provides a tactile feel. Further, these features cannot be copied using other equipment. Many electrographic printers carry out the steps of forming a desired print image on a receiver member utilizing standard size marking particles; and, where desired tactile information is to be formed, selectively prints raised information utilizing marking particles of a substantially larger size than the standard size marking particles of the desired print image [14].

TRACELESS Printing

The Kodak TRACELESS System is a forensically invisible authentication technology that protects against fraud and counterfeiting [15]. It is easy to implement and integrates into a wide range of materials with no disruption to product design or production processes. This technology is based on proprietary KODAK Markers that can be integrated into a wide range of host materials with no impact on material characteristics. These Kodak Markers are only detectable with TRACELESS Readers and they are invisible to standard optical, forensic, or chemical analysis. These uniquely developed TRACELESS Readers are precision built for reliability, durability, and accuracy under extreme conditions. The combined Traceless Markers and Reader system has built-in safeguards to make reverse engineering virtually impossible. Various levels of security features are possible with the same marker and reader —from basic pass/fail to additional levels of security as required.

UV Fluorescent Printing

It is also possible to incorporate certain UV fluorescing dyes and/or pigments in clear toners for security applications. A number of UV fluorescing materials can be added to the toner formulation, which upon being exposed to UV-A or UV-B light, transmits the absorbed excitation in the visible portion of the spectrum. The visible light could range from violet, blue, green, yellow red and even white. Suitable excitation wavelength can be selected depending on the desired final application. This second level security authentication only requires a, typically portable, UV black light. Various applications of this technology are already being used in credit cards, driver licenses, currency, and mailing barcodes. The choice of the UV fluorescent dyes or pigments is dictated by the light stability of these dyes, charging behavior and the cost of the material itself.

The NexPress Digital Production Color Presses is able to apply many anti-counterfeiting measures using the KODAK NexPress Fifth Imaging Unit Solutions [16]. By using a NexPress Digital Color Press, is very easy to implement one or more security features to a print without affecting the characteristics of the end product, providing printers with maximum flexibility for delivering an effective anti-counterfeiting measure for their customers [17].

Conclusions

Electrophotography has established itself as an important technology in the digital printing environment of today. Toners used to print the digital images are essential part of the process and most of the features and appearance in a print is dictated by its composition. The methods used to manufacture toners and their particle sizes influence the toner formulation. Various fusing methods can be in electrophotographic printers, Each fusing technique not only allows fixing of the image to paper, but also affects the color and physical performance of a print.

Clear toner can be used to provide various overt and covert security features to safeguard against counterfeiting and forgery. Many of these features can be simultaneously incorporated in clear toners to provide various levels of protection in the same document. Digital presses, which can print with more than four toners, can easily utilize these clear toners without compromising image quality.

References

1. Galliford, G. J., Proceedings, 9th Annual Toner and Imaging Materials Conference, St. Pete Beach, FL, 2006.

2. Schein L. B., Electrophotography and Development Physics, New York: Springer, 1992.

3. Schaffert R. M., Electrophotography, New York, Focal, 1984

4. Williams E. M, The Physics and Technology of Xerography, New York, Wiley-Interscience, 1984.

5. Diamond A, ed., Handbook of Imaging Science, New York, Mercel Dekker, 1991.

6. Tyagi, D., Fusing technologies and Toner Materials Relationships, Short Course presented at IS&T NIP 29, Seattle, WA, 2013.

7. Kriss M., Ed. Wiley Handbook of Digital Imaging V3, Tyagi, D, Toner Technology and Fusing Concepts. In Press.

8. Kmiecik-Lawrynowicz, G., Chemically Prepared Toners, Short Course presented at IS&T NIP 24, Pittsburg, PA, 2008.

9. Annette, Jaffe, "Digital Technology, Security of Documents and Brand Protection", Tutorial presented at IS&T NIP 22, Denver, CO., 2006.

10. Tyagi, D. Zaretsky, M., Tombs, T., and Lambert P., Use of Clear Toner in Electrophotography for Security Printing, Proc. IS&T NIP 24, pp773-776, 2006.

11. S.-G. Wang, B. Xu, C.-H. Liu, .Halftone image gloss control for Glossmarks,. US Patent 7,180,635 (2007); .Variable Glossmark, US Patent 7,148,999 (2006); .Protecting printed items intended for public exchange with Glossmarks,. US Patent 7,126,721 (2006).

12. D. Schulze-Hagenest, A. Chowdry and D. Tyagi, Digital Watermarking Using Clear Toner, Proc. NIP 23, pg. 554, (2007).

13. D. Schulze-Hagenest, D. Tyagi; A. Chowdry, .Method and device for controlling differential gloss and print item produced thereby, WO Patent application 2006099897 (2006).

14. D. Tyagi, Pat Lambert, M. Zarestky, and Thomas Tombs, Developer composition comprising large toner particles, US Patent 8,435,712. (2013).

15. Kodak press release June 6, 2008, Kodak Previews New Capabilities of KODAK TRACELESS System for Anti-counterfeiting at Drupa 2008, http://graphics1.kodak.com/us/about_gcg/news/2008/080606b.htm

16. Kodak press release April 16th, 2007, .Expanded KODAK NEXPRESS Platform Offers Powerful Choices to Customers for Digital Printing Growth, http://www.kodak.com/eknec/PageQuerier.jhtml?pq-path=2709&pqlocale=en_US&gpcid=0900688a806cf85d.

17. Kodak press release May 29, 2008, Kodak Showcases Innovative Printing Solutions at drupa 2008, http://phx.corporate-ir.net/phoenix.zhtml?c=115911&p=irol-newsArticle_Print&ID=1151669&highlight=