Permanence of Dry Toner Based Documents

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Abstract

The permanence or stability of a document based on dry toner printing technology depends critically on three components that when combined form the image. These factors are the toner, the substrate paper and the fusing process that is used to produce the final document. Archival behavior is not guaranteed by any component alone and those preparing documents intended for long term permanent use have to be aware of all the potential pitfalls that arise in using such a system to make a document of record. The practice of dry toner based electro-photography has changed over the years. While previous experience and history has led to the awareness of the permanence issues with this technology, the technology is not standing still and newer printers incorporate new aspects that provide new challenges to understanding what approach is best for the conservation of these prints. This paper attempts to put the current understanding of image permanence of such prints in a historical perspective.

Introduction

The long term stability of a dry toner based document is of great concern to a number of different groups; those most interested in this behavior are involved in the conservation of printed objects and anyone involved in the retention of prints on paper. Grattan[1] and Subt[2] each provide brief descriptions of the issues encountered in these objects and some general guidelines for managing the preservation of such documents.

The archival behavior of prints made by employing dry toners in the electro-photographic process is dependent on many factors. The toner itself, being based on a pigment dispersed in a polymer, might limit the permanence of a dry toner print. The receiving medium, usually paper, might change as the print ages. Along with these "materials" changes there is the possibility that some aspect of the hardware selected by the manufacturer of the print engine can have a significant impact on the archival properties of the printed document. In this last category the fuser sub-system used in either the laser printer or electro-photographic copier is likely the component that has the most significant impact on document life. Each of these factors and their impact on an archival document are discussed below. The factors also interact with one another and as a whole make for a complicated puzzle for those trying to understand the overall archival document phenomenon. Finally there is an attempt to describe experiments that are performed by the laser printer and copier vendors which are directed at the appropriate aspects of the image permanence issues.

Impact of the Toner

Dry toner particles are composed of approximately 85 to 95% by weight of polymer resin(s) and between 5 and 15% of colorant, usually a pigment. Some toners contain wax which may be considered to be a component of the polymer resin. For black toners the colorant is generally carbon black made from the incomplete combustion of a natural gas source. These carbon blacks are very stable in almost all environments having properties that resemble lamp-black which has been employed in marking many type of objects since antiquity. The materials used to impart color to colored toners are generally synthetic organic pigments which do not always have the same archival quality as a carbon black. The colorants are much like those used in the printing industry and are expected to have a similar lifetime. The colors that generally degrade upon exposure to light are the yellow's which tend to fade to colorless with time and some magenta colorants which darken to a brown color with age. There is a question in the document conservation community whether the presence of iron oxides in a toner has a detrimental effect on the image stability of the print made with these materials (Grattan[1] p 3). Iron oxides are widely used in single component magnetic toners. The present author does not have such concerns about the use of iron oxides in toners as experience with MICR toners containing magnetite at about 30% by weight of a toner counters this question. These heavily loaded MICR materials are used to print checks which have to pass through a number of high speed sorters and yet still survive. A well fused MICR print is like as stable as any based on carbon black pigment.

The polymers (resins) first used to make toner particles in large volumes were styrene-acrylate copolymers. In 1994, Imaging Products Monthly[3] listed the composition of toner resins from 60 manufacturers. This listing contains some toners based on styrene-butadiene copolymers and some that used a polyester base resin. Gregory[4] also listed a similar set of materials included in the composition of dry toner particles. Since that date there was a shift to a greater production volume of styrene-butadiene resins (used in the Xerox DocuTech family of high speed black copier/ printers) and then to polyester resins (such resins are especially favored for use in producing cyan, magenta and yellow color toners). Of interest the latest generation of dry toners, made by chemical processes (CPT - chemically produced toners) are again based largely on styrene-acrylate polymers. All the polymer systems described above are quite stable and do not degrade significantly with time. The films of pigmented resin that constitute the final image on the substrate are stable and the only likely change over time is the possibility that films of these materials become somewhat more brittle. An aspect of these toner layers that is of importance in conservation of the images is that polymers containing styrene and acrylate or butadiene may be plasticized by the compounds used to ensure that polyvinyl chloride, PVC, remains flexible. This leads to the well documented vinyl offset behavior encountered with many electro-photographic prints. Polyesters are not as readily plasticized by such PVC additives and generally offer superior vinyl offset performance to those polymers rich in styrene.

The selection of the polymer in any toner design is governed by the mechanical properties of a film of the material and the ease of production of the toner. Most polymers employed to date for dry toners have a glass transition temperature, T(g), of between 60 and 70°C. These materials are only softened and not melted by heating in the fusing system which operates between 150 and 180°C. The T(g) range given above was selected from experience that shows polymer powders with a T(g) that range may be transported without “caking” between the toner manufacturing site and the final customer. Most toner powder made using a polymer with a T(g) below the given range form aggregates when exposed to the extreme environmental conditions found in some warehouses and trucking operations. It is also known in the industry that the higher the T(g) of a toner resin the more energy is required to fix the toner on the substrate. One additional consequence of this particular glass transition temperature is that it is unwise, from a document stability perspective, to store a printed document at temperatures above 60°C under compression (for example in a bound book) for any extended period of time. This is particularly important if the pages are printed on both sides of the paper when toner-toner contacts may occur. Further discussion of this and related paper-toner offset is given below.

One additional material, generally a polyolefin wax such as polypropylene or polyethylene, is encountered in a number of toner compositions. The wax is added to the toner formulation to assist in releasing the toned print from the heated fuser roll (see the fuser discussion below). In some formulations this addition of wax eliminates the need for using any release oil with the fusing system. The wax is a stable material which can enhance the archival stability of a toner document.

An additional property of the toner that can alter the stability of an image and the archival behavior of the printed document is the toner-paper adhesion which is a function both of the nature of the toner polymer and the surface treatment to the paper. Aspects of this interaction are discussed below.

Paper and Permanence

While the polymer-colorant combination employed in the design of a dry toner is not often the major contributing cause of poor archival behavior of a toned image, the same cannot be said of the paper used to make the print or copy. Today the major use of laser printers and copiers is the creation of “transient” documents. A transient document has a short lifespan and is generally in use for less than a week. This short life means that most of the paper used in such “printers” does not need to be of archival quality but has only to function in the printer (no paper jams or image defects) and be low in cost. Despite this there are some examples of inexpensive papers that have used to make photocopies that have endured for 30 years. These papers were of an “alkaline” type and have not yellowed over time.

The failure of many papers to show archival behavior is well known and efforts to provide guidance on the selection of a “permanent” paper have been documented by ISO [9706:1994 and 11108:1996], ASTM [D 3458-96 Requirements for LE-1000 (Type I – high permanency) Paper] and ANSI/NISO [Z39.48-1992]. Compliance with these standards unfortunately does not ensure that a print made using qualified permanent paper will lead to a permanent printed image. For a document with a life expectation of more than 50 years the interaction between the print engine, the toner and the paper enter into what has to be considered for predicting the permanency of a print.

In an electrophotographic printer or copier the paper has to be fed through the unit and imaged by transferring toner from a drum or belt onto the paper, the toner is then fused to the substrate. These operations function best when the paper contains sufficient moisture to be conductive. Too much moisture in the paper can lead to the loss of the appropriate mechanical “stiffness” which ensures that the sheet can be fed through the paper path in the printer/copier. The adhesion of the toner to the paper surface is facilitated by having an appropriate surface on the paper with a surface energy that facilitates the “wetting” of the surface by the softened polymer. This results in a strong mechanical bond between the toner layer and the paper surface. These interactions may be modified when release oil is used in the fusing system or when wax is added to the toner particles in oil-less toner designs. Wax tends to migrate to the surface of the toner film when such particles are fused and thus modifies the toner-paper interaction.

In the field it appears that users of the current generation of full color dry toner print engines show a preference for the use of coated, high gloss papers. The ANSI standard Z39.48 comprehends this type of paper and using suitably qualified coated papers should allow for the production of archival prints. Many of the coated papers on the market today use a paper coating that contains white inorganic material bound to the paper surface with a styrene-butadiene polymer. This type of coating provides an ideal receptor for toners that are formulated using the standard styrene containing polymers. The coating and the toner resin in this case blend readily and form a very stable system. Polyester based toners are not as readily blended into these styrene-butadiene based coatings. This may limit the archival behavior of prints made with such systems.

It is important also to understand that the papers preferred either for laser printers or copiers differs from region to region throughout the world. In Japan where most of the modern laser printers are designed it is critical for the printer device to work with the very uniformly dense, lightweight, heavily filled paper that is favored in that country. This form of "office" paper is what is used as the basis for evaluating the chosen print hardware. North American papers are less uniform in mass density than are those from Japanese mills and generally have higher basis weight. European office papers are generally even higher in basis weight than in North America. Thus the design of the optimal fusing set points for any print engine is a compromise between the different paper requirements. This compromise may also influence the archival behavior of a particular printed document. Given a well characterized specific "permanent" paper substrate a particular print engine could be tuned to provide an optimally permanent image. In general this is not a practical solution to the image permanence problem.

Influence of Fuser Design

The function of the fuser in a laser printer or copier is to convert a layer of powder (colored toner) into a film that adheres to the paper surface. In the earlier copiers the image was fused by simply heating the paper and the toned image for sufficient time in an oven to fix the toner to the paper. This slow process ensured that the toner-paper interface was almost at the same temperature as the paper and the toner formed a very permanent layer. Fusing technology has gone through many changes over the past years. Some variety of fusing systems emerged as the process speed increased. All these fuser designs had to be able to increase the temperature of the toner-paper interface to a level where the toner would flow and adhere to the paper.

Alternative fuser designs include radiant fusers where the toner is heated directly as it passes under a hot lamp and absorbs the incident radiation. In this case as the paper is reflective it remains relatively cool and the hot toner fixes itself to the cooler substrate. The radiant fusing process does not apply any pressure to the toner layer and is still in use on some web fed print engines.

An alternative to the radiant fusing system has been adopted by most print engine manufacturers. This fusing sub-system is based on heated rolls where the imaged paper passes between the two rolls. Usually the roll directly contacting the toner image is heated and it raises the temperature of the toner-paper interface to the fusing temperature. The other roller, which may or may not be heated, has the purpose of providing a means to apply pressure to the toner paper system. Increasing the pressure assists in maximizing the contact area between the toner layer and the heated roll which in turn assists in the transfer of heat across the toner layer. The extent of toner fix to paper is still governed by the temperature of the toner-paper interface. The actual heated zone, the nip formed between the contacting rollers, is quite short and is usually about 1-2 millimeters long. The time the toned paper is in the fusing nip is only tens of a millisecond thus requiring high temperatures inside the heated roll to allow for sufficient energy at the toner-paper interface. Dual roll fusing systems generally require a release aid to ensure that the hot toner layer adjacent to the heated roller is removed with the paper when the substrate is separated from the roll. This stripping process requires either an oiled roller or a release agent (a wax) embedded in the toner particles. Both approaches have an impact on the archival nature of the final document. There is a penalty to be paid for using a roll fuser; these systems require considerable energy to maintain both their temperature and temperature uniformity during high speed runs. This energy demand increases with the process speed of the print engine. Most of the documents currently being produced on laser printers are fused with roll fusers.

There is another type of roll fusing system that is in use in the field; this is the cold pressure fixing system used in some high speed electronic printers. No heat is applied and the hard metal rollers force the imaged toners into the paper under a applied pressure that is close to that needed for paper calendaring. The documents produced on this equipment are believed not to be archival as the toner layer may be removed by aggressive rubbing.

Recently a number of printer manufacturers have introduced fusers based on heated belts. These belt fusing systems are not run at as high a temperature as the roll fusers and compensate by maintaining contact with the toned paper for a longer time than for a roll fuser. An advantage of the belt fusing system is that this system can be brought to operating temperature far faster than can a heated roll. This behavior of the belt fusing system can be used to make an "instant-on" printer. Far less pressure is applied to the toner-paper sandwich with a belt fuser so the image is not significantly compressed by the system. Prints made with toner and paper designed for roll fusers appear to behave much as they do when fused on a belt fuser. It is uncertain whether the drastically differing conditions experienced by the toned paper in a belt fuser will lead to image permanence that is identical to that of a roll fused image.

Many of the printed documents made using the fusers described above can have their archival behavior enhanced by exposing the fused print to a UV curing step. Passing the print through a unit where it is exposed to intense UV irradiation creates a more durable cross-linked film of polymer than is achieved by thermal fusing alone. Such post print equipment is not readily available but is becoming more accessible in larger print-shops.

Image Permanence Experiments

Most manufacturers of laser printers and copiers evaluate their materials in prototype hardware before launching a product. Some of these tests are relevant to the archival behavior of the final printed document and will be outlined here.

The first evaluation involves the determination of the set-point for the temperature of the fuser. This temperature will be chosen such that the toner is well fixed to the substrate at this temperature. Some manufacturers allow trained service personnel to change this set point after installation. Some machine designs employ sensors to vary the fuser temperature over a limited range in response to input media while the unit is operating. The fuser temperature is usually determined using the design intent toner and a set of papers that the manufacturer knows are of interest to the customer of that class of printer. A range of paper characteristics will be covered by this approach but not all papers can be explored in this pre release investigation. If the desired permanent paper is similar to any of the evaluated papers then papers that meet the standards for archival behavior will function well in the particular hardware. The optimal fuser temperature is set using measures of the "fix" of the toner on the paper. These fix measures are based on abrasion, rub and crease testing of a printed image. The crease test is interesting as it involves the creasing of a test image with a constant action and examining the section around the fold. Usually a poorly fixed toner layer breaks along the crease exposing a wide region of exposed paper. As the fix is improved by increasing the fusing temperature the creased area decreases in width until for an excellent fix no white can be seen by eye. Microscopic examination of the nature of the creased area also provides information on the brittleness of the toner layer. The crease criteria are very important to archival properties of an image,

Most manufacturers have adopted tests to determine whether the toned image is liable to vinyl offset. This test is done by placing an imaged patch up against a clean standard vinyl surface and the sandwich is maintained in a humidity controlled chamber (~70% RH) for up to 7 days while being heated to about 50°C under compressive load. The image-vinyl sandwich is then split and the extent of toner transfer to the vinyl assessed. For this type of test a scale of 0-5 is used, 0 corresponding to no toner transfer to the vinyl and 5 to severe toner transfer.

A similar test is performed to assess the extent of toner-toner and toner-paper offset which is relevant to the situation where documents with print on both sides are stacked together under compression. The printed patterns are designed to allow the examination of print-paper and print-print interaction in a single experiment. The toner patterns are a uniform high optical density patch for black toners and both single color patches along with process color "black" patches (combination of cyan, magenta and yellow all at optimal density) for color printers. The toner-paper samples are then sandwiched together and evaluated under conditions similar to those described for the vinyl offset studies above. Again the offset is measured using scales of 0-5, 0 being excellent and 5 a failing grade for both the toner-paper and toner-toner interactions. As might be expect many toners fail in those areas where toner-toner contact occurs but there are a number of cases where the failure was seen in the toner-paper contact areas. This is generally found for papers with an applied surface sizing designed to facilitate toner adhesion.

Conclusion

The stability and permanence of a dry toner based document has to be considered as a system of interacting variables. The most significant factors are the toner, the paper and the fuser system. The failure of any one of these factors results in loss of image permanence. Production of an archival document requires a stable well understood toner, the use of an archival paper that is compatible the toner and a fusing system that securely attaches the toner to the paper surface.

References

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Biography

Michael Hopper received his M.Sc. and Ph.D. in Physical Chemistry at the University of Natal, South Africa. He spent 28 years at Xerox Research Centre of Canada studying a variety of imaging materials. The last 10 years of this involvement was in the development of processes to make chemical toners and he holds 52 US patents in that technology. He is a member of the IS&T, ACS, AIC and the Soc. Coatings Technology.