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Dry Processing Instant Photographic Systems

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Abstract. The technology, photographic characteristics, applications, advantages, limitations and possible lines of advancement of dry processing instant photographic systems viz. dry silver halide systems, diffusion transfer reversal materials, photothermographic systems, dry film peel-apart photoresists, photopolymers for holographic recording, thermoplastic recording systems and electrophotographic systems have been discussed.

1 Introduction

A photographic system in which a latent image formed by the action of light could be processed in a dry manner, to give a dense, high contrast and high resolution image, may find many applications in a wide range of fields of information storage and retrieval[1,2], reprography[3], instant amateur and professional photography[4], holographic recording[5], lithographic[6] and screen-stencil printing[7], printed circuit technology[8], radiographic recording[9], etc.

The conventional silver halide systems[10-12] with all their enormous advantages have a severe limitation due to the necessity of wet processing. This can be a serious drawback in cases where the quickest possible access is required. Most recent photographic systems have been designed which retain the basic photographic properties of the process but offer not only rapid access but dry processing as well.

A survey of the literature on photographic materials reveals the following few recent photographic systems for instant dry processing-dry silver halide systems[13], diffusion transfer reversal materials[14], photothermographic systems[15], dry film peel-apart photoresists[16], photopolymers for holographic recording[17], thermoplastic recording systems[18] and electrophotographic systems[19].

2. Dry Silver Halide Systems

Dry silver is the most recent process and represents a union between the silver halide system and thermography[20]. A variety of commercial rapid access heat developable materials have been based on this system.

The basic process of the dry silver halide system is very simple[21]. In principle, the imaging layer comprises the following two main components :

(a) A comparatively small amount of photo-sensitive silver halide.

(b) A major amount of non-light sensitive image forming material. This consists of silver behenate (silver soap, silver salt of a long-chain fatty acid such as behenate acid) plus a reducing agent.

The components (a) and (b) must be in catalytic proximity either in the same layer or in separate layers. The chemicals needed for dry silver materials, can be coated on either opaque or transparent materials, therefore, either film or paper can be used as the base support. It is significant to note that dry silver coatings use less than half the silver required for conventional silver halide emulsions.

In the dry silver process[22] (Fig. 1), light-sensitive silver halide is used as the latent image forming material. When the material is exposed, silver halide forms the silver speck or stable latent image. The photolytic silver thus formed from the silver halide catalyses the image forming redox reaction between the silver behenate and the reducing agent so that heating the exposed layer for a few seconds to approximately 100°C will develop a silver image as shown in Fig. 1.

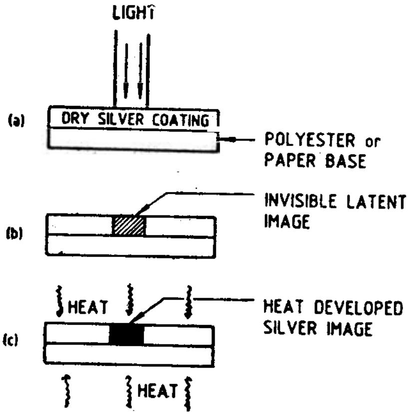
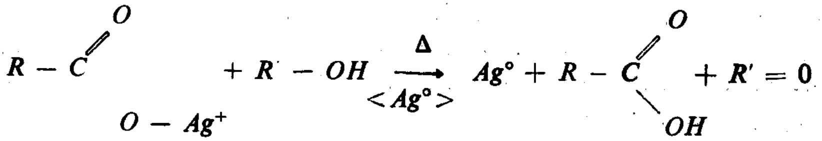


Figure 1. Dry silver process.

The two basic reactions of latent image formation and image development are as follows :

$$2\,(Ag\,X) + h\nu \longrightarrow 2 < Ag^{\circ} > + X_2 \qquad \text{(Latent image formation)}$$



$$R-C\begin{matrix}\diagup O\\ \diagdown O-Ag^{+}\end{matrix} + R'-OH \xrightarrow[<Ag^{\circ}>]{\Delta} Ag^{\circ} + R-C\begin{matrix}\diagup O\\ \diagdown OH\end{matrix} + R' = 0$$

(Image development)

The reducing agent that causes the formation of silver metal from the silver salt is made of developer or antioxidant, plus development accelerator. The antioxidants used in dry silver are weak antioxidants and are not typical of the chemicals used in wet photographic development. A typical example of the type of antioxidant used is 2, 2'-methylene bis-(4-methyl-6-tert butyl phenol).

A couple of significant characteristics of the process are that nothing needs to be added or removed during image formation, and the light capturing mechanism is quite separate from the image forming mechanism, in other words, a catalytic process. Light forms the catalysts which initiate and accelerate image formation, but the catalyst itself does not become part of the image. Since the silver that is light sensitive does not become part of the image, therefore, some of the classical relationships between sensitivity and other characteristics do not exist, but the fact that one form of silver responds to light and another form of silver forms the image is of significance in making a simple-to-use and versatile image forming media.

Because the photosensitive element of the coating is silver halide, it can be dye sensitized to all areas of visible spectrum. It is also possible to use colour developers and to achieve colour coupling. The energy required for the formation of latent image is relatively low, about 10 ergs/cm^2 to achieve $D = 1.0$. The speed of the dry silver materials ranges from 0.001 to 0.1 ASA. The resolution is very high of the order of 80 to 500 lines/mm.

The thermal processors required for the dry silver process are quite simple in principle[23]. The method used to apply heat to dry silver materials is not significant from a kinetic point of view, but temperatures should be controlled, usually to within ± 1 °C and contact with the heating source should be uniform enough to impart this level of heat control to the media itself, so that best photographic quality can be achieved. It does not matter, for instance, whether hot air or a hot surface is used or which side of the media is heated, but there are, however, advantages from an access time and physical handling of the media.

The range of systems based on the dry silver principle comprises film as well as paper of various degrees of photosensitivity, contrast and granularity. There is available a dry silver paper of medium to high contrast as well as low to medium contrast, and a continuous tone grade of dry silver film. Special materials include a green-red sensitive film for laser recording, a higher speed green sensitive film for CRT recording, and a high contrast film for microfilming.

Dry silver halide materials find applications in laser recording, CRT recording, enlarging, micro-filming, document copying, photocopying, etc[24].

The speed of the dry silver halide systems is low as compared to the conventional wet silver halide systems. The sensitivity, stability and shelf-life of dry silver halide materials could be improved. The basic kinetics of the process and the materials needed for the technology do not theoretically limit these improvements. The research efforts carried out at 3M Co., USA, in 1979, have reduced the required exposure energy to less than one erg (speed more than 1 ASA) for $D = 1.0$ and have formulated materials that are stable to adverse environmental conditions, particularly at elevated temperatures[13].

3. Diffusion Transfer Reversal Materials

Diffusion Transfer Reversal (DTR) is a photographic processing technique that produces a finished positive print, directly from the camera, immediately after exposure[25–27]. The method of producing the positive print is, however, totally different from that of the conventional printing process. In this case it is the unexposed and undeveloped silver halide in the negative which is used for the formation of the positive image[28–30].

The principles of DTR process were discovered independently by different routes by Andre Rott[25], of Gevaert (Belgium), and Edith Weyde[26], of Agfa (Germany). This one-step photographic process was perfected by Edwin H. Land[27] for use in instantaneous camera photography to produce silver-image prints. Later, Land and Polaroid Corporation pioneered in the introduction of in-camera colour prints using dye diffusion transfer[31].

In the DTR process[14,32,33] (Fig. 2) an exposed photographic emulsion layer is developed by means of a processing solution (developer) that contains a silver halide solvent while it is in contact with another layer containing catalytic nuclei that is not light sensitive, but which is specially prepared consisting usually of colloidal silver or silver sulphide. In the course of forming a negative image in the exposed layer, the developer dissolves sufficient amounts of the unexposed silver halides (representing the positive image) and forms soluble complex silver ions which are diffused and transferred to the receptor layer, creating a positive image on its surface by reduction of soluble complex ions to metallic silver by the substances usually contained in the second support. In the exposed areas of the negative, all the available silver halide is developed to black silver. No soluble silver compounds can be formed and the corresponding areas in the positive layer remain free from silver.

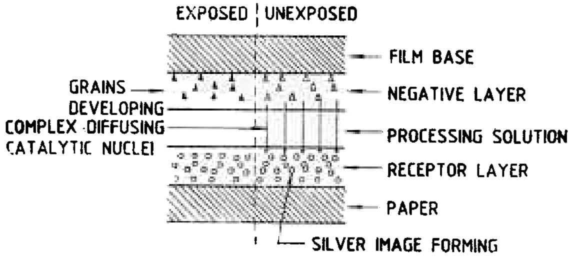


Figure 2. Silver salt diffusion process.

In this process, the image formation depends not only on one but on two types of imaging process[34]. Firstly, the conventional latent image is formed by exposure on the negative layer and secondly, the catalytic nuclei present in the receptor sheet catalyse the reduction of solubilized and transferred, originally unexposed silver halide to metallic silver. The binding agents in the image-receiving layer must act as a vehicle for suspending and dispersing the essential ingredients of the layer. Water soluble starch ethers or carboxymethyl cellulose have been suggested[35,36] as binding agents for the positive layer. The development nuclei act as catalytic sites for the deposition of the silver from the transferred silver complexes. The substances used for the catalytic sites were called 'fogging agents' by Andre Rott[37] because these substances were capable of promoting the reduction of silver halides without requiring the action of light.

Edith Weyde[30] has noted that the number of active silver nuclei in the positive layer determines the rate of silver deposition. According to her, heterocyclic mercapto compounds, which form silver compounds of low solubility, slow the rate of deposition of silver from the silver complexes being transferred by the diffusion. She[38] patented the 5-mercapto-1, 2, 3, 4-tetrazoles, particularly the 1-phenyl-5-mercapto-1, 2, 3, 4-tetrazole for producing black diffusion transfer images.

According to Land[39], the general reactions which take place in the DTR systems are

In the negative or donor layer

$$Ag^+ X^- \xrightarrow{h\nu} Ag^\circ + X$$

(Conventional latent image)

$$Ag^+ X^- \text{ Dev} \xrightarrow{Ag^\circ} Ag^\circ + X^- + \text{Dev} - OX$$

(Exposed) (Negative image)

$$Ag^+ X^- + 2\, S_2\, O_3{}' \longrightarrow [Ag\,(S_2\, O_3)_2]''' + X^-$$

(Unexposed) (Soulble complex silver ion)

In the positive and or receptor layer

$$Ag\,(S_2\, O_3)_2\,] + \text{Dev} \xrightarrow[\text{nuclei}]{\text{catalytic}} Ag^\circ + 2\, S_2\, O_3{}' + \text{Dev} - OX$$

(Soluble complex
from negative layer)

Colloidal silver (Positive image)
or
Silver sulphide.

The processing solution contains high concentrations of developing agents, alkali and silver halide solvent in a viscous medium[40]. In Rott's British patent[41] the processing solution was a thiosulphate monobath containing hydroquinone and metal as developing agents. Agfa[42] introduced developing agents such as 1, 4-dihydroxy-2-cyclohexyl benzene or 1, 4-dihydroxy-2-tertiary-butyl benzene.

The processing solution has two functions : Firstly, it has to develop chemically the emulsion in which a negative silver image is to be produced instantaneously, i.e. before the physical development process starts by virtue of the dissolved silver halide and the diffusion transfer process begins. Secondly, the dissolved silver halide, migrating in the form of a complex silver ion, must also be instantaneously reduced to black silver by the developer. This is accelerated and accomplished by the nuclei of high catalytic activity in the receiving sheet.

In practice, in the Polaroid-Land Camera[43] (Fig. 3) the roll film consists of two types of materials, one is roll of negative film and other is roll of positive paper. The negative film is made of negative type of photo- sensitive emulsion and positive paper coating is not light-sensitive but specially prepared and contains nuclei for precipitating silver during development process. The positive paper also consists of pods of viscous processing solution attached at appropriate intervals.

The two strips travel through the camera independently but are brought into contact after exposure of the negative layer. Pods of processing solution are ruptured when the two strips are pressed into contact between metal rollers and form a very thin layer of developer between the two strips. After a processing period of about 10 seconds, the positive print can be pulled out of the camera and separated from the negative. Normally the negative image is discarded but Polaroid have also introduced a new material which yields a high quality negative after immediate immersion in a solution of sodium sulphite to neutralize the developer[44].

Although the amount of silver per unit area is very low in the positive image, its density is high[45]. This implies that very efficient use is made of the image silver and leads to an exceptionally high amplification factor in DTR systems. Speeds of up to 3000 ASA are common place in commercially available Polaroid black-and-white systems and speeds of up to 20,000 ASA are claimed by Land in 1971, in the process Solubilization by Incipient Development (SID)[46]. These high speeds are beyond those possible with similar negative emulsions developed by conventional means.

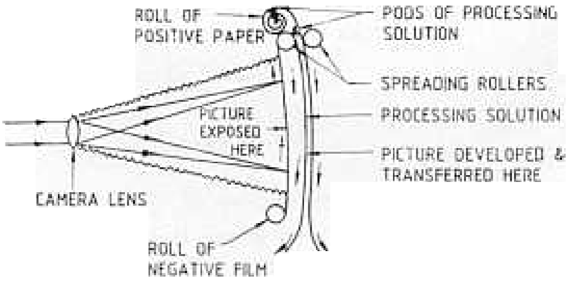


Figure 3. Schematic view of polaroid-land camera.

The extreme sensitivity of DTR materials is due to the following facts[47]:

(a) The image silver is of high covering power. The covering power and colour of the silver image are influenced by the presence of toning agents. A dense image in the receptor layer is due to the presence of active catalytic nuclei and the toners.

(b) The use of an extremely active processing solution containing amidol, phenidone at high concentrations and pH values.

(c) Development is carried out immediately after exposure, this avoids any latent image regression which occurs in conventional negative materials that are often processed weeks/months after exposure.

(d) The image is formed on a paper base which gives an increase in density as compared to a transparent material because light passes twice through the image.

The ease with which positive images are produced by the diffusion transfer reversal technique has led to the investigation of various modifications of the basic process, including some which do not involve the transport of silver ions from the negative to the receiver. Some of these imagenious variations are : the use of water or an alkaline solution as the transfer fluid[48], formation of electrically conducting photographic images[49], negative and positive images by Web processing[50], thermal diffusion transfer[51], dye diffusion transfer for forming photographic images in colour[52], and Kodak instant picture system[53].

The recent development in DTR materials is the Polaroid SX-70 process[54-56] which uses single support materials and does not require stripping apart. The process which gives direct finished coloured possitive print immediately after exposure is named 'Absolute One-step Photography' by Edwin H. Land[54]. The Polaroid SX-70 film has been described as '15 layers of chemicals bound between two sheets of plastic' and is exposed and viewed from the same side using a camera with an optical system to reverse the image so that it would be right-reading in the final colour print. On 20 April 1976, Eastman Kodak Company introduced an instant photography system using a colour print film, 19 layers deep and incredibly complex that W. T. Hanson, Jr., described as having 'fundamentally new imaging technology'[57]. Unlike the Polaroid print film, which has a negative silver halide emulsion layer, the Kodak print film is basedo n a positive-working emulsion. In 1983, Polaroid[58] has introduced a new 'light management' camera with infrared sensing system which employs the most recently developed Polaroid 600 high speed instant colour print film.

Apart from the wide-spread application of the DTR technique for document copying and for amateur and professional photography, many other practical uses have been developed such as in photomicrography, CRT recording, X-ray radiography, slide transparency making, offset printing system, etc[14].

The resolution of the DTR materials is not high and the stability of the DTR positive prints is not equal to the conventional photo-finishing prints. The resolution of the DTR materials should be increased at the expense of the speed which is very high. Some chemical steps should be attempted to make the DTR positive prints as stable as conventional photographic positive prints.

4. Photothermographic Systems

The term photothermography applies to an instant dry process of imaging in which imaging systems are rendered sensitive to heat by exposure to light[59,60]. Mercurous oxalate has been used in photothermographic systems, in which the thermal decomposition is accelerated by first exposing the material to light[61,62]. Mercurous oxalate emulsions are prepared by adding mercurous nitrate solution in the presence of dilute nitric acid to a solution of potassium oxalate in gelatin.

$$2H_g\,NO_3 + K_2C_2O_4 \xrightarrow[\text{dil } HNO_3]{\text{gelatin}} H_{g2}C_2O_4 + KNO_3$$

In this process, a substrate, which has a coating of mercurous oxalate in a suitable binder, is exposed to light to form a latent image. On heating, the latent image is amplified and a visible black mercury image is produced. The amplification of the latent image has been shown to be of the order of 10^4.

Increased development temperature does not increase the photographic speed of the system but decreases the development time. One of the interesting observations made is that mercurous oxalate is much more sensitive to light when it is exposed at a raised temperature. For example, if an emulsion is exposed at room temperature to a given light source for one second, an exposure time of one-tenth of a second would be sufficient to give a comparable density at a higher temperature with the same emulsion. It was found that calcium, barium and uranyl oxalates increased the sensitivity of the system. The binder must be dimensionally stable and must prevent the developed mercury image from evaporating. A copolymer of acryionltrile and polyvinylidene chloride was found to be the most suitable. Using this binder, development temperature of 180°C could be used and development time carried out in five seconds.

The proposed mechanism for the photo-thermal decomposition of mercurous oxalate is that the products of reaction are mercury and carbon dioxide.

$$H_{g2}\,C_2\,O_4 \xrightarrow[\text{Heat}]{\text{Light}} 2H_g + 2CO_2$$

It has not been possible to find a suitable solvent to fix the image thus produced. Materials which dissolved the unreacted mercurous oxalate also removed the developed mercury image. It is possible to transfer the image during the development stage to a receiving sheet containing selenium sulphide or palladium chloride. Another method of fixing is to supercoat the developed print with a layer containing an UV absorber. The system has a resolution of at least 50 lines/mm.

The sensitivity of photothermographic emulsions consisting of mercurous oxalate suspended in gelatin lies in the near ultra-violet region of the spectrum. Efforts to extend the spectral sensitivity have shown that certain dyes produce sensitization in the visible region of the spectrum[63]. The best sensitizers found are Acriflavine, Acridine orange, Acridine yellow and Proflavine. In the case of Phthalein dyes, the order of sensitization is : Erythrosine *B* > Eosin *Y* > Rose Bengal > Phlosin *B*. In general, the spectral range of sensitization for mercurous oxalate is virtually the same as that of silver halide emulsions[64].

Complex oxalates of palladium and cobalt[65] have been shown to exhibit photothermographic properties with amplification factor of 10^3 to 10^4 on development at up to 90°C. The stoichiometry of the reactions is as follows :

$$K_2\,[Pd\,(C_2\,O_4)_2].\ 2\,H_2O \xrightarrow{h\nu} Pd + 2\,CO_2 + 2\,H_2O + K_2\,C_2\,O_4$$

and it has been suggested that the solid photo-products, palladium atoms or aggregates and a *Co* (II) complex oxalate in the case of $K_2\,[Co\,(C_2\,O_4)_3].\ 3\,H_2O$ catalyse the thermal decomposition. In the case of $K_2\,[Pd\,(C_2\,O_4)_2].\ 2\,H_2O$ coatings on glass were produced by air-drying a wet slurry of the compounds applied to the glass with or without a binder of polyvinyl-pyrrolidone.

In the Dual Spectrum photothermographic system[66], the thermographic reaction is controlled by prior exposure to light. It is based on the discovery that there are compounds such as substituted α-nephthols, especially 4-methoxyl-1-nephthol, which can be deactivated by light. They are one of the reactants of a heat system, while the other reactant may be a noble metal salt of an organic acid such as silver behenate. The light inactivation of the naphthol can be increased and extended to longer wavelengths by the addition of halogen containing fluorescein dyes such as erythrosine.

In this photothermographic system, the reactants are usually supported on two different substrates. The dye sensitized α-naphthol is coated on one substrate and is printed by the reflex technique. This exposed sheet is then placed in reactive contact with an opaque substrate having a layer containing silver behenate. Heating this sandwich to the conversion point produces a black image in the regions which were not deactivated, by reduction of the noble metal salt of an organic acid.

The mechanism of the light desensitization of 4-methoxyl-1-naphthol to subsequent thermal reaction with the organic salt is due to the fact that in the presence of a photoreducible dye, the efficiency is increased by oxidation of the dye to its original state by oxygen or peroxides present associated with the organic components of the coating. A dye sensitized decomposition of the naphthol is probably involved, similar to the reactions which take place in the sensitized initiation of photopolymerization[67].

A new type of photothermographic lead compound system[68] involves some interesting properties. At normal room temperature the light sensitivity is negligible. Heating the material, however, up to 80-100°C during imagewise exposure to light of 360-420 nm results in the formation of a clearly visible image. Cooling the material again to room temperature desensitizes completely the photothermographic layer so that the use of an additional fixing step is avoided. The whole process can be repeated many times so that 'add-on' imaging is possible. The active ingredient contains basically a thermosensitive but not light sensitive, organic lead compound, the decomposition temperature of which is lowered by the catalytic activity of an exposed photoconductor.

For these experiments, lead (II) oxide and triisopropanolamine have been used as the thermosensitive compound. A small amount of lead (II) oxide in excess acts as a light-sensitive catalyst. Other photoconductors such as *ZnO* or $Ti\ O_2$ can also be used. When a composition of this type is coated on paper, a deep black image consisting almost entirely of metallic lead is obtained on a nearly white background.

Photothermographic systems find applications in reprography, CRT recording and document copying and can be used only as recording materials for line work. Most of the thermographic materials have spectral response in the near ultra-violet region, attempts can be made to extend the spectral sensitivity of the systems, to the visible region of the spectrum by the incorporation of certain photosensitive dyes.

5. Dry Film Peel-apart Photoresists

This type of dry film photoresist is unique in its processing techniques, as no liquid developing is employed and gives a positive image instantaneously after exposure and thermal development[69]. They are particularly suitable in making printed circuit boards[70], lithographic plates[71], and screen-stencil images[72].

The structure of dry film photoresist is shown in Fig. 4. It has a sensitized photoresist layer sandwiched between a 25 μm thick polyester Mylar film which is defined

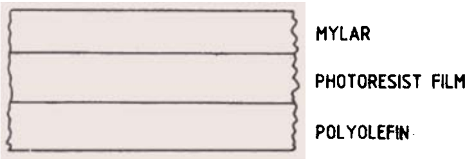


Figure 4. Dry-film photoresist composition.

as 'peel-apart film' and a cover polyolefin film which protects the adherent photosensitive resist layer[16].

The photosensitive layer includes a photo-polymerizable unsaturated monomer, a polymer binder and a sensitizer as essential ingredients which undergo a change in adhesion upon light energy absorption[73,74]. The photosensitive layer thickness is 20-50 μm.

The dry film peel-apart system is developable due to the difference in adhesive forces[75,76]. An increase of the adhesive force between the photo-polymer layer and the peel-apart Mylar film and a prompt decrease of the adhesive force between the photopolymer layer and the substrate surface occur in a layer on exposure and thermal development. The unexposed photoresist layer remains on the substrate and the exposed layer is peeled from the substrate. This is called a positive working photopolymer process.

In practice[77], the polyolefin cover film is removed and the photosensitive resist layer is applied to clean copper surface (Fig. 5 a). This light-sensitive element is exposed to actinic light through a high contrast photomask. When light reacts with the resist resin, it polymerizes and the adhesin to the clear-plastic overlay is increased. The exposed resin undergoes a change in physical properties because of an increase in molecular weight. In the unexposed areas, the resin of course, remains unchanged. After exposure, parts are developed thermally with the Mylar overlay in place. Initially the part is heated. Heating is sufficient to cause flow in the unexposed areas but not in the polymerized exposed areas. While warm, the clear-plastic overlay is peeled from the part. By virtue of the adhesion to the Mylar material caused by polymerization, the exposed image is pulled from the metal surface by the departing plastic overlay as shown in Fig. 5. In the unexposed areas, the heat-softened unpolymerized resin undergoes a cohesive failure with the application of the peeling force. About

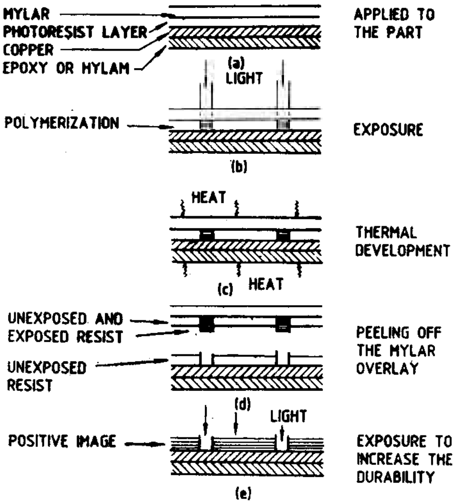


Figure 5. Dry-film peel-apart photoresist process

half of the resin remains attached to the Mylar overlay and is peeled off with the exposed image. The lower half remains attached to the metal substrate and forms the image. Because the unexposed resin remains, the image is positive. In the unexposed areas, the image remains unpolymerized and readily removable. For greater durability towards etching, the final image is exposed.

The image profile is somewhat distorted from the tear-out of the exposed image and the resolution is not high (5 lines/mm), but it is usable in many engineering reproduction applications[78]. Resolution is remarkably effected by the thickness of the photosensitive layer and exposure time. With a normal exposure time, resolution varies inversely with the thickness of the photosensitive film.

The speed of the system is low of the order of 10^{-6} ASA. The spectral sensitivity is basically determined by the absorption of the sensitizer. The actinic range of the present system isfrom a bout 200 to 300 nm. Efforts should be made to increase the speed and resolution of the dry film photoresists. The spectral response can also be extended to the visible region of the spectrum by the addition of suitable sensitizers.

An important advantage of dry film peel-apart photoresist systems is that it solves industrial pollution problem which is generally caused by a large amount of waste volatile developer used in wet photofabrication and photoprinting photoresist systems[77].

6. Photopolymers for Holographic Recording

A photosensitive material capable of high resolution image recording that needs no wet development is desirable for holography, optical data-processing and laser computer output microfilming applications that require the interference of an object with its holographic image or real-time recording. Dye sensitized polymerizable materials have been shown to provide attractive techniques for recording holographs and have attracted the current interest of investigators[79,80].

Photopolymers have very high resolution capabilities and do not require wet processing. Transparent, practically grainless, phase holographs can be conveniently recorded with laser exposures. They can be fixed optically in place, allowing almost instant access[81,82].

The photopolymer system used in holographic recording is a mixture of acrylic monomers and photocatalyst solutions[83].

	Photocatalyst solutions	
Acrylic Monomers	(1)	(2)
Barium acrylate, Lead acrylate, Acrylamide, Solvent water	*p*-toluene sulphinic acid, methylene blue, solvent water	*p*-toluene sulphinic acid, methylene blue, 4-nitrophenyl acetic acid, solvent glycerol

The photopolymer solutions are usually prepared in the volume ratio of five parts monomer solution to one part photocatalyst (1) or 10 parts monomer to one part photocatalyst. (2) Photopolymer samples are prepared by enclosing the photopolymer solution between a pair of 5 cm square glass cover slides. The thickness of the photopolymer film is controlled by an adjustable slide holder and is usually set to a 25 μm spacing.

Polymerization of the acrylic monomers used is initiated by 'photoredox catalysis'[84]. This photoredox catalysis system consists of photo-oxidant dye, methylene blue and *p*-toluene sulphinic acid. Prior to laser exposure, this catalyst is mixed with a water solution of monomers. The mixture remains sensitive only for a few hours, although individually the monomers and photocatalyst solutions have long shelf lives.

The methylene blue is a sensitizing dye which provides high sensitivity for *He-Ne* (633 nm) and ruby laser (694 nm) frequencies. A methylene blue molecule that has absorbed a photon has a high probability of undergoing an inter-system crossing from its normal singlet state to an excited triplet state, which is metastable. Methylene blue has a higher oxidation potential in its triplet state than in the singlet configuration.

A redox reaction, which takes place between the triplet dye molecules and *p*-toluene sulphinic acid, produces free redicals (This reaction does not take place when the methylene blue is in its ground singlet state). The free redicals then initiate polymerization of the monomers. The polymer is a plastic solid after exposure.

The film can be fixed by adding 4-nitrophenyl acetic acid to the photocatalyst solution and illuminating the film with ultraviolet light following the holographic exposure[85]. Ultraviolet photolysis of the 4-nitrophenyl acetic acid yields components that temporarily desensitize the photopolymerization process by reducing the dye to its colourless form so that it no longer absorbs visible light. The images could be fixed with UV exposure of approximately 200 mJ/cm^2 from a mercury are filtered with a No 7-54 corning glass filter. A variation of thermal fixing has also been employed, just before exposure[86].

Holographs made with a catalyst without 4-nitrophenyl acetic acid can be fixed by exposing to room light without destroying the holograph. There is some loss of diffraction efficiency after several hours but usually reconstructed images can be obtained weeks later[87]. The room light completes the polymerization of the unexposed and partially exposed areas; however the index of refraction of the final polymer depends on the rate of polymerization so that the image information is not completely lost[88].

Monomers containing acrylates and acrylamide produce images that initially scatter light but turn transparent, after a few hours in room light forming phase images[89].

The speed of the photopolymer systems is 10^{-4} to 10^{-5} ASA and resolution is of the order of 1000-3000 lines/mm. Photopolymers offer the following advantages over other holographic recording materials[90] : (i) They are self processing, (ii) amplification can be obtained after recording by exposure to a light beam which can be the reconstruction beam, (iii) they have a high diffraction efficiency, (iv) they have a resolution of the order of 3000 lines/mm, (v) they can be coated on large surfaces and bygreat thickness, and (vi) they can be sensitized to most wavelengths of the visible spectrum.

The main drawback of this system is that the image is transparent and invisible and can only be viewed optically.

Efforts can be made to manufacture dry photo-polymer coatings of uniform thickness on glass plates or films similar to conventional photographic systems so that they could be used as such without performing the manual process of making photopolymer samples. The photopolymer systems can be made sensitive to other types of laser source by the addition of appropriate photosensitive dyes in the photocatalyst solution.

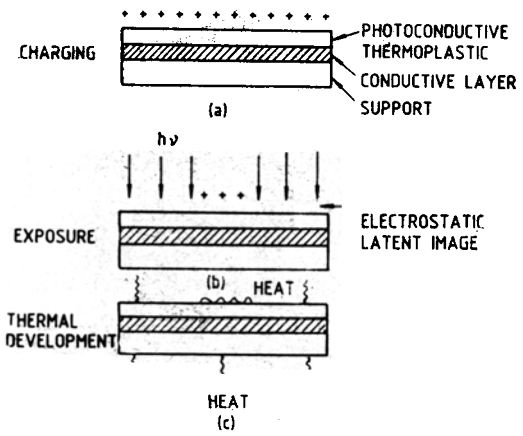


Figure 6. Thermoplastic recording process

point which causes deformation or grooves to be formed in the non-irradiated or unexposed areas, as shown in Fig. 6.

Images are invisible and can be viewed only optically by reflection or transmission methods. Images can be erased by heating to their melting point and the cycle can be repeated.

The primary advantages of thermoplastic recording systems[99] are :

(a) Relatively high diffraction efficiency typical of thin phase holographs.

(b) High resolution (up to 1000 lines/mm) and more important high useful bandwidth, the latter in excess of 1000 lines/mm on some devices.

(c) Suppression of intermodulation distortion as a result of this bandpass response, permitting full use of the high diffraction efficiency without excessive intermodulation effects on the reconstructed images.

(d) Moderate sensitivity : Even with relatively insensitive organic photoconductors, these are the only high resolution recording devices or materials which are quite comparable in sensitivity to silver halide emulsions.

(e) Rapid dry development, including ease of *in situ* development, useful in optical storage and in holographic interferometry.

(f) Reusability, with many thousands of cycles of reuse now attainable.

(g) Replicability by mechanical means (like other surface relief holographs).

(h) Insensitivity of device both prior to charging and after recharging, permitting handling, in ambient light before charging as well as after formation of the stabilized latent image.

The main drawbacks of the systems[99] are :

(a) High sensitivity of device performance to details of fabrication, charging and development, lack of 'development to completion'.

(b) Relatively complex apparatus needed for adequately controlled charging and development.

(c) Lack of unique specification of major response characteristics resulting from the complex interdependence of diffraction efficiency and frequency response, together with their sensitivity to a variety of device and process parameters.

(d) Relatively complex and precisely controlled fabrication techniques required for high quality devices.

(e) Sensitivity of the thermoplastic to abrasion and dust, the latter aggravated by electrostatic attraction of dust during device operation.

(f) Relative ease of accidental erasure by overheating.

(g) Tendency toward ghost image formation by charge trapping, requiring special precautions in cyclic processes.

The characteristics of thermoplastic recording systems are ideally suited to many forms of holographic interferometry and in future they should find increasing applications in that field[100].

8. Electrophotographic Systems

Dry processing instant electrophotographic systems have received much attention and gained great importance in the last two decades and are developing at a rapid rate[101]. They have almost completely superseded the silver halide system in a few areas such as document copying and there are indications that they are likely to become a serious competitor to silver halide systems in other areas.

Electrophotographic systems include xerography[102], photoelectrets[103], persistent conductivity systems[104], migration imaging systems[105], electrothermographic systems[106], electroluminescent systems[107], colour electrophotographic systems[108], etc.

The most important electrophotographic systems, i.e. xerographic processes are based on Chester F. Carlson's invention in conjunction with that of Otto Kornei in 1938, which consisted of a unique combination of photoconductive and electrostatic effects[109].

In these processes photoconductivity is used to convert a light image into an electrostatic image. This is achieved by first charging a photoconductive insulating layer uniformly and then discharging it imagewise by exposure[110]. The present theory of the mechanism of electrostatic image formation is as follows[111].

When a photon of sufficient energy is absorbed by the photoconductive layer, an electron is excited from the valency band to the conduction band, leaving a positive hole. The electrons neutralize the positive surface charge. The remaining positive charge moves by hole migration, driven by the electric field, through the photoconductive layer to the base plate.

The photoconductive materials generally used in xerography are : amorphous selenium in the xerox systems, zinc oxide-binder layers in Electrofax systems and organic photoconductors in the systems proposed by AG Kalle and the IBM corporation.

To initiate this process[102], the system must first be 'sensitized' by charging the photoconductive layer of the photoreceptor. The photoreceptor may be regarded as a sort of electron capacitor in which the photoconductor is the dielectric and the conductive support is one capacitor plate, the other plate normally present in the capacitor, is missing. As the free surface of the photoconductive layer is not laterally conducting, it is necessrry during charging to use special means such as corona discharge to spray ions on to all parts of the surface in order to build up a uniform charge.

In corona charging, fine wires are placed at a short fixed distance from the photoconductor and moved across the surface at a speed of about two inches per second. The corona wires are maintained at a potential above 7000 volts and the electric field on the wire surface ionizes the air molecules near the wire. In the applied field, the ions move to the photoconductor surface and charge it, usually to several hundred volts.

The sequence of steps in the basic xerographic systems (xerox) is as follows[112] (Fig. 7) : (A) Charge, (B) Exposure, (C) Development (deposition of toner particles), (D) Transfer, (E) Fixing, and (F) Cleaning. Whereas the sequence employed in Electrofax systems is as follows[113] (Fig. 8) : (A) Charge, (B) Exposure, (C) Development, (D) Fixing.

The first step after sensitizing the photoconductor is exposure, which can be carried out either by contact, optical projection or a reflex method. The latent image formed on exposure can be converted into a visible image by any of the following development

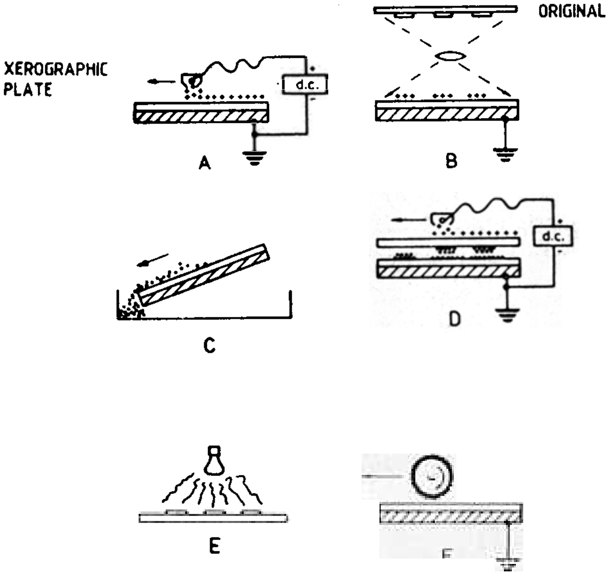


Figure 7. Image-forming steps in xerography

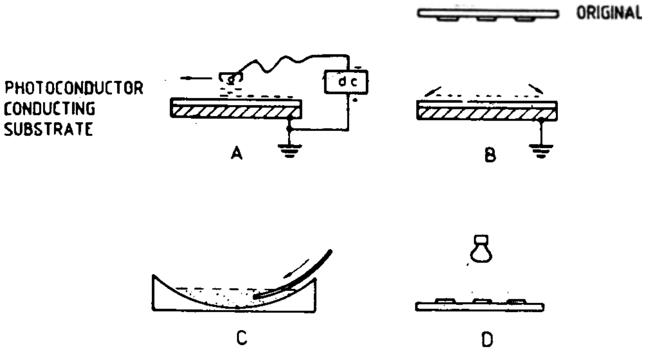


Figure 8. Image-forming steps in electrofax

methods : dry powder[110], liquid developmet[114], electrolytic development[115], and plastic deformation[116].

For most applications of xerography a permanent record is required. With zinc oxide receptors on paper, the photoreceptor itself becomes the permanent support. With re-usable photoreceptors (selenium, etc.), the toner image must be transferred to a permanent surface. Images are usually transferred by placing a sheet of paper over them and applying a high potential to the paper by another application of the corona discharge used to sensitize the receptor. Electrostatic attraction then moves the toner from the photoreceptor surface to the receiving surface (Fig. 7 D). When the paper is peeled away from the photoreceptor, it carries with it a large portion of the toner image.

After transfer to paper, the toner particles are held only by comparatively weak electrostatic forces and could, therefore, be easily removed. The usual technique for fixing the image is the application of heat or exposure to vapours of a volatile liquid if a dry toner is used, and evaporation for electrophoretic liquid developed images. Residual powder which remains after electrostatic transfer must be removed. This can be done by brushing or blowing.

Persistent internal polarization systems (photoelectrets)[117] involve the separation of positive and negative charges within a photoconductive insulator by the simultaneous application of an electric field and irradiation. The positive and negative charges (positive holes and electrons) migrate to the appropriate electrode but may be trapped at certain sites within the photoconductor for either a short or a long period of time, depending on the depth of the traps, to form an internal polarization field. The internal polarization field may be further stabilized by short-circuiting the electrodes which induces charges at the electrodes and neutralizes the internal polarization field, thus inhibiting the recombination of electrons and holes.

In the application of this phenomenon[19] to an imaging process, the electrode system consists of a photoconductor sandwiched between a transparent electrode and removable opaque electrode, which after imagewise exposure to form a latent electrostatic field pattern within the photoconductor, is removed for development of the image by one of the conventional xerographic development techniques. Persistent internal polarization has been observed in a number of photoreceptors such as anthracene dispersed in dielectric resins[118], sodium, potassium and silver chlorides[119], zinc sulphide-cadmium sulphide phosphor[120] and zinc oxide[117]. Two basic methods, polarization and depolarization techniques are employed based on the principle of photoelectrets[19].

A version of electrophotography which differs from xerography or photoelectrets, is persistent conductivity system[121] in which the latent image exists as a state of electrical conductivity in a photoconductive layer and persists as an after-effect of irradiation. The persistent conductivity has been explained as a phenomenon involving shallow traps[104]. Electrons excited during exposure are raised to the conduction band, but many of these electrons remain in shallow traps even after illumination has ceased. These shallow trap electrons can be made fully conductive by subjecting the materials to a strong electric field. The latent conductivity pattern can be used to create a visible image.

The procedure employed using the latent conductivity image to produce an electrostatic image is as follows : the photoconductive surface is directly exposed, i.e. without previous corona charging, to the optical image to form the latent conductivity image˙ An electrical surface charge is applied to the photoconductive surface, i.e. with a corona charging device. The latent conductivity areas will dissipate the surface charge in the previously exposed areas, whereas in the dark areas a surface charge will remain, forming an electrostatic image which is a reversal of the latent conductivity image. The electrostatic image can then be developed by one of the various techniques used in xerography. The photosensitive medium in the persistent conductivity system consists of a layer of photoconductive insulating material like phosphor powders, zinc-cadmium sulphide or zinc-cadmium selenide, coated on a conductive base[122].

The migration photo-imaging system invented by Goffe[105], called photoelectrosolography, produces visible images by positioning particles imagewise in the depth of a thermoplastic layer. In this softenable layer which is supported on a transparent base, the photosensitive selenium particles are embedded either as a layer one or more particles deep or dispersed throughout the layer.

The steps in the formation of an image with this system comprise : (a) sensitization, by corona charging positively or negatively to 80-200 V, (b) image exposure from the front or rear, (c) development by either heating at 80-120°C for 1-30 sec or exposing to solvent vapour at room temperature for 1-30 seconds. Development results in the formation of a 'migration image'. The image consists of particles which have migrated from their initial positions to take up positions imagewise in the depth in the softenable layer.

In electrothermographic system[106], the electrostatic print is obtained by imagewise dissipation of the charge by heat rather than by light. The original, having radiationabsorbent are as on a white background, is first brought into close contact with a dielectric surface to which an electrostatic charge has been applied. Then a short exposure of high intensity rich in infrared radiation is given through the original or the dielectric base. During exposure, the radiation absorbed is converted to heat; this raises the temperature of the corresponding areas in the dielectric, thus lowering its resistivity. The heated areas in the dielectric lose their orginal charge, and a charge pattern which closely resembles the original density results, and can be developed in the usual manner.

The main application of the phenomenon is in the copying of documents containing an IR absorbing ink. Other applications are electrostatic in the reproduction of scanned or television images and memories in analogue or digital computers. For quick erasure of the electrostatic signal, the choice of a suitable dielectric heating method just beyond the transition point of the material provides an efficient method.

Ranby and Ellerbeck[107] have described electroluminescent systems which could be used for recording X-ray radiation. Using these systems a direct X-ray image could be viewed without any processing stage and the image could be erased by switching off the applied voltage. The electroluminescent panels are re-usable and have a sensitivity approaching that of conventional X-ray film material. The panels in generdl comprise a thin layer of phosphor such as zinc sulphide sandwiched between a transfer electrode and a base electrode coated with a zinc oxide photoconductor.

Exposing the panel to radiation of the appropriate wavelength whilst simultaneously applying an alternating current between the electrodes causes imagewise electroluminescence. Images persist for an hour or more at room temperature but their lifetimes can be increased to over 24-hours by storage at low temperatures. Permanent records of the images can however be obtained by photographing them. Prior to re-using the panel the image can be erased thermally by heating to 80-150°C or by exposure to infrared radiation. With appropriate selection of the photoconductor such panels may be made sensitive to ultraviolet radiation.

Electrophotographic systems are potentially useful for producing colour prints, and can usually meet the requirements, for colour reproduction[123]. The photoreceptor in he two main systems, namely Xerography and Electrofax can be made sensitive to the appropriate regions of the visible spectrum and the correct colour can be produced by using suitable dyes and pigments.

In the electrostatic colour process invented by Tulagin[108], development toner particles are used which are themselves photoconductors. Toner particles which respond to radiation in the spectral region complementary to their own colour have been produced. These toner particles, in the basic three colours, are charged and spread on the surface of a suitable base and exposed to a colour transparency. The particles which have a colour corresponding to that of the exposing light remain charged while the other particles are discharged. The discharged particles can then be removed from the surface by a vacuum technique. This principle has been improved by using liquid developers, i.e. electrophoretic development.

In the colour xerography process[19] (Fig. 9), when an image is projected through one of the transparent electrodes (tin oxide on glass), the particles become photoconductive in the regions of the spectrum in which they absorb light. They then undergo a nett change in their charge polarity and migrate from the positive electrode to the negative electrode producing a colour image. A typical layout for a xerographic colour copier is shown in Fig. 10.

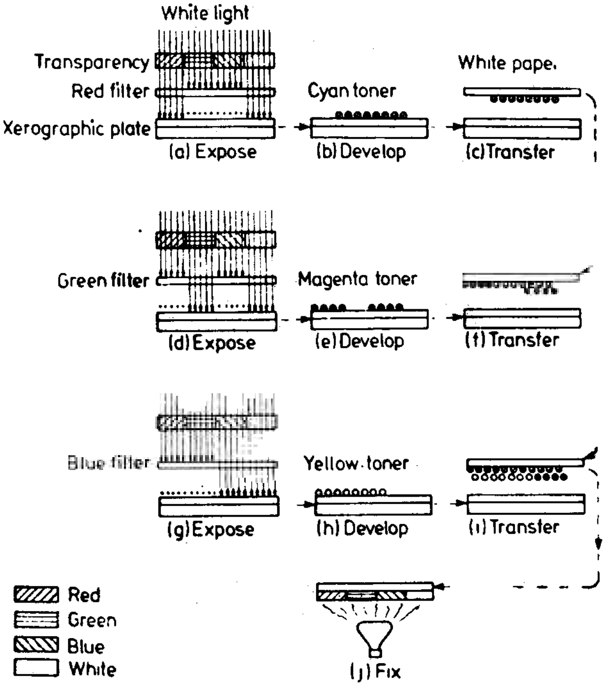


Figure 9. Steps in colour xerography,

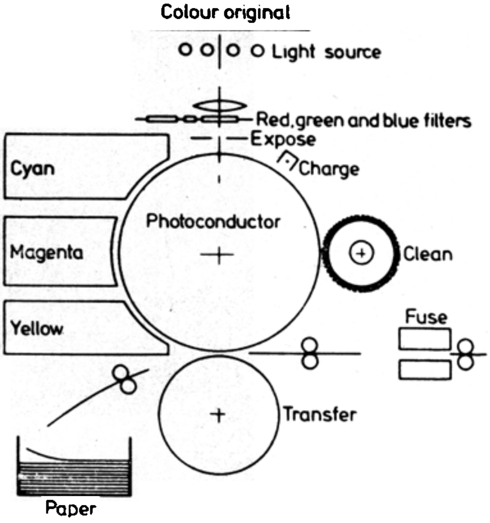


Figure A xerographic colour copier.

3 M Co has introduced a colour in colour process[123] which employs a photoconductive coating as an intermediate (e.g. zinc oxide). On the other side there are large areas of cyan, magenta and yellow dyes. Exposure of the original through a red, green or blue filter causes a conductive image to be formed, and this image is developed with a black toner. If the material is passed over an infrared lamp the dye directly behind the toner image migrates to a receptor sheet. The intermediate is then advanced to the next dye area and the second exposure given and the development and transfer are carried out as before. A third cycle then gives the final reproduction. Thus where red light is used the cyan dye is transferred, where green light is used, the magenta dye is transferred and where blue light is used, the yellow dye is transferred, thus forming a colour replica of the original analogous to that obtained by the subtractive method of colour photography.

The applications of existing electrophotographic systems are becoming almost as diverse as silver halide systems and include the following examples : document copying[124], hard copy from microfilm[19], producing microimages[125], lithographic printing[126], photoengraving[127], radiographic recording (electroradiography, xeroradiography)[9], printing from photographic negatives[128], computer output printing[129], rapid access display[130] and holographic recording[131].

9. Conclusion

Dry processing instant photographic systems viz., dry silver halide systems, diffusion transfer reversal materials, photothermographic systems, dry film peel-apart photoresists, photopolymers, thermoplastic recording systems and electrophotographic systems, play a very vital role for taking instantaneously permanent records of objects of optimum photographic quality in a wide range of important applications such as, information storage and retrieval, reprography, instant amateur and professional photography, holographic recording, lithographic and screen-stencil printing, printed circuit technology, radiographic recording, etc.

References

Doyle, L. B., 'Information Retrieval and Processing' (Melville Pub. Co,, Los Angeles, California), 1975.
2. SPSE, Symp. on Photography in Information Storage Retrieval, Washington, 1965.
3. Burden, J. W., 'Graphic Reproduction Photography' (Focal Press, London), 1980.
4. Haist, G., 'Modern Photographic Processing, Vol. 2' (Wiley Interscience, New York), 1979, p. 372.
5. Thompson, B. J. & De Velis, J. B., Proc. SPIE Seminar on Developments in Holography, Boston, Massachusetts, 1971.
6. Gamble, C. W., 'Modern Illustration Processes' (Sir Issac Pitman & Sons, Ltd., London), 1953, p. 216.
7. Mertle, J. S., & Monsen, G. L., 'Photomechanics and Printing' (Oxford & IBH Pub. Co., New Delhi), 1969, p. 357.

8. Denstman, H. & Schultz, M. J., 'Photographic Reproduction' (Mc Graw-Hill, New York), 1963, p. 85.

9. Dryden, V. W., SPSE 2nd Intern. Conf. on Electrophotography, Washington, 1974, p. 181.

10. Carroll, H. H. Higgins, G. C. & James, T. H., 'Introduction to Photographic Theory' (Wiley-Interscience, New York), 1980.

Clerc, L. P., 'Photography : Theory and Practice, 4th ed., 7 Vols.' (Focal Press, London), 1970-71.

12. James, T. H. & Higgins, G. C., 'Fundamentals of Photographic Theory, 2nd ed.' (Morgan & Morgan, New York), 1960.

Morgan, D. A., Proc. SPIE on Laser Printing, Vol. 169, Los Angeles, California, 1979, p. 105.

14. Rott, A. & Weyde, E., 'Photographic Silver Halide Diffusion Processes' (Focal Press, London), 1972.

15. Gold, R., SPSE Symp. on Unconventional Photographic Systems, Washington, 1964, p. 1.

16. De Forest, W. S., 'Photoresist : Materials and Processes' (Mc Graw-Hill, Inc., New York), 1975, p. 163.

17. Wopschall, R. H., 'Photopolymer Films for Recording Holograms' (Op. Soc. Am. Meeting, Tucson, Arizona), 1971.

18. Urbach, J.C., 'Thermoplastic Hologram Recording, in Holographic Recording Materials, Ed., Smith, H. M,, Vol. 20' (Springer-Verlag, New York), 1977, p. 161.

19. Schaffert, R. M., 'Electrophotography' (Focal Press, London), 1974.

20. Morgan, D. A., '3M's Dry Silver Technology' (Institute of Image Electronics Engineers of Japan Meeting, Tokyo), 1980.

21. Harriman, B. R., SPSE Symp., Unconventional Photographic Systems, Washington, 1967.

22. Barry, D. C., 'Dry Silver Technology' (Institute of Image Electronics Engineers of Japan Meeting, Tokyo), 1980.

23. Jacobson, K. I. & Jacobson, R. E., 'Imaging Systems' (Focal Press, London), 1976, p. 122.

24. Anwyl, R. D. & Walker, P., 'Radiation Sensitive Systems, in SPSE Hand Book of Photographic Science & Engineering, Ed., Thomas, W., Jr. (Wiley-Interscience, New York), 1973, p. 371.

25. Rott, A., *Sci. ed Ind. Photo.*, **13** (1942), 151.

26. Weyde, E., *Foto-Kino-Technik*, **2** (1948), 229.

27. Land, E. H., *J. Opt. Soc. Am.*, **37** (1947), 61.

28. Land, E. H., *PSA J.*, **13** (1947), 370; *Photo. J.*, **90** (1950), 7.

29. Varden, L. E., *PSA J.*, **13** (1947), 551.

30. Weyde, E., *Phot. Korr.*, **88** (1952), 203.

31. Crawley, G., *Brit. J. Phot.*, **110** (1963), 76.

32. Land, E. H., 'Photographic Silver Halide Transfer Product and Process', U. S., Pat. 2, 698, 236 and 2, 698, 237 (1954).

Land, E. H., & Morse M. M., 'Photographic Silver Halide Transfer Process', U. S., Pat. 2, 774, 667 (1956).

34. Land, E. H., 'Photographic Product and Process for Making a Positive Transfer Image', U. S. Pat. 2, 698, 245 (1954).

35. Weyde, E. 'Verfahren zur Herstellung direkter Positive nach dem Silbersalzdiffusionsverfahren', Ger. Pat. 1, 055, 953 (1959).

36. Weyde, E., 'Production of Transfer Images by the Silver Salt Diffusion Process', U. S. Pat. 3, 067, 033 (1962).

37. Rott, A., 'Photomechanical Printing, Process and Printing Material for Carrying out the Same', U. S. Pat. 2, 352, 014 (1944).

38. Weyde, E., 'Photographic Process for the Direct Production of Positive Images', U. S. Pat. 2, 699, 393 (1955).
39. Land, E. H., 'Photographic Processes for Producing Prints by Transfer', U. S. Pat. 2, 702, 244 (1955).
40. Land, E. H., 'One Step Photographic Transfer Process' U. S. Pat. 2, 647, 056 (1953).
41. Rott, A., 'Improvements in or relating to Photographic Processes', Brit. Pat. 614, 155 (1948).
42. Agfa, 'Improvements in or relating to the Production of Direct Positive Photographic Images by the Silver Salt Diffusion Process', Brit. Pat. 767, 978 (1957).
43. Varden, L. E., in 'Photography, Its Materials and Processes, 6th ed., Ed., Neblette, C.B.', (Van Nostrand, New York), 1962, Chap. 28.
44. Land, E. H., 'Photographic Processes for Producing Prints by Transfer and Products Useful in connection Therewith', U.S. Pat. 2, 740, 715 (1956).
45. Duffin, G. F., 'Photographic Emulsion Chemistry' (Focal Press, London), 1966, p. 219.
46. Land, E. H., Farney, L. C. & Morse, M. M., *Photogr. Sci. Engng.*, **15** (1971), 4.
47. Land, E. H., 'Photographic Diffusion Transfer Reversal Processes', U. S. Pat. 2, 704, 721 (1955).
48. Weyde, E. & Konig, A.V., 'Photographic Material', *Brit. Pat.* 1, 111, 492 (1968).
49. Herd. H. H. & Sun, T. I., 'Method of Making an Electrically Conductive Silver Image', *Brit. Pat.* 1, 234, 847 (1971),
50. Boller, B.K., Smith, E.A. & Sorem, A.L., 'Photographic Web Processing', U.S. Pat. 3, 573, 048 (1971).
51. König, A.V., Mader, H. & Weyde, E., 'Light-sensitive Material with Incorporated Developer', U.S. Pat. 3, 415, 651 (1968).
52. Land, E.H., 'Photographic Products, Processes and Compositions', U.S. Pat. 3, 647, 437 (1972).
53. Kodak, *PSA J.*, **42** (1976), 9.
54. Land, E.H., *Photogr. Sci. Engng.*, **16** (1972), 247.
55. Land, E.H., *Brit. J. Photogr.*, **119** (1972), 495.
56. Land, E.H., *Photogr., J.*, **114** (1974), 338.
57. Hanson, W.T., Jr., *Photogr. Sci. Engng.*, **20** (1976), 155.
58. *Polaroid News*, **2** (1983), 1.
59. Helwich, O., IInd International Congress for Reprography, Cologne, 1967.
60. Vrancken, M.N., *Photogr. Sci. Engng.*, **14** (1970), 347.
61. Sullivan, P.T., SPSE Symp., Unconventional Photographic Systems, Washington, 1964, p. 57.
62. Gilman, P.B., Jr., Vaughan, P.A. & Van der Meulen, P.A., *Photogr. Sci. Engng.*. **3**, (1959). 215.
63. Van der Meulen, P.A. & Countrymen, R.C., *Photogr. Engng.*, **4** (1953), 104.
64. Van der Meulen, P. A. & Brill, R.H., *Photogr. Sci. Engng.*, **2** (1958), 121.
65. Spencer, H.E. & Hill, J.E., *Photogr. Sci. Engng.*, **16** (1972), 234.
66. Jacobson, K.I. & Jacobson, R.E., 'Imaging Systems' (Focal Press, London), 1976, p. 139.
67. Oster, G., *Photogr. Engng.*, **4** (1953), 173.
68. Brinckman, E.M., SPSE Symp., Unconventional Photographic Systems, Washington, 1964, p. 13.
69. Takahashi, Y., Hasegawa, E. & Nagae, T., Proc. Photo and Electro-imaging, Tokyo, 1977, p. 26.
70. Herzog, J.F., Proc. EIPC Conf. Printed Circuit Manufacturing, 1970, p. 108.
71. Heiart, R.B., U.S. Pat. 3, 060, 026 (1962).
72. Du Pont., Brit. Pat. 905, 700 (1962).
73. Brug. M., U.S. Pat. 3,060,023 and 3,060, 025 (1962).

74. Schoenthaler, A.C., U.S. Pat. 3, 469, 982 (1969).
75. Woodruff, R.W., Jeffers. W. & Shedeker, R.A., *Photogr. Sci. Engng.*, **11** (1967), 93.
76. Woodward, D.W., Chambers, V.C. & Cohen, A.B., *Photogr. Sci. Engng.*, **7** (1963), 360.
77. Mizuki, E., Proc. 13th International Congress, High Speed Photogr. & Photonics, Tokyo, 1978, p 165.
78. Ikeda, T., 1st Technical Conf. Photopolymers, Tokyo, 1976, p.141.
79. Oster. G., *Nature*. **173** (1954), 300.
80. Chaberck, S., Shepp, A. & Allen, R.J., *J. Phys. Chem.* **69** (1965), 641.
81. Shepp, A., Chaberck, S. & Mac Nell, R., *J. Phys. Chem* , **66** (1962), 2563.
82. Margerum, J.D., Miller, J.J. & Rust, J.B., *Photogr. Sci. Engng.*, **12** (1968), 177.
83. Jenney, J.A., *J. Opt. Soc. Am.*, **60** (1970), 1155.
84. Rust, J.B., Miller, L.J. & Margerum, J.D., *Poly. Engng. Sci.*, **9** (1969) , 40.
85. Margerum, J.D. & Petrusis, C.T., *J. Am. Chem. Soc.*, **91** (1969), 2467.
86. Brault, R G., Jenney, J.A., Margerum, J.D., Miller, L.J. & Rust, J.B., Proc. SPSE Seminar on Applications of Photopolymers, 1970, p. 113.
87. Close, D.H., Jacobson, A. D., Margerum, J.D., Brault, R.G. & Mc Clung, F.J., *Appl. Phys. Letters*, **14** (1969), 159.
88. Kogelnik, H., Proc, Symp. Modern Optics, Brooklyn, New York, 1967, p. 605.
89. Urbach, J.C. & Meier, R.W., *Appl. Opt.*, **8** (1969), 2269.
90. Christy, J.P., Sagant, J. & Tribillon, J.L., SPIE, 1st European Conf. on Optics Applied to Metrology, 136 (1977), 355.
91. Kogelnik, H., 'Reconstructing Response and Efficiency of Holograms Gratings' (Polytechnic Press, Brooklyn), 1967, p. 606.
92. Bartfai, J.J. Ozarow. V. & Gaynor, J., *Photogr. Sci. Engng.*, **10** (1966), 60.
93. Holographic Recording Materials, Final Technical Report, Electro-optics Operation, Harris Electronic Systems Div., 1974.
94. Terrell, D.R., *Photogr. Sci. Engng.*, **21** (1977), 66.
95. Gaynor, J.G. & Aftergut, S., *Photogr. Sci. Engng.*, **7** (1963), 209.
96. Colburn, W.S., & Dubow, J.B., Photoplastic Recording Materials, Technical Report, Air Force Avionics Laboratory. Air Force Systems Command, 1973.
97. Gundlach, R.W. & Claus, C.J., *Photogr. Sci. Engng.*, **7** (1963), 14.
98. Gaynor, J., *IEEE Trans. Electron Devices, ED.*, **19** (1972), 512.
99. Urbach, J.C., Advances in Holograms Recording Materials in Developments in Holography, Proc. SPIE Seminar, **25** (1971), 31.
100. Bellamy, J.C., Ostrowsky, D.B., Poindron, M. & Spitz, E., *Appl. Opt.*, **10** (1971), 1458.
101. SPSE, 4th Intern. Conf. on Electrophotography, Washington, 1981.
102. Dessauer, J.H. & Clark, H.E., 'Xerography and Related Processes' (Focal Press, London), 1965.
103. Fridkin, V.M. & Zheludev, J.S., 'Photoelectrets and the Electrophotographic Process' (Van Nostrand, Princeton), 1966.
104. Dessauer, J.H., Photographic Sci. Symp., Zurich, 1961.
105. Goffe, W.L., *Photogr. Sci. Engng.*, **15** (1971), 304.
106. Cassiers, P.M., *Photogr. Sci. Engng.*, **4** (1960), 199.
107. Ranby, P.W. & Ellerbeck, R.P., *J. Photogr. Sci.*, **19** (1971), 77.
108. Tulagin, V., *J. Opt. Soc. Am.*, **59** (1969), 328.
109. Carlson, C.F., 'Electrophotography', U.S. Pat. 2, 297 .691 (1942).
110. Dessauer, J.H., Mott, G.R. & Bogdonoff, H., *Photogr. Engng.*, **6** (1955), 250.
111. Fridkin, V.M., 'The Physics of the Electrophotographic Process' (Focal Press, London), 1972.
112. Claus, C.J., *Image Technol.*, **11** (1969), 11.
113. Greig, H.G., U.S. Pat 3,052, 539 (1962).