SSDT — A New Plate for Direct (Filmless) Exposures

S.B. Doyle
P.J. Watkiss

SSDT, or Single Sheet Diffusion Transfer, is a new litho plate developed at Howson-Algraphy for exposure by projection, either through film or from copy, or by a laser. It uses the well known technology of diffusion transfer platemaking, but in a new way. Both receptor and donor layers, normally separate sheets of aluminum and photosensitive paper in conventional DTR applications, are combined into a presensitized configuration. Unlike other single sheet DTR products, which are paper or plastic based, we have used our expertise in graining and anodising to produce a lithographic aluminum substrate. By doing this we have achieved the convenience of a single sheet product and the excellent press characteristics of electrochemically grained and anodised aluminum.

Although filmless plates have been available for some years using electrostatic technology, the advantages offered by the SSDT system are simplicity of processing, low cost of equipment, and the ability to make multiple exposures.

The product described in the paper has been designed for camera exposure or for exposure by an Argon-ion laser outputting at 488 nm and has an energy requirement of approximately 10 microJcm^{-2}. It is capable of giving a resolution of up to 10 micron lines and giving press runs in excess of 50,000 impressions. We are currently involved with a number of field trials in both commercial and newspaper accounts.

* Howson-Algraphy

1 Background

Direct-to-plate systems, which do not require a film intermediate in the conventional sense, have been available for many years in the form of diffusion transfer plates and electrostatic plates. These can be considered as true filmless plates since, because they are positive-working, they enable the user to image paste-up copy directly onto the plate using a camera fitted with a reversal facility. Exposure requirements for such plates are generally of the order of 1-20 microJcm^{-2} and have peak spectral sensitivities in the blue-green to green region of the light spectrum. Conventional light-sensitive diazo materials, used as the coating for the majority of today's printing plates, typically have energy requirements of 200,000 to 400,000 microJcm^{-2}.

More sensitive organic systems are based on light induced radical polymerisations of monomers (Potts, 1987). Such systems have energy requirements of the order of 10,000 microJcm^{-2}, though in theory sensitivity 30 times this can be achieved (Shimizu, 1986). Photo-polymerisable plates are being developed by plate manufacturers generally with the objective of using them for step-and-repeat projection exposures on equipment such as the Opti-Copy Imposer. Monomer plates are negative-working which means that direct camera exposure from paste-up copy is not possible. However, laser exposure becomes a possibility since the exposure can be positive or negative. Also, because the radical formation in these photosensitive compositions can be spectrally sensitised to visible light, exposure to visible light lasers becomes a possibility (Shimizu, 1986), though the relatively high energy requirement for exposure currently limits their use to high powered and expensive water-cooled argon-ion lasers (Table 1).

TABLE 1. Uses of Lasers in Graphic Arts

Laser	Power	λ(nm)	Cost ($)	Application
CO_2	500 W	10,600	75,000	Gravure
Nd-YAG	18 W	1,060	40,000	Laser Mask
Ar^{++} (Water cooled)	2 W (10 W)	361 (488)	40,000	Monomer Plates
Ar^{+} (Air cooled)	10 mW	488	7,000	Silver halide Electrostatic
HeNe	10 mW	633	500	Silver halide Electrostatic
Ir diode	10 mW	780	100	Silver halide Electrostatic

Truly camera-direct systems, for the present at least, must rely on the traditional, highly light-sensitive technologies of electrophotographic and silver halide materials.

In lithographic printing processes silver halide has found use commercially only in diffusion transfer products (also referred to as DTR or chemical transfer plates). This is perhaps surprising in view of the wealth of knowledge accumulated on silver halide imaging over the past century and the undoubted versatility of these materials. Several applications appear in the patent literature on the use of silver halide materials in printing plate processes other than diffusion transfer systems and these are summarised in Table 2.

TABLE 2. Some Applications of Silver Halide to Printing Plates

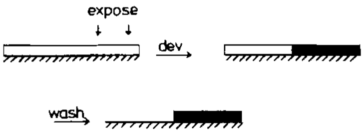
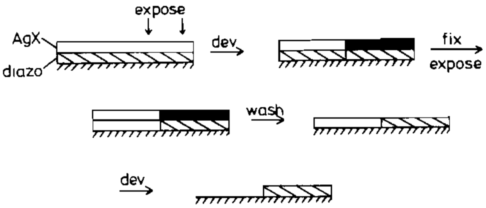
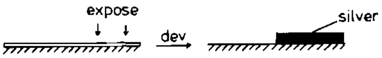
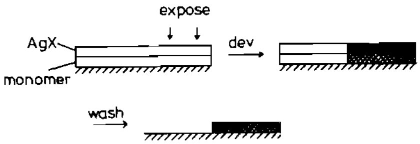
Process	Description	Reference
1 Tanning	Oxidised Developer cross-links gelatin or binder	e.g. Plambeck (1980)
	 	
2 Overcoated Diazo	A coating of silver halide emulsion acts as a mask for the diazo layer	e.g. Shiba (1980)
	 	

Table 2 cont.

Process	Description	Reference
3 Physical Development	Latent image on silver halide grains acts as catalyst for physical development in developer containing silver nitrate 	Gracia (1975)
4 Radical Polymerisation	Vinyl monomer polymerised by radical intermediate produced by silver halide reduction 	Maeda (1985)

The impetus to use silver halide as the foundation of a printing plate lies in the advantages silver halide has to offer. Silver halide is a pre-sensitised material, that is to say it can be exposed to light without prior treatment. Additionally, because the latent image formed in silver halide grains is stable for many months, multiple exposures can be made and delays between exposure and processing are not a problem. Electrophotographic plates do not possess these benefits and have to rely more heavily on equipment, the consequence of which is greater capital investment. Figure 1 shows schematically the processing differences between an electrophotographic plate and what is possible with a pre-sensitised silver plate.

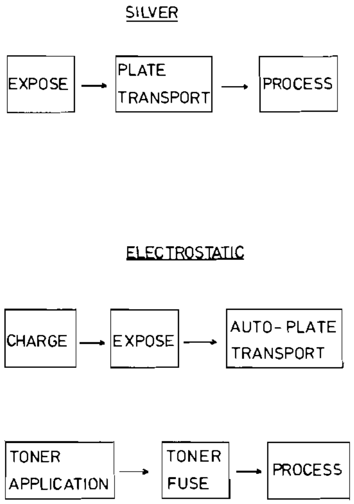


FIGURE 1. Comparison of Electrostatic and Silver Plate Processing

Provided the systems illustrated in Table 2 fulfil the basic criteria of high speed (50 microJcm^{-2} or less) and high sensitometric contrast (i.e. similar in response to lith or rapid access films) then they are potential candidates for direct-to-plate. We are actively investigating applications of silver halide emulsions since we believe they offer a new concept in plate-making.

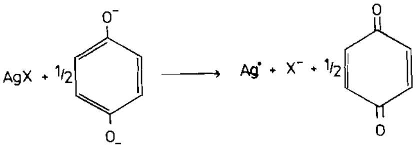
2 The Diffusion Transfer Process

Despite the fact that diffusion transfer products have been used for many years (Schultze, 1979) we believe that this technology is still capable of being used in new ways.

Diffusion transfer mechanisms are well documented by Rott and Weyde (1972) and only a brief resume is required here. A silver halide crystal on exposure to light forms a latent image, usually on the surface of the crystal, which comprises a cluster of 4 to about 10 photolytically reduced silver atoms. This acts as an electrode for the reduction of the entire crystal by the action of an organic reducing agent, usually hydroquinone. Reduced silver formed this way by chemical development plays no further part in the diffusion transfer process. In conventional B&W processing, unexposed silver halide is dissolved by the fixer bath. In DTR processing the hypo of the fix bath is included in the developer. Unexposed crystals are converted to silver thiosulphate complexes which are able to diffuse in the emulsion layer. If these come into contact with a catalyst or nucleation site the reducing environment of the developer converts the silver thiosulphate complex to silver. Silver formed by physical development in this way is more densely packed than chemically developed silver and in this form is oleophilic and capable of accepting ink. Table 3 summarises the chemical processes occurring in a DTR system.

TABLE 3. Chemistry of the DTR Process

1 Chemical Development of Exposed Grains

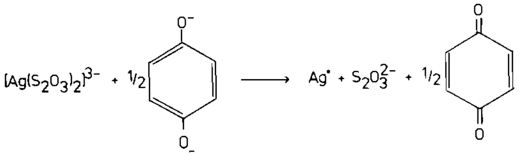


2 Fixation of Unexposed Grains

$$AgX + 2S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-} + X^-$$

TABLE 3. Cont.

3 Physical Development of Silver Complex



Printing plates made by the DTR process can be classed as either single sheet or two sheet plates. In single sheet assemblies currently on the market the nucleation layer is in a surface hydrophilic layer (or lithographic layer) with the emulsion layer beneath it. The substrate for all these products is either polyester reinforced paper or plastic (polyethylene terephthallate). Dissolved silver complex in the unexposed areas diffuses to the nucleation layer where it precipitates as physically developed silver, Figure 2.

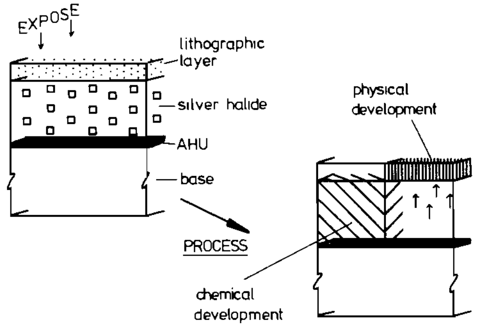


FIGURE 2. Single Sheet Paper and Plastic Plates

In two sheet systems the nucleation layer is formed on a grained and anodised aluminium plate and the emulsion layer is coated onto a separate sheet of paper. After exposure the paper and aluminium sheets are brought together in a processor, trapping a layer of developer which allows the thiosulphate complex to diffuse to the nucleation layer where it is precipitated as lithographic silver, Figure 3.

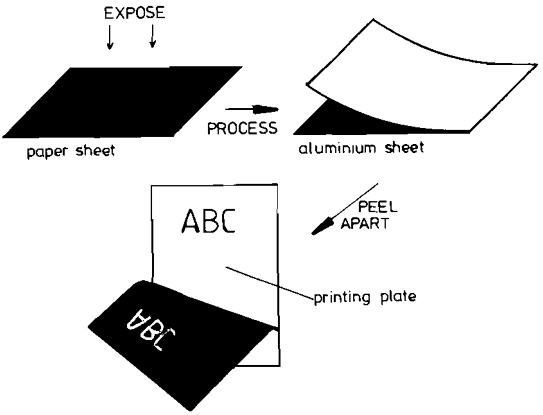


FIGURE 3. Two Sheet Aluminium Plates

3 Description of the SSDT Plate

Both categories of printing plate described above, although widely used, have inherent disadvantages. Plastic and paper plates can give rise to press handling difficulties, particularly if the press is not dedicated to these plates, and although the plastic plates are quite tough, run length is generally less than aluminium plates. The two sheet aluminium plates are easier to run on a press but because the two sheets have to be accurately registered and manually peeled-apart the process is a little inconvenient.

We have designed a system in which an aluminium, lithographic substrate is coated firstly with a nucleation layer and then with a silver halide emulsion layer plus any other coatings such as non-stress or development agent containing layer, Figure 4.

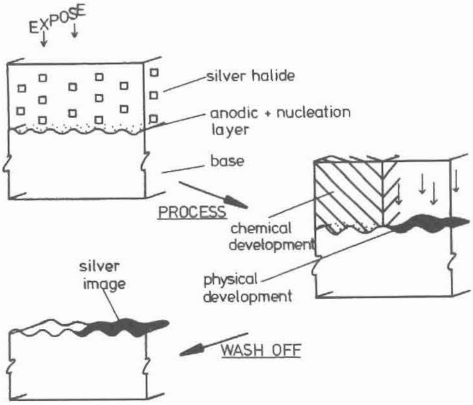


FIGURE 4. Structure and Processing of the SSDT Plate

On development, or activation, the silver thiosulphate formed in the unexposed areas can diffuse downwards to the nucleation layer to form lithographic silver which is strongly adhered to the anodic layer. After washing to remove the chemically developed background a positive image of silver is left on the plate, Figures 4 and 5.

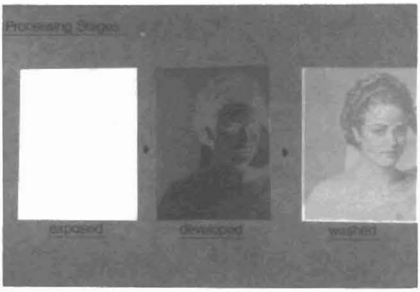


FIGURE 5. A Plate at Various Stages of Processing

Thus, with the SSDT plate we have the convenience of a pre-sensitised configuration and the lithographic quality of anodised aluminium substrate. Although such an assembly was anticipated in the patent literature (Yackel, 1972), the novelty of the plate lies in the way the nucleation and emulsion layers are configured and the special considerations required to make the plate a viable, commercial product.

4 Technical Discussion

Having described the plate in general terms some of the characteristics and behaviour of this type of assembly will be discussed in this section.

4.1 Anodic Layer

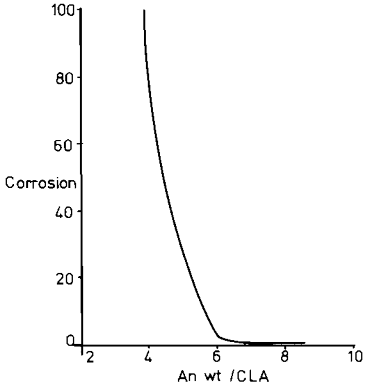
Of great importance with an assembly in which a silver halide emulsion is coated onto an aluminium surface is the nature of the anodising and barrier layer. A highly sensitive inorganic material such as silver halide in close contact with a reactive metal like aluminium can lead to undesirable interactions. Likewise, having formed a metallic silver image on the substrate corrosion becomes a problem. Thus, the halide composition of the emulsion and the nature of the anodising are of prime importance. A high chloride content in the emulsion grains can lead to corrosion of the aluminium on storage as shown in Table 4.

TABLE 4. Substrate Corrosion due to High Chloride in the Emulsion

	Corrosion	
%Cl in Emulsion	**An.Wt. 2.5 gmm^{-2}**	**An.Wt. 4.5 gmm^{-2}**
100	> 100	> 100
90	60	50
80	60	40
60	30	10
40	5	0
30	0	0

The results were obtained by storing plates at 30°C and 95% RH for 14 days and counting the number of corrosion specks covering an area of 150 cm^2.

Metallic silver adhered to the anodic layer of the substrate can result in a corrosive metallic couple if there is electrical contact with the aluminium substrate or possibly with metallic impurities in the anodising. Corrosion can be demonstrated by the observation of pin-holes in the image areas surrounded by a region of weakly adhered silver. The extent of corrosion is dependent on the roughness of the grain and the anodic weight (Watkiss 1987). Plotting the ratio of anodic weight to roughness against the number of corrosion spots in Figure 6 shows a rapid onset of corrosion below a numerical ratio of about 6.



+Roughness corresponds to the CLA, in microns, measured with a Taylor-Hobson Talysurf 10.

The anodic weight, in gmm^{-2}, is measured by weight difference after chemically stripping the anodic layer.

FIGURE 6. Dependence of Corrosion on Grain and Anodising Conditions

From these results it is clear that conditions exist which favour a stable arrangement of substrate and silver halide emulsion, despite the proximity of two reactive materials. It is because of the conditions of substrate preparation that a product having good shelf-life and stable printing image can be made.

4.2 Nucleation Layer

A nucleation site is required for the physical development step to take place. Typically used as nuclei are sols of metals such as silver or gold (Vincent, 1963) , or metal sulphides such as silver or nickel sulphide (DeJaeger et al, 1983) or palladium sulphide (Mitsubishi Paper Mills, 1973).

The sol plays an important role in the overall process, contributing to the sensitometric properties of the transfer image and to the mass of silver deposited. The rate of silver deposition is determined by the size of the nucleating particles and their number (Rott and Weyde, 1972 pp 196-197), though if the reaction were to proceed to completion the final mass of silver is independent of the nuclei size or number. In a real system a slow deposition rate is likely to lead to losses of silver thiosulphate complex by lateral diffusion, diffusion into the developer or by precipitation of silver in the emulsion layer.

DTR systems have the high contrast required for camera-direct plates partly through emulsion design and partly because of the competition, in mid-wedge areas, between chemically developed silver and the nucleation layer for the physical development of the silver complex. Thus, with the SSDT plate, the total scale (Altman 1977) of the emulsion is 0.9 logE while that of the positive image on the plate is 0.45 logE.

For a given development time and temperature the amount of silver deposited, expressed as a percentage of image silver to silver coating weight, rapidly reaches a steady value as the concentration of the nucleating particles on the anodic layer is increased, Figure 7.

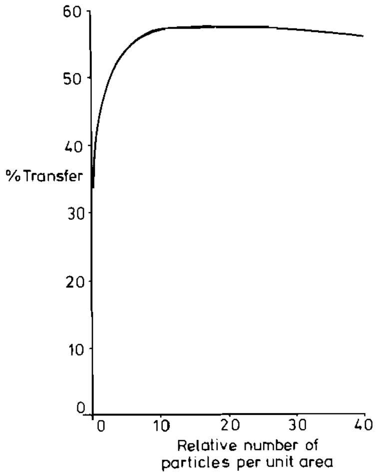


FIGURE 7. Image Transfer vs Number of Nuclei.

4.3 Emulsion Coating

Of importance in obtaining a plate which will run well on the press and which will give run lengths in excess of 50,000 impressions are the amount and morphology of the silver deposited on the anodic substrate. Not only does the sol coating play a part in this as discussed above, but also of importance are the condition and use of the developer and the coating weight of the silver halide emulsion. Diffusional processes which result in the formation of the image are also responsible for loss of material into the developer and laterally into adjacent, chemically developing areas. As the coating weight (or thickness) increases so the efficiency of image transfer decreases as shown in Figure 8.

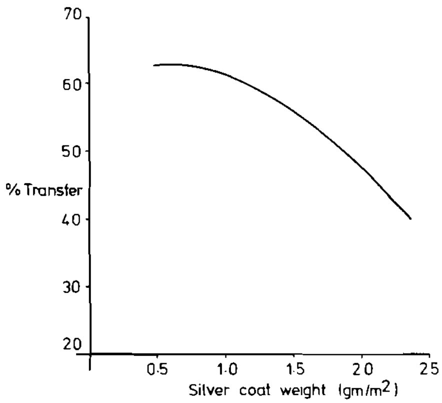


FIGURE 8. **Efficiency of Image Transfer vs. Coat Weight.**

In solid areas lateral diffusion is not as important, but in halftone areas losses by this process can be quite large. Boyack (1983, 1987) has calculated the effects of lateral diffusion on image reproduction in the Polaroid Polachrome system on varying layer thickness, incremental swelling and effects of non-isotropic diffusion. He has shown that, as expected, lateral diffusion becomes more important as the thickness of the diffusion layer increases and as the swelling of the layer becomes greater. Lateral diffusion in DTR assemblies leads to loss of image resolution and consequently a lower MTF response than in conventional photographic films.

Figure 9 shows how the mass of silver transferred in the image areas decreases as the image becomes finer. The results were obtained by contact exposing the plate with line screens of rulings up to 50 line pairs mm^{-1}.

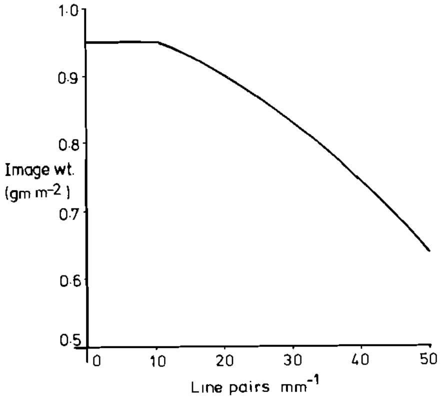


FIGURE 9. Loss of Silver Image in Fine Lines

4.4 Nature of the Lithographic Silver

The form which the physically developed silver takes determines the strength of the image. Because the density of silver is 10 $gmcm^{-3}$ and typical image weights are about 0.8 to 1.0 gmm^{-2} the thickness of the silver in the image areas is only about 0.1 micron or so; a truly lithographic process. An electron micrograph of a dot in Figure 10a shows that the grain structure is clearly visible in the image areas. Figure 10b is a close-up inside the image and shows the silver to be in the form of discrete 'clumps' of silver. These appear to be well adhered to the substrate in contrast to the electron micrograph in Figure 10c which shows deposits of silver in the form of needles not attached to the substrate. This latter picture was of an image formed with exhausted developer, which, although the image transfer is good, the plate performs less well on the press because of the different image morphology.

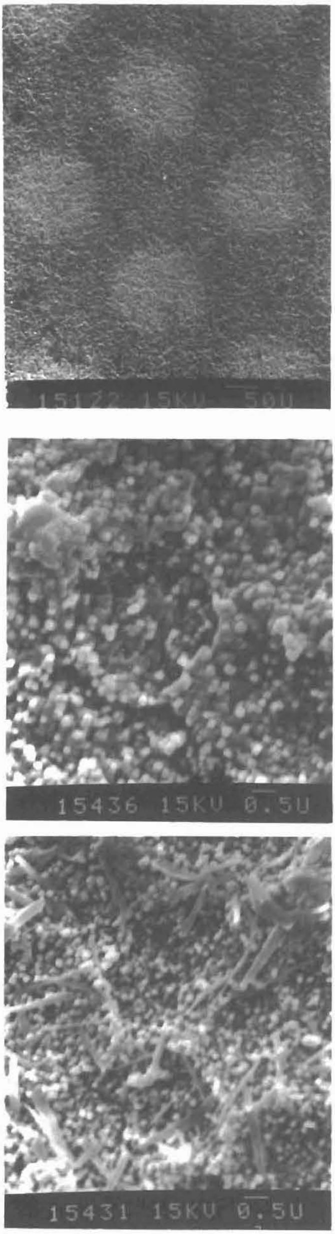


FIGURE 10. **Electron Micrographs a) Half-tone dots; b) Image silver; c) silver deposited with exhausted developer**

4.5 Finisher

Having formed the lithographic silver image by development and removal of the background by washing, the silver must be treated to render it oleophilic. Commonly used reagents include cationic surfactants and mercapto compounds. In the case of mercaptans a complex with silver is believed to form which has the effect of increasing the surface oleophilicity of the silver and also protecting the silver image against atmospheric tarnishing (Li).

5 Properties of the SSDT Plate

Table 5 summarises the properties of our current plate.

TABLE 5. Properties of SSDT Plate

Property	Value
1 Spectral sensitivity	490 nm peak
2 Safelight	Amber
3 Sensitivity	
a) 488 nm Ar+ Laser	7 microJcm^{-2}
b) Pulsed Xenon	60 lux. sec
c) Tungsten halogen	120 lux. sec
4 Resolution	
a) Contact	62 line pairs mm^{-1}
b) Laser	25 line pairs mm^{-1}
c) Camera	14 line pairs mm^{-1}
d) Projection	25 line pairs mm^{-1}
5 Press run length	
a) Cold-set ink	60% Aq. Neg.
b) Heat-set ink	70% Aq. Neg.
c) UV ink	120% Aq. Neg.
6 Shelf-life	1 year

Blue spectral sensitivity was chosen for the convenience of amber safelights and for argon-ion laser exposures. It is also very well suited to pulsed-xenon lamps and can be used with high colour temperature tungsten lamps. Resolution is determined by the optics of the exposing device and by the spread of the image due to diffusional processes. The inherent resolution limit can be determined by contact exposure to a Brunner target as 10 micron lines. This would suggest reproduction of 5-95% 60 lpcm halftones could easily be achieved if the optics of the exposing device were of very high resolvability. Run length is, as might be expected, limited to short to medium runs as the comparison with Howson-Algraphy's aqueous negative plate shows. Solvent resistance is, of course, very good but under cold-set inks and with high damp levels image wear is accelerated and the print endurance falls short of a standard negative plate.

6 Systems

Despite run length limitations indicated in Table 5 under cold-set inks we have been running a test installation on an offset web press using these conditions and regularly achieving run lengths in excess of 50,000 impressions, giving us great confidence in our product under adverse conditions.

The system in use at this installation is a camera with reversal facility and a stand-alone processor for manual operation as shown in Figure 11.

7 Conclusions

We have shown in this paper that a high speed presensitised plate, using the well known technology of diffusion transfer, can be made as a single sheet configuration using lithographic quality electrochemically grained and anodised aluminium substrate, the first of its kind.

Factors that are of importance are:

i) The grain and anodising conditions which ensure a stable product.

ii) A nucleation layer of sufficient number density to provide rapid deposition of physically developed silver.

iii) An emulsion coat weight to give good silver transfer weights with minimum losses in highlight areas.

The advantages of such a plate are speed of processing and simplicity of handling and a versatility which is not found with electrostatic plates. Disadvantages include the need for safelight working, medium run lengths and careful control of developer ageing.

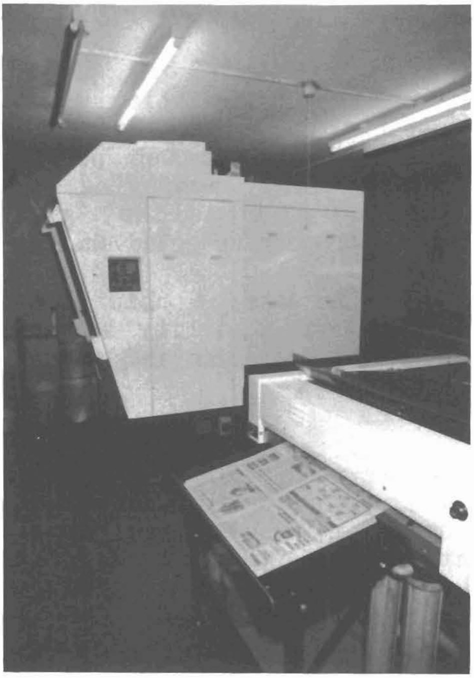


FIGURE 11. Camera and Processor in Use

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