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THE PHOTOCHEMISTRY OF ARYLDIAZONIUM SALTS: FUNDAMENTAL ASPECTS AND APPLICATIONS TO REPROGRAPHIC PROCESSES

The solution photochemistry of aryldiazonium salts is described in terms of two principal mechanisms, i.e. photohomolysis and photoheterolysis. The quantum yields of both pathways are discussed with reference to their dependence upon solvent, and the chemistry of the various reactive species produced during irradiation is outlined. The importance of these compounds in reprographic technology is summarised according to the types of process based on particular intermediates and products, and the discussion includes dye-line processes (both positive and negative), physical development systems for metal images, vesicular processes and lithographic processes (both positive and negative) including photopolymerisation techniques.

1 — INTRODUCTION

The susceptibility of aryldiazonium salts $ArN_2^+X^-$ to decompose on exposure to light of energy corresponding to the principal long-wavelength absorption band has long been known. The photolysis proceeds readily, in high quantum yield (always exceeding 0.1), whether the aryldiazonium is in fluid or rigid solution, or in the form of microcrystals: although nitrogen gas is always the sole nitrogen-based product, the other photolysis products depend on the medium employed. It is the ready photodestruction of the diazonium salt which forms the basis of its extensive usage in the so-called dye-line or diazotype process. In this, a master copy, usually in the form of an original line drawing or typescript on tracing or other reasonably translucent paper, is placed between the irradiation source (a fluorescent lamp) and the copying paper, which consists of a good quality paper which has been coated with a weak solution of a (normally yellow) diazonium salt and then dried. The light transmitted by the master copy bleaches out the diazonium salt, but that *not* transmitted through the opaque portions of the master leaves a corresponding yellow image on the copy. This residual positive image of diazonium salt is then developed to an intense blue, brown or black colour by coupling with a suitably reactive compound, such as a hydroxyaromatic or a compound bearing an active methylene group, at pH $\geqslant 7$ (depending on coupler reactivity) to give the coloured azo-compound, for example with phenol itself,

$$ArN_2^+X^- + C_6H_5OH \xrightarrow{OH^-} Ar-N= \\ =N-C_6H_4OH \quad (1)$$
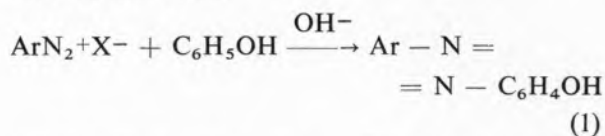
In this review we shall summarise both the principal pathways by which an aryldiazonium salt responds to irradiation and some of the recent developments in the applications of these useful compounds in reprographic technology.

2 — ENERGY LEVELS OF ARYLDIAZONIUM CATIONS

Benzenediazonium cation shows a major band at 259 nm (assigned to a $^1A_1 - {}^1A_1$ transition) and a minor band at 295 nm (assigned to a $^1A_1 - {}^1B_1$
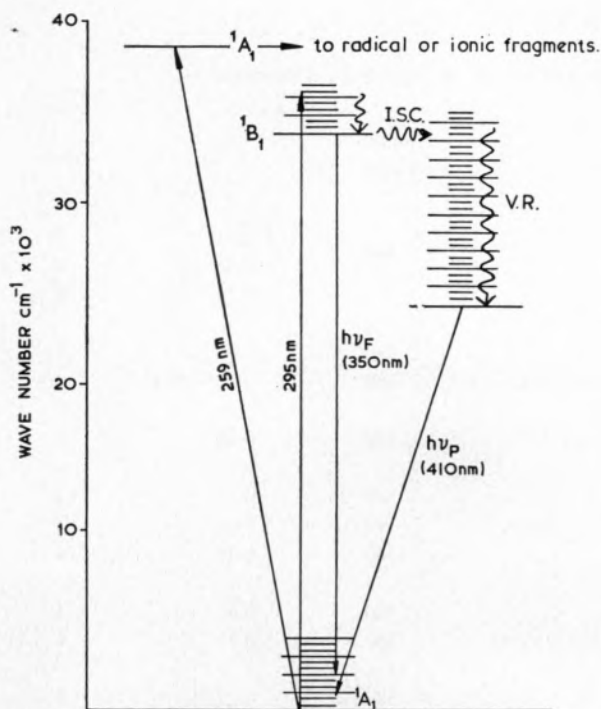
Fig. 1

Simplified Jablonski diagram for lower-energy states of the benzenediazonium cation based on data of Reference [1]

transition) [1]. Irradiation in the latter band in ethanolic solution produces both fluorescence (λ_{max} ca. 345 nm) and, at 77 K, phosphorescence (λ_{max} ca. 410 nm). However, irradiation in the more intense 259 nm band yields no emission but instead, at 77 K, the alcoholic matrix became strongly paramagnetic, yielding a broad singlet electron spin resonance (e.s.r.) spectrum near $g = 2$, sugges-

tive of a phenyl radical [1]. Clearly there is no conversion from the more highly excited state, $^1A_1$, to the lower energy fluorescent $^1B_1$ state (Fig. 1).

## 3 — PRIMARY PHOTOCHEMICAL ACT

The e.s.r. spectrum mentioned above provides clear evidence that, at least in frozen alcoholic solution, the main pathway for photodecomposition of diazonium cation is (2).

$$ArN_2{}^+X^- \xrightarrow[\varphi_2]{h\nu} Ar\cdot + N_2 + \cdot X \tag{2}$$
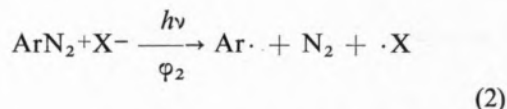
Whether or not (2) is significant at room temperature has long been debated, the principal rival mechanism being that of ion-formation (3).

$$ArN_2{}^+X^- \xrightarrow[\varphi_3]{h\nu} Ar^+ + N_2 + X^- \tag{3}$$
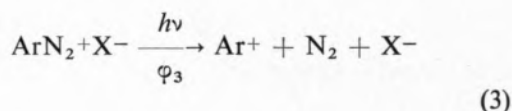
That (3) operates in aqueous and dilute aqueous acid media is suggested by the recovery of the corresponding phenol in high yield, implying the hydrolysis

$$Ar^+ + 2H_2O \longrightarrow ArOH + H_3O^+ \tag{4}$$
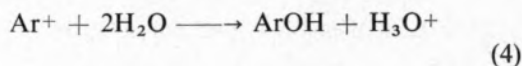
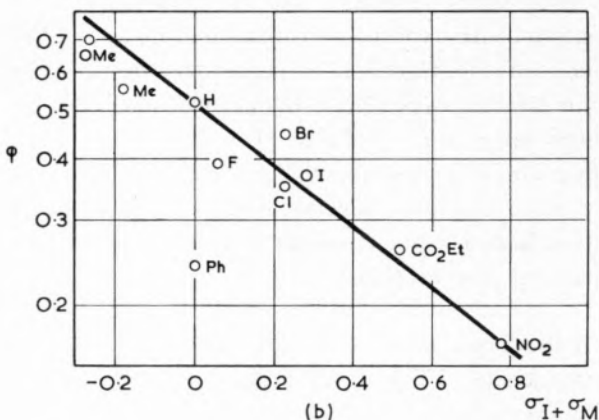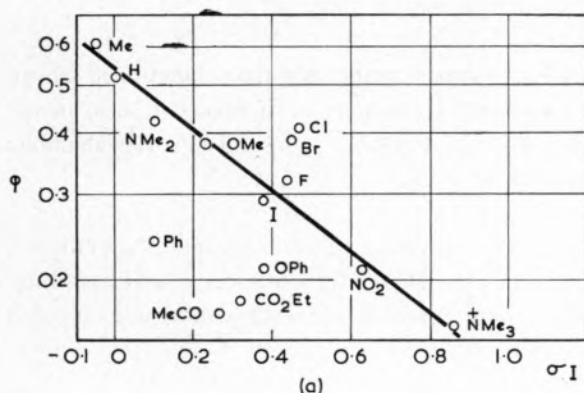(Working in neutral or slightly alkaline solution prompts the coupling reaction (1) with unreacted

Fig. 2

Hammett plots relating quantum yields for the photodecomposition of aryldiazonium salts in dilute aqueous acid with σ-parameters: (a) p-substituent; (b) m-substituents. Reproduced with permission from Reference [2]

Table 1

Photodecomposition quantum yields, φ_{dec}, for diazonium salts of technological importance

Benzenediazonium cation	Anion	Medium	Irradiation wavelength/nm	φ_{dec}	Ref.
4-diethylamino	$ZnCl_4^{2-}$	Aq. H_2SO_4	380	0.41	3
				0.48	4
		Polymer film	379	0.25	8
4-morpholino	$ZnCl_4^{2-}$	Aq. H_2SO_4	380	0.60	4
	$ZnCl_4^{2-}$	Acidified aerated ethanol	380	0.74 ± 0.03	4
4-morpholino	BF_4^{-}	Polymer film	380	0.30	4
2,5-diethoxy-4-morpholino	BF_4^{-}	Aq. H_2SO_4	380	0.33	4
		Acidified aerated ethanol	380	0.67	4
		Polymer film	380	0.38	4
2,5-diethoxy-4-morpholino	$ZnCl_4^{2-}$	Aq. H_2SO_4	380	0.34	4
		Acidified aerated ethanol	380	0.72	4
2,5-dimethoxy-4-morpholino	BF_4^{-}	Aq. H_2SO_4	380	0.27	4
		Acidified aerated ethanol	380	0.77	4
		Polymer film	365	0.43	7
			398	0.43	7
			425	0.41	7

The data for aqueous H_2SO_4 refer to argon-finished solutions, with $[H_2SO_4] = 0.05$ м.

ArN_2^+ ions). The quantum yield of (3), denoted φ_3, has been measured both for a series of simple *m-* and *p-* substitued benzenediazonium salts [2] and for some of the more highly substituted salts [3, 4], used in the dye-line process, all determined in dilute aqueous acid. The results for the former series provide a fair correlation with the nature of the substituent as measured by a modified form of the Hammett σ parameter (fig. 2). The commercially-used diazonium ions also display high values for φ_3 (Table 1).

In ethanol (or other alcoholic solvents) the situation is more complex. Several lines of evidence point to at least a major preponderance of the homolytic pathway (2), as follows:

(i) Products. In ethanol, the principal photolysis products at 273 K from p-nitrobenzenediazonium ion (as its $SnCl_4$ complex) are nitrobenzene (76.6 %) and acetaldehyde (74.1 %) [5]. These originate in steps (5) and (7) shown below. Also found are products indicative of radical coupling, e.g.

$p-O_2NC_6H_4CHOHCH_3$ and $(CH_3CHOH)_2$, and, interestingly, some $p-O_2NC_6H_4OC_2H_5$, implying neutralisation of an aryl cation. (See reaction (8) below). Addition of I_2 results in the production of 65 % of $p-O_2NC_6H_4I$, implying efficient capture of the $p-O_2NC_6H_4$ radical, but does not reduce formation of $p-O_2NC_6H_4OC_2H_5$, indicating this to have a non-radical origin.

(ii) E.s.r. experiments. We have mentioned above the reported [1] formation of phenyl radical in the photolysis of $C_6H_5N_2^+$ ions in a frozen alcoholic solution at 77 K.

(iii) Quantum yields. In pure, argon-flushed ethanol, the quantum yields φ_2 for a number of aryldiazonium salts exceed unity [4], implying a short radical-chain reaction, viz.

$$ArN_2^+X^- \xrightarrow[\varphi_2]{h\nu} Ar\cdot + N_2 + \cdot X$$

(2)

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$$Ar\cdot + CH_3CH_2OH \rightarrow ArH + CH_3\dot{C}HOH \tag{5}$$

$$CH_3\dot{C}HOH + ArN_2{}^+X^- \rightarrow CH_3\overset{+}{C}HOH + \\ + Ar\cdot + N_2 + X^- \tag{6}$$

$$CH_3\overset{+}{C}HOH + 2H_2O \rightarrow CH_3CH(OH)_2 + H_3O^+ \\ \downarrow \\ CH_3CHO \tag{7}$$
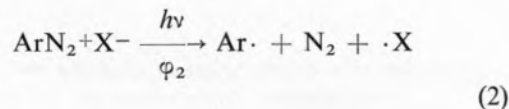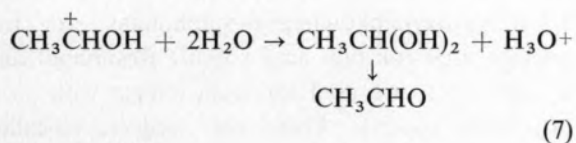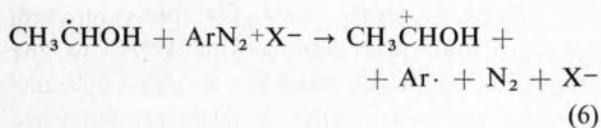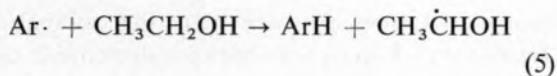
Each quantum removes one molecule of diazonium salt in (2), and the aryl radical so generated attacks the solvent to yield a reducing solvent radical which consumes further $ArN_2{}^+$ in (6). Termination is by radical — radical reactions to give $ArCHOHCH_3$, etc.

However, (2) is by no means exclusive, as indicated by formation of $p\text{-}O_2NC_6H_4OC_2H_5$ in (i) above, formed via (8):

$$p\text{-}O_2NC_6H_4{}^+ + 2C_2H_5OH \rightarrow \\ \rightarrow p\text{-}O_2NC_6H_4OC_2H_5 + C_2H_5OH_2{}^+ \tag{8}$$

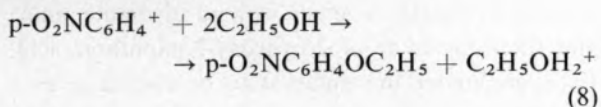Several workers [4, 6] have found the importance of the homolytic fission (2) to be reduced both by acidification of the medium and admitting O_2. PAYNE [4] reports initial quantum yields for benzene-diazonium fluoroborate in ethanol to be reduced on such treatment from the high value of 5.4 to a level (of 0.59) more commensurate with those found in aqueous solution, and results on a series of *m*- and *p*-substituted derivatives displayed a not dissimilar Hammett ρ value of -0.26 ± 0.02. Evidently O_2 is removing $Ar\cdot$, although the suppressant effect of acid is harder to rationalise. The same pattern emerged with the more complex commercial diazo salts (Table 1).

Several groups have studied the photodecomposition of diazonium salts in polymer films (a medium increasingly exploited in the dye-line industry). Various 2,5-dialkoxy-4-morpholinobenzenediazonium fluoroborates gave φ_{dec} of ca. 0.43 at λ (irradiation) from 348 to 460 nm [7], whilst a series of p-dialkylaminobenzenediazonium tetrachlorozincates yielded φ_{dec} from 0.19 to 0.72 [8]. PAYNE [4] has examined both simple and complex aryldiazonium tetrafluoroborates in cellulose acetate film, finding φ_{dec} to be insensitive to change of ring-substituent. He also found the irradiated films at 77 K to display e.s.r. spectra suggestive both of trapped aryl radicals and of triplet ground-state aryl cations, which indicate reactions (2) and (3) to operate in parallel under these conditions.

4 — APPLICATIONS

These are highly diverse, extending to both the initial and final products of the photodecomposition as well as to the photobleaching process itself [9], as set out in the scheme below.

We shall treat each of the processes and species 1-5 outlined in the scheme in turn.

$$ArN_2{}^+PF_6{}^-$$

$h\nu$ (1. Photobleaching process to leave $ArN_2{}^+$ image)

$+ \quad \cdot PF_6$ 　　　　　 2. Phenol

$Ar\cdot \quad + \quad N_2$ 　　　　 Azo-dye image

3. Radical initiator and reducing agent 　　 4. Gas release

$ArF \quad + \quad N_2 \quad + \quad PF_5$

5. Lewis acid
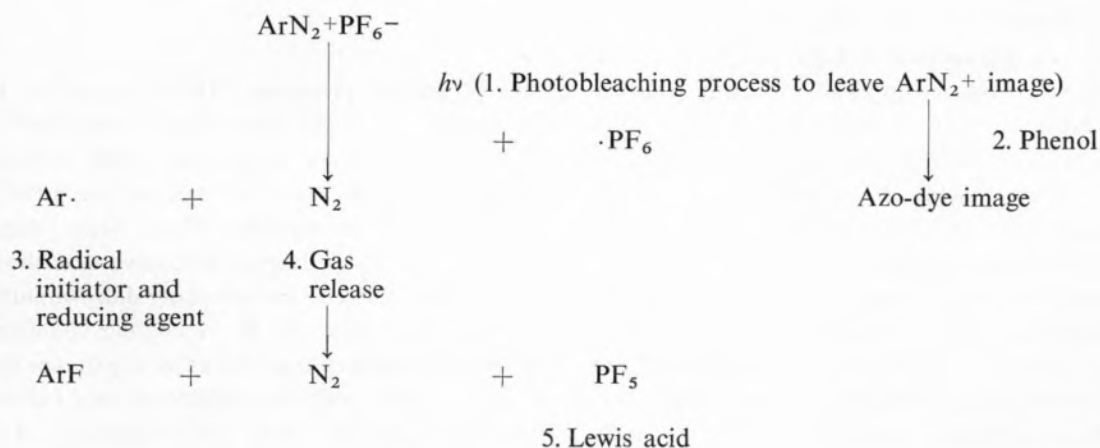
(i) Photobleaching of $ArN_2^+X^-$ and (ii) coupling with hydroxyaromatic. The basic imaging system described in the introduction contains only the diazonium salt and is referred to as a one-component system, depending on a subsequent development of the positive image of unreacted diazonium salt with a phenolic coupler (eqn. 1.). The coupler can be incorporated into the original coating (to give the so-called two-component system) provided the medium is maintained at low pH by addition of an organic acid to inhibit coupling. After exposure, the image is developed by inducing diazo-phenol coupling on raising the pH by exposure either to ammonia gas or an involatile amine such as ethanolamine [10]. Other procedures for increasing the basicity of the medium include the use of thermolabile compounds, such as urea, which release NH_3 on warming. A notable innovation has been the use of diazo-coated transparent plastic films (usually on polyethylene terephthalates) which provide more robust copies.

The image colour of the dyeline print depends on both the type and quantities of diazonium salts and couplers used, and also on the conditions of development, and any colour can be produced. The group of diazonium salts used are all of the same general structural type, and the flexibility in selecting line colour is largely due to the coupler. In general, dihydroxynaphthalene-2-hydroxynaphthoic acid derivatives give blue dyes, pyrazolones give red dyes, whilst acetoacetylamines yield yellow dyes. Brown dyes are formed by resorcinol and its derivatives.

As regards the aryldiazonium salt, it is essential to match its absorption maximum with the spectral output of the irradiation source (usually maximal at 360-420 nm). For one-component systems it is desirable to incorporate a high coupling activity because, to prevent creeping of dye away from the image areas through diffusion of the diazonium salt, it is essential that the relatively less-soluble dye is formed quickly. It is advantageous to use diazonium salts of lower water solubility than those used in two-component processes. A diazonium salt frequently used in one-component formulations is 2,5-diethoxy-4-tolythiobenzenediazonium chlorozincate. Diazonium salts for two-component processes should be of relatively low coupling speed in order to eliminate premature reaction with the

coupler (which is also present in the coating) and 2,5-diethoxy-4-morpholinobenzenediazonium chlorozincate is frequently used.

The coupling agents used for one-component processes must react rapidly with ArN_2^+ to give a dye of limited water solubility, and phloroglucinol is often used. Less active couplers are employed in two-component processes. Naphthols, e.g. sodium 2,3-dihydroxynaphthalene-6-sulphonate, are frequently used for blue line colour. Resorcinol and its derivatives are used for sepia images with good ultraviolet opacity. These are used as so-called «intermediates», i.e. coatings on film or transparent paper which are used for making further dyeline copies.

Negative dyeline materials can be produced either by the use of a diazo-sulphonate or naphthoquinone diazides. *Trans*-diazosulphonates do not couple, but on irradiation rearrange to the *cis*-form, which is in equilibrium with the free diazonium ion, enabling coupling to occur. A negative material described by KALLE [11] illustrates the process. Sodium 3-chloro-4-diethylaminobenzenediazosulphonate is coated together with an involatile amine and the o-anisidide of 2-hydroxy-3-naphthoic acid. Exposure under the material to be copied gives a blue image in the exposed areas. The material is then treated with acid vapour and re-exposed to ultraviolet light which effects the isomerisation of the *trans*-diazosulphonate to the *cis*-form, but coupling is prevented by the acid and the diazo compound is destroyed by light.

On exposure to light, naphthaquinone diazides form indenecarboxylic acids which couple very rapidly with undecomposed diazo compound to give a dye in the exposed areas, i.e. to give a negative image.

(iii) Reducing properties. On exposure to light, diazonium salts and some diazo compounds give reducing substances which have been utilised by KALLE [12] to reduce metal salts to the metal, e.g. silver nitrate to metallic silver. More recently, JONKER and his colleagues [13] have described the production of metal images using diazosulphonates or diazothioethers (fig. 3). A coating containing a diazosulphonate or diazothioether is exposed imagewise to light: reducing substances are formed in the light-exposed areas, and treatment with a

metal salt solution forms a latent image of metal in the image areas, the intensity of which can be increased by treatment with a solution of a metal salt containing a mild reducing agent, e.g. metol. A typical formulation for the coating of a resin-coated polyester sheet is as follows:

0.1 mol sodium 2-methoxybenzenediazosulphonate
0.0167 mol lactic acid
0.0167 mol cadmium actate
10 g Lissapol N
distilled water to 1000 ml.

This solution is applied as a coating which is then dried and exposed to u.v. light. The exposed material, containing reducing substances in the light-exposed areas, is treated with the following solution:

0.1 mol mercurous nitrate
0.01 mol silver nitrate
0.1 mol nitric acid
distilled water to 1000 ml.

It is then rinsed with water and the latent image of mercury is developed by treatment with the following developer, which deposits silver:

0.1 mol metol
0.1 mol citric acid
0.05 mol silver nitrate
distilled water to 1000 ml.

When development is complete, the material is washed with water. This process is useful in the production of printed circuits.

(iv) Gas evolution. The release of N_2 on decomposition of aryldiazonium salts was utilized by KALLE [14] in 1932. Diazonium salt was coated together with gelatin on film: imagewise exposure to light followed by heating, produced areas of small bubbles in the exposed regions (fig. 4). Films of this type give a positive image of the original when viewed by reflected light because of light-scattering by the bubbles. Viewed by transmitted light, a negative image of the original is seen. The Kalle process is rather unsatisfactory because gelatin is moisture-sensitive. G.A.F. pointed out [15] that the choice of resin is important (it must be both thermoplastic and hydrophobic), and also that it is better to disperse the diazonium salt in the resin rather than dissolve it. The small particles form nuclei for bubble production. The

PHYSICAL DEVELOPMENT SYSTEM

I. UNEXPOSED

DIAZOSULPHONATE →
ADHESIVE LAYER →
POLYESTER BASE →

$\underline{TRANS} - ArN = NSO_3 Na$

hν

II. EXPOSED

CIS DIAZO COMPOUND IN EXPOSED AREAS

$\underline{CIS} - ArN = NSO_3 Na \rightleftharpoons Ar\overset{+}{N} \equiv N + SO_3^{2-}$

III. NUCLEATION

METAL LATENT IMAGE (METAL NUCLEI)

$SO_3^{2-} + Hg_2^{2+} \rightarrow Hg SO_3$ COMPLEX + Hg
or
$SO_3^{2-} + 2Ag^+ \rightarrow Ag_2 SO_3$ (further reduced by developer)

IV. DEVELOPMENT

ELECTRODELESS PLATING OF FURTHER METAL
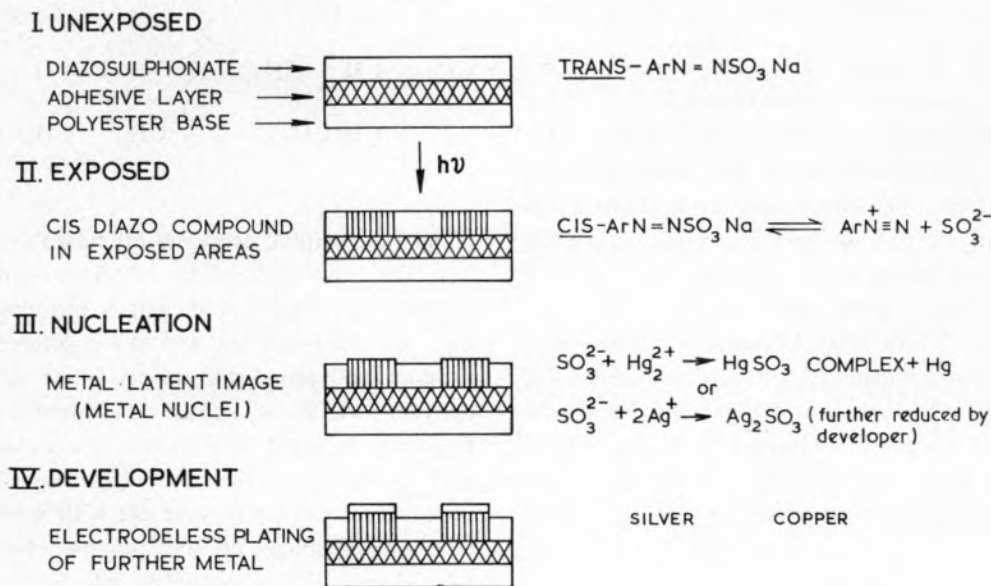
SILVER   COPPER

Fig. 3

Block diagram illustrating reaction sequences involved in the physical development system

VESICULAR (GAS - BUBBLE) DEVELOPMENT.

HYDROPHOBIC THERMOPLASTIC AND DIAZO

SUBSTRATE

$h\upsilon$ $h\upsilon$

LATENT IMAGE (N_2 NUCLEI)

HEAT EXPANDS BUBBLES

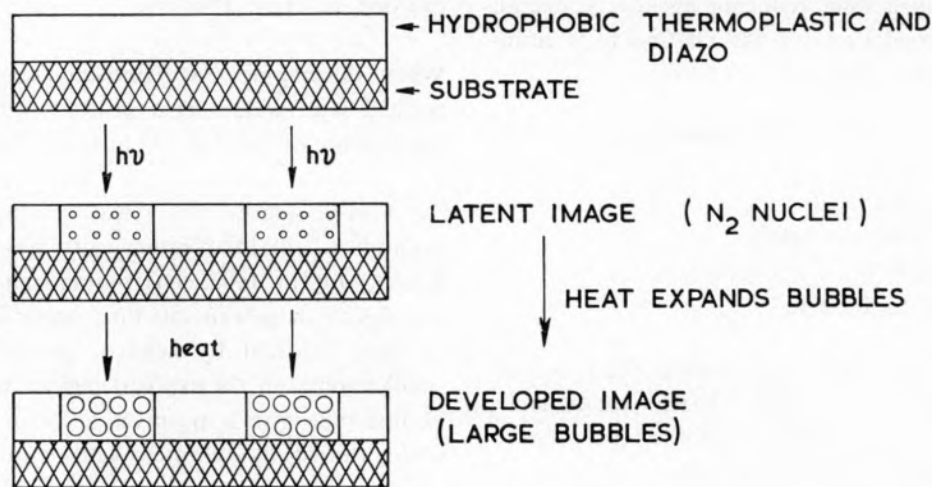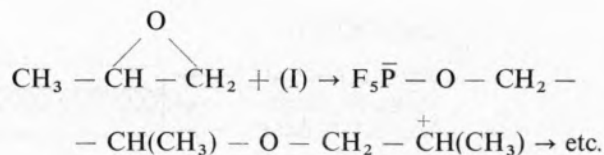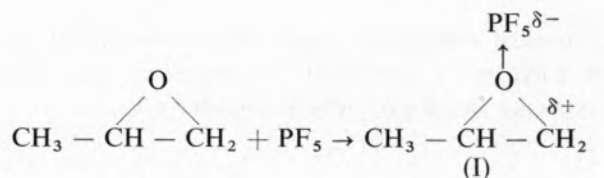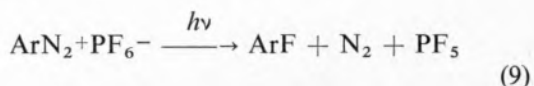heat

DEVELOPED IMAGE (LARGE BUBBLES)

Fig. 4

Sequence of processes involved in vesicular development

degree of permeability of the resin to gas is also important. When the material has been exposed and then heated to produce the image, it is re-exposed without heating to decompose the diazonium salt in the non-image area. In the absence of heat the nitrogen gas formed slowly diffuses through the resin without forming bubbles. Suitable resins are polyvinyl chloride and polyvinyl acetate [16].
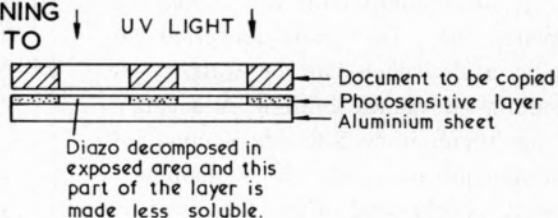
(v) Reaction of Lewis acids. Diazonium cations are usually associated with complex anions to increase their stability. Certain anions (Lewis salts) afford the corresponding Lewis acid following photolysis (eqn. 9), which acts as a catalyst for cationic polymerisation. For example, a coating containing an epoxy resin, e.g. the Shell product «Epikote 1007» (a bisphenol-A-epichlorhydrin condensate) and 2,5-diethoxy-4-tolylthio-benzenediazonium hexafluorophosphate will harden and become less soluble in the light-exposed regions due to the catalytic effect of the PF_5 released by the decomposition of the diazonium salt [17]. The photocatalysis is quite general for epoxides, e.g. for 1,2-epoxypropane:

$$ArN_2{}^+PF_6{}^- \xrightarrow{h\upsilon} ArF + N_2 + PF_5$$

(9)

$$CH_3 - \overset{\displaystyle O}{\overset{\displaystyle /\backslash}{CH - CH_2}} + PF_5 \rightarrow CH_3 - \overset{\displaystyle \overset{\textstyle PF_5{}^{\delta-}}{\uparrow}{O}}{\overset{\displaystyle /\backslash}{CH - CH_2}}{}^{\delta+}$$

(I)

$$CH_3 - \overset{\displaystyle O}{\overset{\displaystyle /\backslash}{CH - CH_2}} + (I) \rightarrow F_5\bar{P} - O - CH_2 -$$
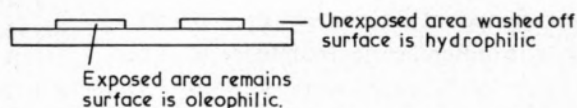$$- CH(CH_3) - O - CH_2 - \overset{+}{CH}(CH_3) \rightarrow etc.$$

Other lithographic processes are based on solubilisation (or insolubilisation) of diazonium salts on exposure to light. A negative lithographic process [18] depends on the water-soluble reaction product between 4-diazophenylamine and formaldehyde, which is coated on aluminium sheet. Exposure to light insolubilises the exposed areas, presumably by further polymerisation. The unexposed areas can be washed off with water to leave a negative image of the original, treatment of which with oily lithographic ink gives a negative plate from which prints can be made. The sequence is set out in fig. 5.

NEGATIVE LITHOGRAPHIC PROCESS

I SENSITISED PLATE IS EXPOSED
TO ULTRAVIOLET LIGHT SHINING
THROUGH THE DOCUMENT TO
BE COPIED.

UV LIGHT

— Document to be copied
— Photosensitive layer
— Aluminium sheet

Diazo decomposed in
exposed area and this
part of the layer is
made less soluble.

II UNEXPOSED PORTIONS
WASHED OFF

— Unexposed area washed off
surface is hydrophilic

Exposed area remains
surface is oleophilic.

III DEVELOPED PLATE TREATED
WITH OIL-BASED INK.

Ink adheres only to oleophilic areas
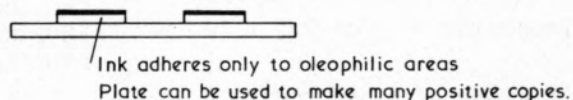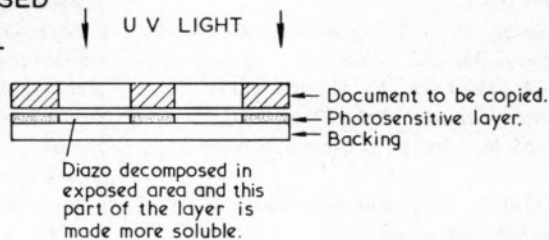Plate can be used to make many positive copies.
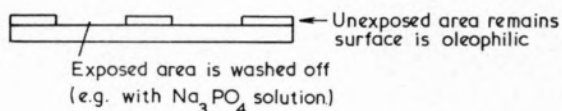
Fig. 5
Sequence of processes in preparation of negative lithographic plates

POSITIVE LITHOGRAPH PROCESS

I SENSITISED PLATE IS EXPOSED
TO ULTRAVIOLET LIGHT
THROUGH THE DOCUMENT
TO BE COPIED.

UV LIGHT

— Document to be copied.
— Photosensitive layer.
— Backing

Diazo decomposed in
exposed area and this
part of the layer is
made more soluble.

II EXPOSED PORTIONS
WASHED OFF.

— Unexposed area remains
surface is oleophilic

Exposed area is washed off
(e.g. with Na_3PO_4 solution.)

III DEVELOPED PLATE
TREATED WITH OIL-
BASED INK.

Ink adheres only to oleophilic areas.
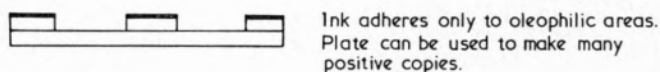Plate can be used to make many
positive copies.

Fig. 6
Sequence of processes in preparation of positive lithographic plates

A positive process is based on 1,2-naphthaquinone-4-diazide-5-sulphonyl esters and amides which are oleophilic and insoluble in dilute sodium phosphate solution [19]. If these compounds are coated on aluminium plate, they are photo-converted to indenecarboxylic acids which can be washed off with dilute sodium phosphate solution. A negative image of 1,2-naphthaquinone-2-diazide-5-sulphonyl ester or amide remains and, since this is oleophilic, a positive image is obtained when the plate is treated with lithographic ink (as illustrated in fig. 6).

Finally, sheets of paper of film coated with diazonium salt often show a difference in receptivity to toner in the exposed and unexposed portions [20]. Depending on which diazonium salt is used, toner dusted on an exposed print will adhere to the unexposed or exposed portions of the print and quite good images can be produced in this way.

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RESUMO

A decomposição fotoquímica dos sais de arildiazónio em solução é interpretada na base dos dois mecanismos mais importantes: foto-homólise e foto-heterólise. Discute-se a variação dos rendimentos quânticos dos dois mecanismos com a natureza do solvente e apresentam-se reacções químicas das várias espécies reactivas produzidas durante a irradiação luminosa. É realçada a importância destes compostos na tecnologia da reprodução gráfica de acordo com o tipo de mecanismo e com base na natureza dos intermediários e produtos, nomeadamente na tecnologia dos processos de reprodução do tipo ozalide (positivos e negativos), sistemas de revelação física para gravuras em metal, processos de reprodução vesiculares e processos litográficos (positivos e negativos) abarcando as técnicas de fotopolimerização.