OFFSET NEGATIVE PLATES -

THE MOVES TO AQUEOUS PROCESSING CHEMISTRY

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Abstract: A brief summary will initially be given, of the different types of photosensitive materials which have been used over the years in solvent developed negative plates. This will be followed by a description of subsequent advances which enabled the use of water/solvent mixtures as developers.

The push towards eliminating solvent from the developer altogether has, however, continued and a resume of the state of the art will be presented. The two main chemical approaches for achieving total aqueous development, namely the use of diazo resins and the use of photopolymerisable unsaturated materials, such as acrylates, will be discussed in full. Particular emphasis will be placed on a novel approach to aqueous development pursued by Howson-Algraphy. The approach is based on the use of a difunctional monomer which has both a vinyl polymerisable double bond and separately, a second reactive group. The chemisty of either functionality can be exploited independently without affecting the latent utility of the other group. This duality of function has enabled novel, light sensitive diazo polymers of varying properties and of varying molecular weight, to be synthesised. Groups with hydrophilic or hydrophobic character can be simply introduced into the polymer; acidic groups, basic groups and even photochromic groups can likewise be incorporated. In essence, an aqueously developable, light sensitive coating can be chemically, rather than (as in the past) physically assembled.

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Traditionally, presensitised negative working lithographic plates were solvent developed. Their coating chemistry was based on the use of very hydrophobic materials such as poly(vinyl cinnamate), azide sensitised epoxy resins and copolymers of p-phenylene diethoxyacrylate and 1,4-di(hydroxyethoxy)-cyclohexane.

Insolubilisation of these materials occurs by a photocrosslinking mechanism to produce very tough, durable images of high molecular weight. An example of the chemistry (poly(vinylcinnamate)) is detailed in (Figure 1). Typical solvents for developing these

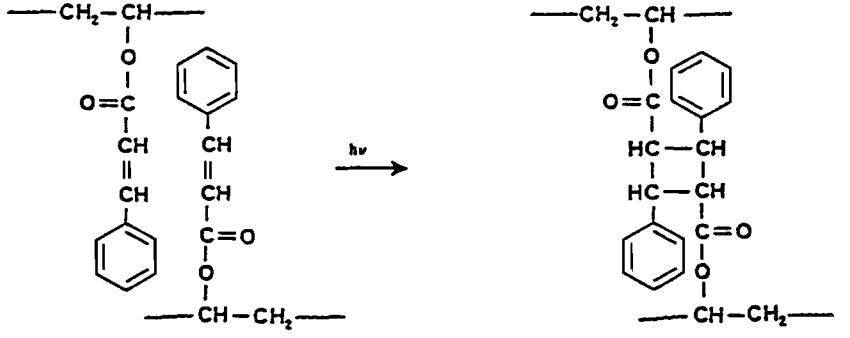


Figure 1. Poly(vinylcinnamate)

types of photopolymer would be 2-methoxyethanol or γ-butyrolactone.

In the mid 1970's some progress was made towards reducing the solvent content of the developer for long running negative plates. Hoechst (as Kalle or Enco) introduced a diazo resin based plate and 3M introduced a plate based on the use of an unsaturated oligomer (or monomer). Both plates relied on the incorporation of significant proportions of the very tough poly(vinyl formal) as a binder to promote the required long runs and hydrophobic images. However, both these plates had as their active compounds, materials which had sufficient hydrophilic character to permit the introduction of water into the developer and in fact the developers were an approximate 30:70 mixture of alcohol and water. Despite their similarity in performance and processing chemistry, the two plates generated their images in different ways - diazo plates

operate by photoinsolubilisation (loss of the solubilising diazo group as shown simplistically in Figure 2) and monomer plates by photopolymerisation (polymerisation of an unsaturated oligomer or monomer).

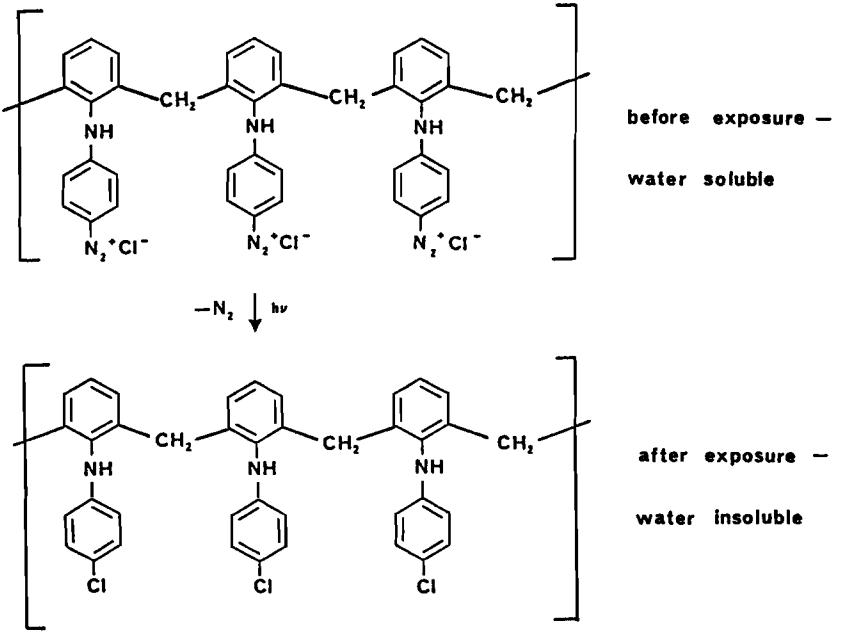


Figure 2. Diazo Resin

Both the Kalle plate and the 3M plate differed in their modus operandi from the photocrosslinkable solvent developed systems described earlier.

In the late 1970's the demand for totally solvent free developers, particularly from Scandinavia, and to some extent from the UK, grew. Both the Hoechst approach and the 3M approach appeared to suggest ways in which the elimination of volatile, smelly solvents from developers could be achieved. This demand for "aqueous plates" generated a tremendous amount of activity amongst the European based plate manufacturers particularly in the field of diazo chemistry. In order to achieve this total aqueous development, the plate manufacturers initially found it necessary to completely eliminate from the coating formulation the presence of a binder resin (which was hampering development) and to rely on the diazo resin alone to

provide the printing image. In the absence of the reinforcing (or binder) resin, the plates of course had their limitations. Light sensitivity was poor (because of the presence of very high proportions of active diazo which in turn, required high levels of light energy to complete insolubilisation), image blinding occurred under certain circumstances and perhaps most important of all, the plates were only capable, at best, of achieving medium run lengths. At about this time (1980) there was also a flurry of activity in the field of water (or tap) developed plates. To achieve water development the coatings had to be even more hydrophilic and thus the problems seen with the aqueously developed plates were compounded and water developed plates were not really a commercial success.

To improve the press performance and oleophilic properties of the aqueous diazo plates, it was clearly necessary to incorporate in some way, a reinforcing resin. However, because of patent restrictions many plate manufacturers were unable to use combinations of conventional diazo resins (diazo diphenylamine/formaldehyde condensates) with reinforcing resins and hence there was fresh activity in the search for new diazo materials. Of particular interest in the patent literature are descriptions of the use of materials based on the condensation of 3-methoxy-4-diazodiphenylamine with methylol derivatives (Teuscher of Hoechst, 1975), diazos derived from bis-acid chlorides (Philpot et al of Kodak, 1979) and diazos made from a similarly novel approach based on the use of polyfunctional isocyanates (Stanton et al of Howson-Algraphy, 1981).

In order to achieve the desired, improved performance and yet to retain total aqueous development, it is necessary to include with the diazo resin, binders which have some hydrophilic character. This can be achieved by incorporating within the binder functional groups such as carboxylic acid (-COOH), sulphonamide ($-SO_2NH-$) or sulphonic acid ($-SO_3H$). There is a wealth of patent literature on this subject and patents of possibly commercial importance relate to:

i) the use of carboxylic acid group containing acrylic polymers, such as the terpolymers methacrylic acid/methyl methacrylate/n-hexylmethacrylate, described by Faust (1974) and methacrylic acid/methyl methacrylate/2-hydroxy-

ethyl methacrylate/acrylonitrile described by Naratomi et al (1978);

ii) the use of poly(vinyl acetals) as reacted with carboxylic acid anhydrides to generate half-esters (Pawlowski 1985), and the carboxylic acid group containing poly(vinyl acetals) of Mattor (1974); and

iii) the use of sulphonamide group containing polymers generated by the reaction of, for example, sulphonyl isocyanates with free hydroxyl containing polymers as described by Klupfel et al, (1973a, 1973b).

The presence of significant (>50 percent by weight) amounts of these types of reinforcing resins can, however, still lead to image blinding problems or lack of hydrophobicity and a balance must be struck between on the one hand the quantity and hydrophilic quality of the reinforcing resin and on the other hand the press performance, light sensitivity and oleophilicity of the plate. The requirement to retain total aqueous development perturbs this finely balanced equation. Increasing the diazo resin content aids aqueous processing but, as already pointed out, impairs light sensitivity and possibly reduces run length; reducing the diazo content speeds up the coating but promotes image blinding which may itself, in turn, restrict run length.

Some presensitised plate manufacturers have now tackled this problem by reverting to the use of developers which contain low levels of organic solvents (the use of low levels of solvent mean that declarations relating to their presence are not always necessary). The use of solvents (typically benzyl alcohol or phenoxyethanol) enables a reduction in the hydrophilic character of the support resin to be made and blinding is thus less of a problem. This reduced tendency to blind means that the proportion of binder can be increased significantly, generating plates of greater light sensitivity and durability.

However, in general the supported diazo approach to the problem does not necessarily provide a complete answer and work has continued on seeking alternative ways of providing good press performance, good light sensitivity and totally solvent free development.

The most important alternative approach is, of course, the one based on photopolymerisation - a chemistry successfully exploited, as already described, by 3M with their aqueous/solvent XN plate in the late 1970's. The great advantages proferred by this type of system are as follows:

i) the use of low molecular weight unsaturated oligomers means aqueous development should be possible;

ii) long press runs should be achievable;

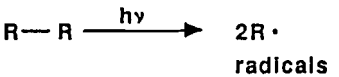
iii) high sensitivities should be achievable - the photopolymerisation reaction is a "chain reaction" - hence image insolubilisation occurs from minimal energy input; and

iv) the composition can easily be spectrally sensitised. This is clearly of value in producing presensitised plates of the same master composition for different exposing units - conventional frames, u.v. and visible light lasers, projection systems etc.

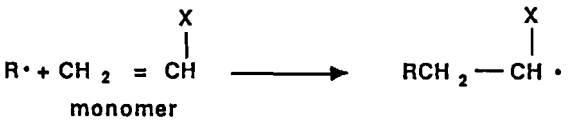
There is a wealth of patent literature on photopolymerisable systems and they have proved to be of value in many fields of application - u.v. curing inks, varnishes, paints, lacquers, can coatings etc. Most, if not all, of the commercial products are based on oligomeric acrylates or methacrylates and clearly these materials would be of great value in lithographic coatings. However, their use does, in general, have a major drawback and that is that their (photo)polymerisation is inhibited by the presence of oxygen. Oxygen terminates the chain reaction by producing an unreactive or stable radical (Step 4, Figure 3) and this can lead to incomplete curing. A great deal of research effort has been directed towards overcoming this problem but generally ineffective or inefficient results have been obtained. Areas which have been studied and which have been put forward as offering solutions to the problem include the use of photoinitiating systems which are less prone to oxygen quenching such as the bis(halomethyl)benzophenones of Pacifici et al (1977, 1978), combinations of benzophenone and amines as described by Osborne (1973) and Gaske (1974, 1975a, 1975b) and α-sulphonyloxymethyl

-benzoins of Gaur et al (1984). The use of oxygen scavengers such as triphenyl phosphine (Hahn, 1978),

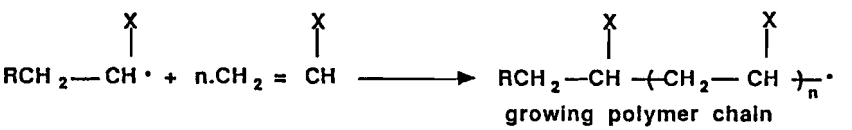
Step 1 - Generation of the primary initiating species



Step 2 - Initiation of the chain reaction



Step 3 - Propagation of the chain reaction



Step 4 - Chain termination by
(i) Combination of two growing chains
or (ii) Oxygen Inhibition

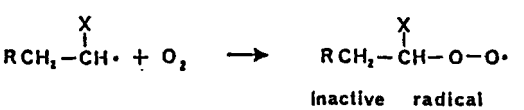


Figure 3 Photopolymerisation process/oxygen inhibition

and mercaptobenzothiazoles or mercaptobenzoxazoles (Chambers 1981) has been evaluated, as has the use of singlet oxygen (generated initially by, for example, red-light irradiation in the presence of a dye-sensitiser) scavenging by materials such as 1,3-diphenylisobenzofuran (Decker, 1979).

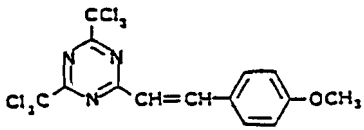
As far as presensitised litho plates are concerned, however, the most effective, although still far from ideal, way of overcoming oxygen inhibition appears to be by the application of an oxygen impermeable overlayer to the light sensitive coating. This approach

has been described in the literature by Alles of Du Pont (1969), Klupfel et al of Kalle (1973c) and others and has been successfully commercialised by Kalle and Polychrome.

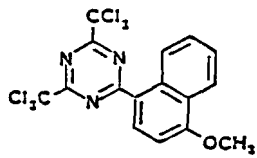
Preferred photopolymerisable compositions for negative plates (both as described in the literature and as used in practice) would appear to comprise a polyfunctional urethane (meth)acrylate, a carboxylic acid acrylic terpolymer support resin (to provide good coating compatibility and durability and to promote aqueous development) and an initiator and/or sensitiser.

The initiating/sensitising system is an extremely important part of the composition as it determines both the final light sensitivity of the composition and its spectral response. The majority of the commercial photoinitiators available for u.v. curing have their light absorption maximum at too short a wavelength to be of great value in coating compositions for presensitised printing plates. Plates need to absorb typically in the region 350-450 nm. For visible laser light longer wavelengths still (488 nm; 514 nm) are required. These requirements have led to a great deal of research activity within the Graphic Arts industry as companies strive to "tune" the spectral sensitivity of their compositions to the desired wavelengths. Limited success has been achieved by the spectral sensitisation of conventional photoinitiators (for example by combinations of Michler's ketone (max 366 nm) and benzophenone) but more importance is now being placed on the use of photoinitiators which have the inherently correct absorption characteristics.

Specific patents of value in this respect are related to the conjugated trichloromethyl-s-triazines (Figure 4; I) described by Bonham et al of 3M (1976a, 1976b), the polycyclic trichloromethyl derivatives (Figure 4; II) from Buhr of Hoechst (1980), the acridines (Figure 4; III) also from Hoechst (Bauer et al, 1973) and the trichloromethyl phenacrylidenes (Figure 4; IV) and perester phenacrylidenes (Figure 4; V) from Howson-Algraphy Wade et al (1985, 1984). All the materials absorb well into the visible region of



(I)



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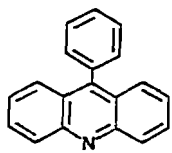

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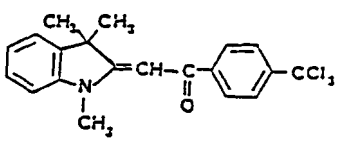

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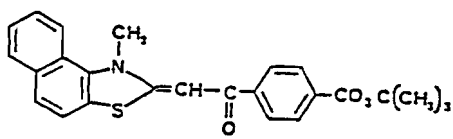

(V)

Figure 4. Photoinitiators

the spectrum and are therefore of particular value in printing plate compositions. The trichloromethyl group containing photoinitiators have an additional advantage in that they generate sufficient acidity to be of value in acid curing systems and will also trigger coating colour changes on exposure in the presence of indicator dyes.

However, despite these advances made, currently neither conventional supported diazo compositions nor photopolymerisable compositions are able to provide an ideal solution to the search for a totally aqueously developable long run negative plate of high light sensitivity. Existing aqueous diazo systems currently offer only a medium-long run press performance and photopolymerisable systems suffer from the already mentioned major drawback of oxygen inhibition of the photoreaction. Compositions relating to hybrid (diazo/monomer) systems have been patented and indeed, commercialised but they too suffer from disadvantages.

Work has therefore, continued on seeking alternative solutions to the problem. A novel approach pursued by Howson-Algraphy has been to try and combine both the light sensitive diazo function and the reinforcing resin into one material - in essence to chemically, rather than physically, assemble the light sensitive coating.

The basic concept behind this novel approach was to try and build into a polymer molecule, the various composite parts of a supported diazo formulation. The polymer would need diazo functionality, clearly, to provide an inherent light sensitivity, hydrophilic character to promote aqueous development and hydrophobic character for oleophilicity. The proportions of these features could, by polymer synthesis, be varied and in conjunction with careful selection of molecular weight, it was believed that a light sensitive product could be optimised. The material selected as the keystone or building block for the diazo group containing polymers was isocyanatoethyl methacrylate (IEM; Figure 5). IEM is a difunctional monomer with a reactive isocyanate group and a vinyl polymerisable double bond. In effect, the chemistry of either functionality can be exploited independently without affecting the latent utility of the other group. The intention thus being to use the vinyl group

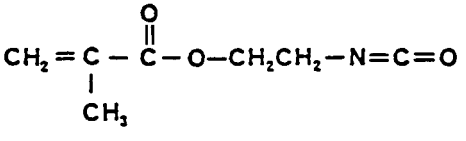

Figure 5. Isocyanatoethyl methacrylate

to generate the polymer (possibly in conjunction with other comonomers) and the isocyanate group to generate the diazo functionality.

The isocyanate group of IEM itself is similar to other aliphatic isocyanates regarding its reactivity with, for example, primary alcohols. Very low levels (0.2percent w/w) of catalysts such as dibutyl tin dilaurate and dibutyl tin diacetate promote the reaction effectively.

The reactivity of the pendant isocyanate group in an IEM homopolymer (Figure 6) or an IEM copolymer (with methyl methacrylate, for example (Figure 7)) remains

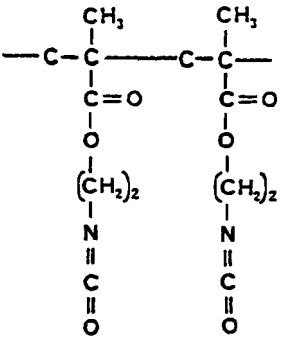

Figure 6
IEM homopolymer

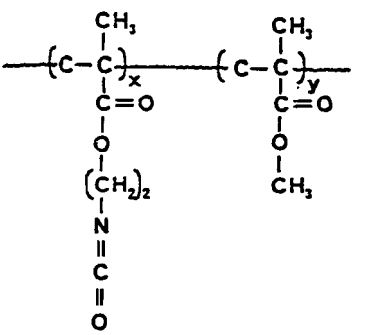

Figure 7
IEM copolymer

quite high (with aliphatic alcohols, reactivity is about 50percent of that of monomeric IEM) and the retention of the NCO functionality in IEM polymers can be very high (90–95 percent) provided water and other active compounds are carefully excluded from the polymerisation.

Thus, IEM is a very versatile compound and its potential has already been exploited in various fields of application, including coating technology. For a presensitised negative plate, we could envisage a diazo polymer represented in one of its most basic and simplest forms according to the structure (Figure 8).

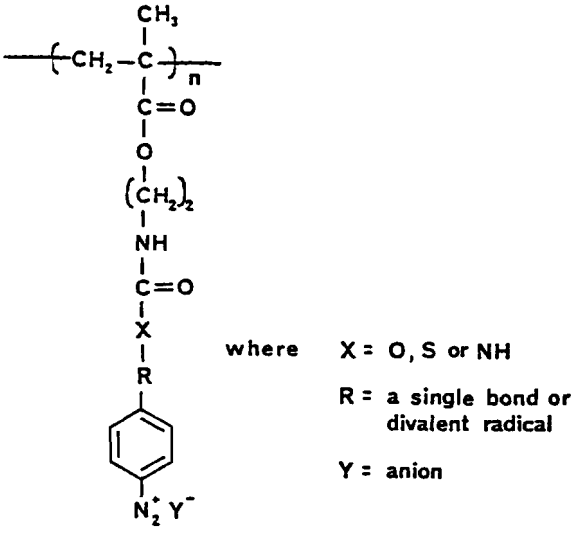

Figure 8. Diazo polymer

Compounds of this type could be prepared by two very convenient methods. In the first method IEM could be polymerised, the isocyanate groups of the resulting polymer could then be reacted with a compound containing both a latent diazo group and an -OH, -SH or $-NH_2$ moiety and then the diazo group could be subsequently generated. In the second method, IEM could be reacted with a compound containing both a latent diazo group and an -OH, -SH or $-NH_2$ group, the resulting compound could then be polymerised and the diazo group, again, subsequently generated.

Clearly the characteristics, of the final diazo polymer could be adjusted by the incorporation at the polymerisation stage (in either method) of various comonomers. Vinyl compounds such as methyl methacrylate, lauryl methacrylate, acrylic acid, and acrylonitrile could be simply incorporated. The levels of comonomers of this type could be finely tuned to give a balance between oleophilicity, aqueous developability and adhesion.

The approach appeared to have a lot of potential and a research program was thus initiated. Howson-Algraphy had previously identified the compound 4-(N-ethyl-N-hydroxyethyl)aminoacetanilide (Figure 9) as a very

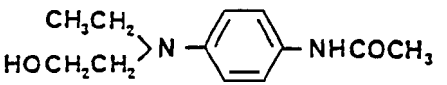

Figure 9. 4-(N-ethyl-N-hydroxethyl)aminoacetanilide

useful diazo precursor. This material, with its hydroxyl functionality appeared to be ideally suited for reaction with the isocyanate group of either IEM itself with subsequent polymerisation or with the isocyanate groups of the IEM polymers. Subsequent processing would involve deacetylation of the protected amine and then diazotisation. The total reaction scheme could be represented as either Appendix 1 or Appendix 2.

Initial work was centred on the homopolymerisation of IEM (molecular weight typically 30,000) with subsequent reaction with the diazo precursor and then conversion to a solvent soluble diazo polymer as shown in Appendix 2 (the anion was typically p-toluene sulphonic acid). The resultant material developed satisfactorily with a totally aqueous developer but lacked oleophilicity and had inadequate press performance and light sensitivity. Various comonomers were progressively introduced into the diazo polymer precursor to try and improve matters. Eventually, a terpolymer comprising methyl methacrylate (7 parts) IEM (2 parts) and lauryl methacrylate (1 part) was identified as looking particularly promising. Light sensitivity of the resulting diazo polymer was very good and medium-long press runs were obtained. Unfortunately, however the preferred aqueous developer was incapable of developing aged plates - in effect, the shelf life of the product was inadequate. Adjustment (downwards) of molecular weight was seen as a possible solution.

The factors affecting the synthesis of varying molecular weight IEM homopolymers had been studied at

an early date in the project. At the high polymerisation temperatures (80-100 degree C) necessary to avoid gel formation, no obvious correlation had been observed between molecular weight and reaction temperature. Similarly the monomer addition time appeared to have little effect. A study of the effect of concentration of IEM on molecular weight indicated, as would be expected from basic kinetic theory, that the use of more dilute solutions assisted the production of low molecular weight polymer; however, this was at the expense of high isocyanate retention. The partial loss of isocyanate functionality could be explained by the reaction of isocyanate groups with the small quantities of water still present in the solvent; at lower concentrations of IEM, this reaction clearly became increasingly important.

The results of experiments with chain-transfer agents were very encouraging with respect to the synthesis of low molecular weight polymers, giving products within the target range of 5,000-15,000, although quite large amounts of agent were required (ca 10percent w/w IEM) and adverse effects on the retention of isocyanate functionality were observed. Making use of the reaction solvent as a chain-transfer agent was also considered; 2-ethoxyethyl acetate appeared to act as a better transfer agent than the otherwise preferred N-methylpyrrolidone (NMP).

However, it was also established that the initiator concentration had the largest effect of any factor on the molecular weight of the final product (molecular weight decreasing as the initiator concentration increases) and this parameter was therefore adopted as the means for controlling and hence decreasing the molecular weight of the diazo polymer.

New lower molecular weight polymers were thus synthesised using the basic 7:2:1 methyl methacrylate: IEM:lauryl methacrylate composition and indeed improvements in developability (effectively shelf life) were observed as the molecular weight fell from ca 30,000 to 15-20,000. Unfortunately, however, the improvements were insufficient and a new tack had to be adopted.

It seemed possible that incorporation of materials such as acrylic acid or methacrylic acid at the

polymerisation stage might aid aqueous developability of the final diazo polymer and so this idea was considered in some detail. Clearly, the synthesis method depicted in Appendix 2, used most extensively up until this time, was unlikely to be suitable - the competing reaction between the isocyanate grouping and the carboxylic acid grouping would most likely cause problems during the initial polymerisation. Hence the scheme shown in Appendix 1 was adopted and polymers having compositions of the form 7:2:1:1 methyl methacrylate:IEM:lauryl methacrylate:methacrylic acid were synthesised and evaluated. Marked improvements in developability were observed for the methacrylic acid containing diazo polymers but there was some loss, possibly as expected, in oleophilicity - this was manifest as an observed reduction in light sensitivity.

Further optimisation of the relative amounts of the comonomers improved the situation somewhat and a preferred composition of 7:1.5:1:0.5 methyl methacrylate:IEM:lauryl methacrylate:methacrylic acid has currently been established. This diazo polymer forms the basis of a litho plate which has very good light sensitivity (ca 200 mJ/cm^{-2}), very good press performance (long runs), is insensitive to oxygen, has a reasonable shelf-life and can be developed by a totally aqueous developer.

polymerise
i hydrolysis
ii diazotisation
DIAZO
POLYMER

polymerise
condense with :
i hydrolysis
ii diazotisation
DIAZO
POLYMER

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