

# **Synthesis of Non-Ionic Water-Dispersible Resins for Use in Intaglio Inks Curing by Electron Beam Radiation**

**Brian Dickens  
Barry J. Bauer  
Walter J. Pummer**

**U.S. DEPARTMENT OF COMMERCE  
National Institute of Standards  
and Technology  
Materials Science and  
Engineering Laboratory  
Polymers Division  
Gaithersburg, MD 20899**

**Prepared for:  
The Office of Research and Technical  
Services  
Bureau of Engraving and Printing  
Department of the Treasury  
Washington, DC 20226**

**U.S. DEPARTMENT OF COMMERCE  
Robert A. Mosbacher, Secretary  
NATIONAL INSTITUTE OF STANDARDS  
AND TECHNOLOGY  
John W. Lyons, Director**

**NIST**



# **Synthesis of Non-Ionic Water-Dispersible Resins for Use in Intaglio Inks Curing by Electron Beam Radiation**

**Brian Dickens  
Barry J. Bauer  
Walter J. Pummer**

**U.S. DEPARTMENT OF COMMERCE  
National Institute of Standards  
and Technology  
Materials Science and  
Engineering Laboratory  
Polymers Division  
Gaithersburg, MD 20899**

**Prepared for:  
The Office of Research and Technical  
Services  
Bureau of Engraving and Printing  
Department of the Treasury  
Washington, DC 20226**

**Annual Report of September 30, 1987**

**Issued May 1991**



**U.S. DEPARTMENT OF COMMERCE  
Robert A. Mosbacher, Secretary  
NATIONAL INSTITUTE OF STANDARDS  
AND TECHNOLOGY  
John W. Lyons, Director**



## Table of contents

Executive summary . . . . .	V
1 Introduction . . . . .	1
2 Background . . . . .	1
3 Syntheses . . . . .	2
3.1 Phosphazenes . . . . .	2
3.2 PMMA backbones . . . . .	4
3.3 Siloxanes . . . . .	4
3.4 Urethane/polyethylene oxide/methacrylates . . . . .	6
3.4.1 Effect of water . . . . .	6
3.4.2 Aliphatic urethanes . . . . .	8
3.4.3 Resin stabilizers . . . . .	9
3.4.4 Crosslinkers . . . . .	10
3.4.5 Design of an ink varnish . . . . .	10
Table 1. Viscosities of urethane resins . . . . .	12
Figure 1. Viscosity vs. composition of urethane resins . . . . .	13
3.4.6 Spreadsheet for urethane synthesis . . . . .	13
3.4.7 Example of spreadsheet. . . . .	15
4 Water wipeability . . . . .	16
5 Cure Speed . . . . .	16
6 Conclusions . . . . .	17
References . . . . .	17
Appendix 1: Synthesis of urethane/PEO/methacrylates . . . . .	19



## Executive Summary

Syntheses have been devised and carried out to produce liquid resins which are water dispersible and which cure under the action of an electron beam. The resins disperse pigments used in intaglio inks.

Four types of resin have been synthesized. All contain polyethylene oxide (PEO) units capped at one end with acrylate or methacrylate groups and joined at the other end with a variety of chemical linkages to give molecules with two or more polymerizable groups. Samples of all types of resin have been provided to BEP.

The first type of resin is based on a phosphazene  $(PN)_3$  center bonded to six PEO arms capped with methacrylate groups.

The second type of resin is of the comb type with a poly methyl methacrylate (PMMA) backbone. The pendant PEO arms are capped with acrylate ends.

The third type is based on a tetrafunctional siloxane center extended with pendant PEO arms capped with methacrylate ends.

The fourth type of resin is based on urethane bonds between PEO units which are capped with methacrylate groups.

The most successful type of resin is where the PEO arms are joined with urethane linkages and the resin system is stabilized against premature polymerization with BHT (butylated hydroxy toluene) and benzoquinone. These resins are di- or trifunctional in terms of polymerizable groups and contain 62 to 72% by weight of poly ethylene oxide, depending on the formulation. When used alone, this type of resin gives weak films. When 20% by weight of a commercial trifunctional crosslinker is added, the cured film is smooth, flexible, non-sticky, and does not scuff. A trial resin, diluted about 50% with crosslinker, gave an ink which dispersed in Dalmar solution and cured with two megarads of 165 KV electrons. When cured, the ink did not transfer color when wiped under heavy pressure with rough paper.





## 1 Introduction

This work describes the design and synthesis of four types of liquid resins which disperse in neutral water when uncured and which cure under the action of an electron beam. All resins contain polyethylene oxide (PEO) units capped at one end with acrylate or methacrylate groups. The first type of resin is based on a phosphazene (PN)<sub>3</sub> center and has six PEO arms capped with methacrylate groups. The second type of resin is of the comb type, with a poly methyl methacrylate (PMMA) backbone and PEO arms capped with acrylate ends. The third type is based on a tetrafunctional siloxane center extended with PEO arms capped with methacrylate ends. The fourth type of resin is based on urethane bonds between PEO units which are capped with methacrylate groups. The urethane resins are divided into two subtypes: those prepared with little or no participation of water in the reaction, and those in which water was an important ingredient.

## 2 Background

Inks are applied wet and are then dried. The inks currently used to print US postage stamps on web presses are dried by heat evaporation of solvents. The emission of volatile solvent into the atmosphere is limited by Local and Federal Government Regulations.

There are two ways of reducing these emissions to an acceptable level. In the first option, a solid ink resin is dissolved in an appreciable amount of solvent or solvents, the formulated ink is applied, and the evaporated solvent is destroyed using catalytic afterburners. Evaporation of solvent using infrared ovens suffers from the drawback that light colors absorb heat less readily than dark colors and are less readily dried.

The second option is to use ink resins which themselves are liquids but which can be transformed into solids by chemical reactions. Much less solvent, if any, is needed in these inks. Web inks must dry very quickly, so the chemical curing reactions must be very rapid. Radiation curing can fully crosslink a liquid resin in a fraction of a second. Crosslinking forms chemical bonds between molecules to produce infinitely large molecules. Crosslinked inks can not be removed satisfactorily using solvents. This report is concerned with radiation-curable resins and inks.

An electron beam is more or less uniformly absorbed by inks and has good penetrating power. Thus, it cures all colors equally well and cures great thicknesses of ink. The prototype resins in our approach have been designed to cure in 2 megarads or less exposure to a 165 KV electron beam.

A mercury lamp now commercially available from Fusion Systems<sup>1</sup> has double the previous output (600 watt per inch instead of 300). Use of this lamp may allow curing of intaglio inks by UV instead of by electron beam. As far as the resins are concerned, the two approaches are very similar, so resins can be developed simultaneously for both systems.

Inks for BEP intaglio presses must be compatible with an aqueous cylinder wipe system. Thus, the inks must wash off a wiping cylinder and remain in suspension until removed from the press. The standard wiping solution used for cylinder wipe presses at the BEP is water containing one percent each of sodium hydroxide and surfactant. Water wiping ability may be conferred by the presence of several types of chemical groups, e.g., carboxylate groups, hydroxyl groups, ether groups, and so on.

The properties required of an intaglio ink resin include low toxicity, a viscosity of about 5 to 30 Pa.s (50 to 300 poises), the ability to disperse the extenders and pigments during manufacture of the ink, satisfactory pot life of the formulated ink, good flow, satisfactory dispersion of the ink from the wiping cylinder using the liquid cleaning system, reasonably fast cure speed, and good mechanical strength in the cured film.

### 3 Syntheses

#### 3.1 Phosphazenes

Resins containing phosphazene moieties give polymers which are very stable. Reviews of phosphazene chemistry and properties have been written by Shaw et al.<sup>2,3</sup>, and Allcock<sup>4</sup>.

The synthesis of a phosphazene with arms based on HEMA (hydroxy ethyl methacrylate) was reported by Anzai and Ohashi<sup>5,6</sup>. Following their procedure, stoichiometric amounts of phosphonitrile chloride trimer,  $(-N=P(Cl_2)-)_3$ , and HEM10<sup>1</sup> (hydroxy ethylene oxide methacrylate with an average of 10 PEO units per molecule) were reacted at 40 °C. The reaction was carried out in a 100% volume excess of toluene to reduce the viscosity and in the presence of 10% molar excess over the stoichiometric amount of pyridine to take up the hydrogen chloride liberated.

The reaction was initially fast, as reported by Anzai and Ohashi<sup>5,6</sup>, but replacement of the last chlorine atoms on the phosphorus took several days, as judged from the IR spectrum. The pyridine hydrochloride was then filtered off. Excess pyridine was removed under low pressure while a small stream of air was bled through the reaction mixture to prevent gelation. (Air is necessary to stop acrylate resins gelling under low

pressures because the stabilizers in the resins are only active against oxygenated radicals.) An attempt was made to precipitate the remaining pyridine by bubbling dry hydrogen chloride through the liquid reaction mixture. This was partially successful. We did not continue the process for long to prevent the hydrogen chloride reacting with the methacrylate double bond. (In one case where we bubbled the hydrogen chloride through the resin solution for about 2 to 3 hours, the solution turned brownish.) After some of the excess pyridine had been removed in this way, the resulting liquid was held in a rotary evaporator at about 20 mm of air. The resultant liquid contained traces of toluene and pyridine and had a viscosity of 0.6 Pa.s (6 poises). This viscosity is far below the 4 to 5 Pa.s (40 to 50 poises) needed in an intaglio ink resin or the 10 to 30 Pa.s (100 to 300 poises) needed in a resin which is to be diluted.

A green ink was made from the phosphazene resin. Both the resin and the ink made from the resin were easily water dispersible and also dispersed the pigments and extenders in the ink without the aid of a dispersing agent. The ink cured very slowly, needing some 30 megarads of electron beam radiation to become non-tacky to the touch. The cured ink was very resistant to prolonged soaking (several months) in water, toluene, and acetone. However, because of the slowness of the preparation reaction, the several steps in the reaction sequence, the low viscosity of the product, and the slow cure of the resulting resin, the phosphazene approach was not continued. Some consideration was given to using linear phosphazenes, such as the 10-mer or 20-mer, but phosphazenes in this size range are not stable. They rearrange to trimers and tetramers<sup>2,3,4</sup>. Also, the resultant resins may have been too highly functional to be stable against premature polymerization of the methacrylate groups.

The slow cure of the phosphazene-based resin may have been due to chain transfer reactions. The pH of the resin was about 4, possibly because of the presence of P-O-H groups<sup>2,3,4</sup>. The P-O-H groups may have acted as transfer agents in hindering the polymerization of the methacrylate groups. Traces of toluene, pyridine and any unreacted P-Cl groups may also have acted as chain transfer agents. The P-O-H groups were probably generated from the action of water in the reactants on the P-Cl groups, although the reactants had been treated with calcium sulfate and molecular sieves. The importance of water in the reaction provided another reason to curtail this approach. Ethoxylated compounds are hygroscopic. The HEM10 material is difficult to dry because it is rather viscous and because its equivalent weight is 520, compared with 9 for water. Thus 0.2% water in HEM10 corresponds to an equivalents ratio of about 1:8 of water to HEM.

### 3.2 PMMA backbones

The second approach used to develop a prototype water dispersible intaglio ink resin was to synthesize a comb polymer with a poly (methyl methacrylate) backbone and polyethylene oxide arms terminated with acrylate groups. The methacrylate groups in the HEM10 monomer were polymerized to give the poly (methyl methacrylate) backbone. A mercaptan transfer agent was used to stop the polymerization of a particular backbone at about the 5-mer level. This gave a material with a short PMMA backbone and with arms of polyethylene oxide terminated with alcohol groups. This material was then acrylated using acryloyl chloride, and the liberated hydrogen chloride was taken up with triethyl amine. Triethyl amine was used because the odor of pyridine is too objectionable to allow it to be used in an ink, even in small quantities. The excess amine was precipitated using hydrogen chloride gas produced by blowing a stream of nitrogen through concentrated hydrochloric acid.

It proved impossible to synthesize a sufficiently viscous resin from the HEM10 material available at the time. Attempts to use less transfer agent to give a longer backbone invariably produced a gel. The problem appeared to be a significant amount of dimethacrylate in the HEM10 material. The amount of dimethacrylate is expected to increase with time because of transesterification reactions. The equilibrium composition of HEM is expected to be 25% diester, 25% dialcohol, and 50% monoester.

HPLC analyses of the HEM material using high pressure liquid chromatography showed that the HEM10 contained an appreciable quantity of hydrophobic material. This hydrophobic material was probably the dimethacrylate ester (HEM10 is the monomethacrylate ester). HPLC was then used to separate the monofunctional from the difunctional and zerofunctional materials. The monofunctional HEM10 separated in this way did not gel when polymerized in the presence of a chain transfer agent. However, purification using HPLC was deemed too complicated a step to be practical if there were other ways of attaining the objective, so the comb polymer approach was discontinued. These resins were among the best for producing stable dispersions in water.

### 3.3 Siloxanes

Another approach involved synthesis of siloxanes. They are formed through a condensation reaction between silicon tetrachloride and hydroxyl groups present in HEM10 and, if the viscosity had to be increased by increasing the molecular weight, polyethylene glycol. This reaction is  $\text{SiCl}_4 + \text{ROH} \rightarrow \text{SiOR} + 4\text{HCl}$ . The equilibrium is shifted to the right by capturing the HCl with a base. This approach is similar to the phosphazene approach. The molecular weight of the product and therefore its

viscosity and curability are controlled by the stoichiometry of the reaction mixture of silicon tetrachloride and the glycols and HEM10.

The first series of syntheses involved addition of  $\text{SiCl}_4$  to a solution of HEM10 and glycol in dry toluene. A 10% molar excess of triethyl amine was added to the solution to capture the generated HCl. A heavy white precipitate of triethyl ammonium chloride formed and was removed by filtration. Most of the toluene and excess triethyl amine was removed on a rotary evaporator. The resulting resins were slightly hazy, probably due to a small amount of triethyl ammonium chloride precipitating upon concentration of the resin. The resins had higher viscosities than that of HEM10 but were much less viscous than the urethane resins (see later).

To eliminate the problem of incomplete removal of triethyl ammonium chloride and toluene, the reactants were mixed without solvent or amine in a bottle connected to a tube containing Ascarite II, which is sodium hydroxide supported on silica. The HCl formed was captured in the vapor phase by the sodium hydroxide, thus eliminating the filtration and evaporation steps of the previous synthesis. The resulting resins were clear, with increased viscosity over the previous samples.

Some of the resins were exposed to an electron beam to measure cure rate. The siloxanes were very slow to cure, being only poorly cured with 5 Mrads exposure. The probable cause is reduced methacrylate functionality. The resins had a noticeable odor of methacrylic acid, probably released through transesterification. Also, silicon-oxygen bonds are hydrolytically unstable.

At this point, we had also begun to investigate urethane/poly ethylene oxide/methacrylate monomers (Section 3.4). The condensation products of urethanes and siloxanes differ in the hydrophobic residues joining the HEM10 segments. The siloxane residue is a silicon atom having a molecular weight of 28 and a functionality of 4. The isocyanate part of the urethane resin has a molecular weight of about 540 and a functionality of 3. Thus, for condensation products of similar type, the siloxanes have much lower hydrophobic content and therefore a much greater water dispersibility.

The strength of the cured film is very important. This is dependent on factors such as the crosslink density and the glass transition temperature of the cured film. Siloxanes and polyethylene oxide sequences tend to lower the glass transition temperature and urethanes tend to increase it. Thus, urethane resins are expected to produce stronger films than the siloxanes.

To some extent, the viscosity of the uncured resin is related to the glass temperature of the cured film. The siloxane resins were not viscous enough to be made into intaglio inks. The urethane resins were significantly more viscous.

Although the siloxane resins have superior water dispersibility, they have inferior viscosity and cure rate compared with the urethanes, and are expected to have poorer mechanical properties. The siloxane approach was therefore abandoned in favor of concentrating efforts on the urethanes.

### 3.4 Urethane/polyethylene oxide/methacrylates

The reaction between HEM10 and isocyanate is a simple one-step process which gives resins of the urethane type. These resins are more viscous than the resins previously discussed, because the urethane linkage is known to be "stiff".

Our experience with surfactants has shown that about 60 to 70% PEO content by weight is needed to confer water dispersibility. Both HEM10 and HEM5 were used as sources of PEO and methacrylate groups. Several isocyanates were tried. When the HEM materials had been dried over molecular sieves, all isocyanates reacted satisfactorily to give liquid products rather than gels.

#### 3.4.1 Effect of water

The HEM materials are hygroscopic. As received, they contain about 0.2% water. This water reacts rapidly with aromatic isocyanates to give a foamy gel. Therefore, aromatic isocyanates can not be used with undried HEM. Also, urethanes based on aromatic isocyanates discolor with time. Work with aromatic isocyanates was therefore curtailed after some initial trials.

Although the amount of water in the HEM material can be reduced using drying agents such as calcium sulfate and molecular sieves, it is not practical to try to dry the HEM material so that there is effectively no water in it, because the equivalent weight of HEM10 is 560 and that of water is 9 or 4.5, depending on whether or not only urea linkages are formed or whether biurets are also formed. Thus, 0.2% water corresponds to a ratio of equivalents of about 1:4 to 1:8, depending on the mechanism by which water reacts with isocyanate groups at the temperatures (30-40°C) used in these preparations.

Water reacts much more slowly with aliphatic isocyanates<sup>7</sup>. Among the more successful isocyanates when undried HEM material was used were hexamethylene diisocyanate (HMDI) and a much more

viscous material, known as Mobay Desmadour 3200<sup>1</sup>, formed from a high temperature reaction between HMDI and water to give an urea-containing isocyanate with a functionality of approximately three.

Attention was then focussed on the aliphatic isocyanate HMDI. The problem was to introduce bonds between the isocyanate molecules to make the resulting urethane molecules longer, and hence make the resin more viscous, while preserving or enhancing properties such as the flow of the resin, its water dispersibility, and its cure rate.

Several attempts were made to use the water in the HEM material along with added water to form ureas with the isocyanate groups. This should stiffen the resin and increase its viscosity over that obtained from a dry HEM10 reacted with HMDI. Resins of about 4 Pa.s (40 poises) were obtained but were very cloudy. Other resins in which the molecule was extended using PEG 400, a polyethylene glycol, and glycerol, a trifunctional alcohol, also had viscosities of about 4 Pa.s (40 poises). This is probably too low for an intaglio ink resin. In addition, the PEO content and methacrylate content of the product are lowered when alcohols such as glycerol and PEG400 are included in the reaction. (For each OH group, PEG400 attaches only 4 ethylene oxide units whereas HEM10 attaches 10 ethylene oxide units. Glycerol attaches no ethylene oxide units.)

The order of reactivity of primary alcohol groups, water, ureas, and urethanes with an aromatic isocyanate is about 500 : 100 : 85 : 1. Tin catalysts such as dibutyl tin dilaurate speed up the relative rate of reaction of the alcohol groups. Tertiary amines such as triethylene amine or triethylene diamine speed up the relative rate of reaction of water.

Triethylene diamine (DABCO<sup>1,8</sup>) was used as a catalyst to speed up the reaction of water with isocyanate so that its rate of reaction would be more nearly equal to that of primary alcohol groups with isocyanate. These preparations invariably gelled because there is too much water present in undried HEM. Similar results were obtained for HEM dried over calcium sulfate when the water-isocyanate reaction was accelerated with triethylene diamine. Drying over calcium sulfate was considered because it is a very simple procedure which could perhaps be tolerated in a production process. Similar results were obtained using HEM material through which a stream of dry air had been passed for 2 hours. It was therefore concluded that the reaction of isocyanate with the water in the HEM material would have to be suppressed by using a tin catalyst to speed up the isocyanate/alcohol reaction.

pH measurements carried out on various resin preparations suggested that the best curing resins (made from the driest HEM) had pHs in the range of 8.5, while resins made from undried HEM

had pHs in the range 7 to 8. Triethylene diamine was added to some preparations after the isocyanate reaction was complete to increase the pH, but the effect seemed to be small.

### 3.4.2 Aliphatic urethanes

One solution to the problem of extending HMDI to give resins with higher viscosities is to use a mixture of HMDI and Desmadour 3200<sup>1</sup>. In the manufacture of Desmadour 3200, extension of the isocyanate groups in HMDI is accomplished by using water to form amines from some of the isocyanate groups. The amine groups then react immediately with other isocyanates to form ureas, and the urea groups are reacted with some of the remaining isocyanates to give crosslinks in the form of biurets. The end result is HMDI extended with the least possible amount of hydrophobic material to give a trifunctional isocyanate.

Undried or partially dried HEM was reacted with aliphatic isocyanate in the presence of a tin catalyst to highly bias the reaction path to be primary alcohol reacting with isocyanate. Resins were made in which both trifunctional isocyanate (to give a higher viscosity) and difunctional isocyanate (to give better water dispersibility) were used with a 3% excess of primary alcohol groups from the HEM material. Mixtures of isocyanates were used so that a one step process could be developed. These preparations did not gel during the urethane synthesis and gave resins which had viscosities of about 2 to 40 Pa.s (20 to 400 poises), depending on the relative amount of trifunctional isocyanate. The resins were very stable against premature gelling during storage.

The pattern which emerged was that 1) HEM10 rather than HEM5 was necessary to confer water dispersibility, 2) the urethanes based on HMDI were easily dispersed in water but were not viscous enough (viscosity about 2 Pa.s=20 poises) and 3) the urethanes based on the trifunctional isocyanate were dispersible in water with some difficulty, at least partly because of their high viscosity of about 40 to 100 Pa.s (400 to 1000 poises).

Various resins were made from mixtures of HMDI and Desmadour 3200. Cure studies using a UV photoinitiator system suggested that HEM10 urethane resins with ratios of 1:1 and 1.4:1 in tri- to difunctional isocyanates (Desmadour 3200 to HMDI) cured well compared with commercially available dental resins based on methacrylates. Cure studies using the electron beam showed that the resins still needed 4 or more megarads to become non-tacky (they contained about 1% of BHT) and that the cured film did not have good enough mechanical properties. We therefore made resins with higher proportions of trifunctional isocyanate and lower BHT content. Using a trifunctional isocyanate should increase the crosslink density. Using less BHT should increase the cure speed. Preparations of various ratios of tri- to difunctional



isocyanates were synthesized (Table 1). Because a viscosity of at least 20 Pa.s (200 poises) was required, we then concentrated on the 10:1 preparation.

### 3.4.3 Resin stabilizers

BHT (butylated hydroxy toluene) retards the cure reaction as well as stabilizing the resin against oxidative cure. Resins were made successfully with low amounts of BHT. The resin based on the trifunctional isocyanate cured after 2 megarads of exposure to the electron beam, which was satisfactory. Much higher exposures, in excess of perhaps 5 megarads or so, seriously weaken the paper on which the ink is printed. The resin based on HMDI cured in less than 2 megarads. (These cure rates are approximate and are very dependent on the amount of stabilizer added to the resin.)

Several other materials were evaluated as potential stabilizers, but none protected the resin during the urethane synthesis. Tests using methyl ether of hydroquinone (MEHQ) instead of BHT to protect the HEM during the isocyanate reaction produced gels within hours, showing that the MEHQ is rapidly consumed by the isocyanate. Using benzoquinone as the sole stabilizer during the isocyanate reaction also rapidly produced gels.

BHT contents of 0.1% seemed feasible in small resin preparations where air is fairly freely accessible to all parts of the resin. The resins were stored in clear glass containers and thus were subject to photolysis. Resins containing less than 0.5% of BHT gelled within one or two weeks when stored in clear glass bottles in a lighted lab, whereas resins with 3% of BHT were more or less infinitely stable under these conditions, but were slow to cure in the electron beam.

BHT is necessary to keep the resin from gelling during the formation of the urethane, but preparations of viscous resins with moderate or lower amounts of BHT invariably gelled in the bottom of the container after several weeks of storage. This strongly suggested the need to include a chain transfer stabilizer to inhibit anaerobic polymerization, where the BHT is not very effective.

Such a stabilizer system will include about 0.05% BHT to protect the resin from gelling during the isocyanate reaction because of polymerization of the methacrylate groups. A resin preparation was carried out with 0.05% by weight of BHT and 0.05% by weight of various additional stabilizers added in solution in pentaerythritol triacrylate, which itself was then present as 20% of the resin formulation. The following stabilizers were tried: (1) more BHT, (2) benzoquinone, (3) ageing, (4) n-hexyl vanillate, (5) ascorbyl palmitate, and (6) methyl ether of

hydroquinone (MEHQ). The intent was to find stabilizers which could be added before the resin preparation reaction. The resin containing BHT and benzoquinone remained liquid long after the others had gelled.

A cure test carried out using a photoinitiator and a visible light source showed that the 0.05% BHT / 0.05% benzoquinone resin cured as well or better than other resins we had made, and thus indicated that the benzoquinone did not poison the cure significantly when an appreciable amount of initiation occurred. The film produced from the resin was elastomeric, and had a somewhat tacky feel, even when well cured. This is a consequence of the low glass transition temperature conferred by the polyethylene oxide linkages in the resin, and is an unfortunate side effect of using these sequences to confer water dispersibility and rapid cure (for methacrylates). The effect of crosslinkers was then investigated.

#### 3.4.4 Crosslinkers

A series of 10:1 urethane resins with 0.05 to 0.1% BHT, 0.05 to 0.1% benzoquinone, and 10 to 20% of pentaerythritol triacrylate were cured in the electron beam. All cured fairly well at 0.5 Mrad, and well at 2 Mrad. As expected, the films with low amounts of the trifunctional crosslinker, pentaerythritol triacrylate, were rubbery. Those with 20% of this material all cured to a smooth film which did not have much friction when rubbed, and which seemed qualitatively to be reasonably hard.

Tests were then carried out on a series of crosslinkers in resins stabilized with 0.1% BHT and 0.1% benzoquinone. The crosslinker was kept at 20% by weight of the urethane resin. Three crosslinkers were used: 1) pentaerythritol triacrylate, which has a free hydroxyl group and therefore is expected to give a slightly tacky if well adhering film, and which is water insoluble; 2) trimethylol propane triacrylate, which has no such hydroxyl group, and which is also water insoluble; and 3) PEG400 diacrylate, which is water soluble. The first two gave better films than the third, as expected since they are trifunctional and contain no PEO.

#### 3.4.5 Design of an ink varnish

The urethane resin is essentially acting as a reactive surfactant. When it is polymerized alone or diluted with PEO-containing diluents such as PEG400 diacrylate, weak films are obtained. 20% w/w of a trifunctional crosslinker dissolved in the urethane resin gave a film which was sufficiently non-tacky

and strong. Trimethylol propane triacrylate was selected as the crosslinker because it is believed to be less toxic than pentaerythritol triacrylate.

It was then found that the intended application required a less viscous vehicle. The choices were to dilute the vehicle further with a water soluble, small molecule monomer, or to change the viscosity of the urethane resin by including some diisocyanate in the reaction. Table 1 shows that the gain in PEO content and hence in water dispersibility for the urethane resin is small compared with large decreases in viscosity. Addition of a non-viscous diluent also causes very large decreases in viscosity. An ink was made from the urethane resin based entirely on the trifunctional isocyanate, with 20% w/w trimethylol propane triacrylate as a crosslinker and diluted with 50% w/w of polyethoxylated trimethylol propane triacrylate as a reactive and water soluble diluent. The ink dispersed in water containing a surfactant and cured very well with two megarads of 165KV electrons. The resultant film was flexible and did not smear. No color could be scrubbed off onto a bond-like paper.

The dispersibility of the ink in water containing no additives was not satisfactory. Tests showed that the vehicle containing the water-soluble small molecule crosslinker had poorer water dispersibility than the urethane/trimethylol propane triacrylate mixture alone, presumably because the water soluble monomer was not concentrating in the micellar interface and hence was not acting as a surfactant. We therefore synthesized a resin based entirely on difunctional isocyanate and HEM10 with the reaction mixture diluted with 20% w/w tri methylol propane triacrylate. This resin is expected to have better surfactant properties and can be mixed with the trifunctional urethane resin to give a mixture of appropriate viscosity. Ink trials will be necessary to establish the required viscosity. The urethane/crosslinker mixture can then be synthesized in a one step procedure.

Table 1 Viscosity vs. composition of urethane resins

Viscosity at 20°C and PEO content vs. composition  
for urethane/HEM10 oligomers

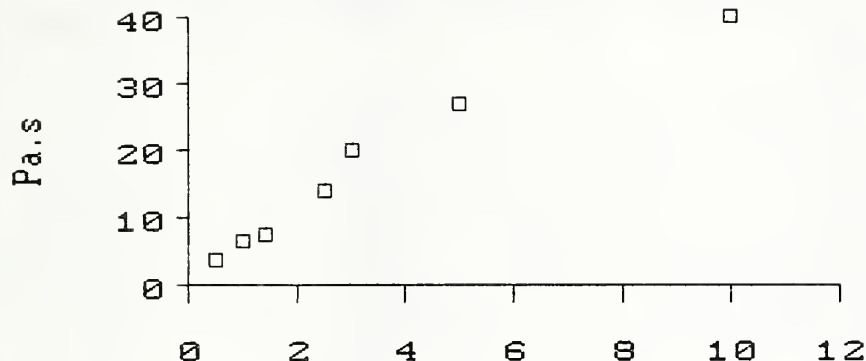
ratio of tri:di isocyanate equivs	viscosity (Pa.s)*	% PEO w/w
0:1	1.6	72.1
0.5:1	3.2	68.8
0.5:1	3.6	
0.5:1	3.9	
1:1	5.0	
1:1	6.5	66.9
1:1	7.0	
1.4:1	7.5	66.1
2.5:1	13.5	64.8
2.5:1	14.0	
2.5:1	14.0	
3:1	19.0	64.5
3:1	20.0	
3:1	20.0	
5:1	27.0	63.7
10:1	40.0	63.1
1:0	100?	62.3

Viscosity of trifunctional urethane +  
20% w/w crosslinker = 38 Pa.s at 20°C

Viscosity of trifunctional urethane +  
50% w/w crosslinker = 3.5 Pa.s at 20°C

\* 10 poises = 1 Pa.s

## Viscosity of urethane mixtures



Tri:di isocyanate

Viscosity of urethane resins (vertical axis) vs. ratio of tri to di functional isocyanate used (horizontal axis)

### 3.4.6 Spreadsheet for urethane synthesis

A spreadsheet (Figure 3.4.7) was used to generate "recipes" for urethane resins. The user types the number of molecules in the reaction formula into the 4th column of the spreadsheet. This column is labeled "recipe (molecules)". The compounds are identified in column 1. The number of reactive groups per molecule is given in column 2 and the equivalent weight of the molecule is given in column 3. The information in columns 1, 2 and 3 is changed only when a new reactant is to be used. The number of equivalents in the recipe is calculated and displayed in column 5. The user should check the net equivalents given at the bottom of column 4 to ensure that he has specified the numbers of equivalents correctly and that there is an excess of OH groups. To facilitate this checking, isocyanate equivalents are given as negative numbers and OH groups are given as positive numbers. Hence the sum of equivalents should be slightly positive for a recipe in which OH groups are in slight excess.

The spreadsheet uses molecular ratios. The resin oligomer is "designed" by drawing a stick diagram of the intended product and entering the appropriate quantities into the spreadsheet. Urethanes with such equivalents ratios of tri to di isocyanate as 1.4:1 and 2.5:1 were synthesized. For a particular ratio of tri to di isocyanate equivalents such as 1.4:1, the numbers of

molecules of the two isocyanates, given by  $1.4/3$  and  $1/2$ , respectively, are entered as formulae (i.e., as  $1.4/3$ , not as the result of dividing 1.4 by 3) directly into the equivalents column of the spreadsheet. "Recalculate" is pressed with zeros elsewhere in the equivalents column. The total number of isocyanate equivalents is obtained from column 5. This number is entered as the number of equivalents of HEM10, and "recalculate" is pressed again. The recipe will then have balanced equivalents of isocyanate and alcohol.

Because the PEO materials (such as the HEMs) are hygroscopic, and because the equivalent weight of water is so small compared with those of the HEM materials, the stoichiometry of the HEMs is perturbed by the presence of even a small amount of water. The percentage of water in HEM10 is typed into the spreadsheet cell at the bottom of column 8 (.22 in the example). Water may also be added separately as a reactant. The total percentage of water from these two sources is displayed in column 6 just below the data entry part of the spreadsheet.

The total amounts of material to be made are provided by the user at the bottoms of columns 7 and 8. These are the volume and the weight of material respectively (15 and 100 in the example). The formula weights in column 6 are scaled to these quantities in columns 7 and 8 respectively. This allows the user to specify in one spreadsheet two total amounts to which the amounts of the individual components will be scaled. Typically, the synthesis was first carried out on a small scale of 5 to 15 mLs before being scaled up to 100 to 150 mLs or grams. Volume was typically used for the smaller amount so that the formulation would fit comfortably in a small vial (2 or 4 dram).

The weight percentage of PEO in the final resin is given at the bottom of column 4. Just below, also in column 4, is the ratio of equivalents of tri- to di-functional isocyanate in the recipe. The cure speed is estimated assuming that pure trifunctional methacrylate resins cure at two Mrads, and that the cure rate will change in proportion to the concentration of reactive groups in the resin. Acrylate groups are assumed to cure 3.5 times faster than methacrylate groups.

The weights of additives when added in 0.05%, 0.10% and 20% w/w are given at the bottom of columns 7 and 8.

### 3.4.7 Example of Spreadsheet for urethane synthesis

Weights of material needed to make U/HEM/TDI/PEG resins

Jul 17, 1987 5:10 PM

cmpd	gps/mol	USER TYPES HERE			formula weights	weights scaled to vol	weights scaled to wt
		equiv weights	recipe (molecules)	calc. equivs			
Des3200	3	181	3.33	-10.00	1809.82	3.972	24.07
HMI	2	84	.50	-1	84	.184	1.12
TDI	2	87	0	0	0	0	0
SiCl4	4	42.45	0	0	0	0	0
A-174	3	82.80	0	0	0	0	0
CHdiNCO	2	111	0	0	0	0	0
PEG400	2	200	0	0	0	0	0
C3H5(OH)3	2	46	0	0	0	0	0
HEM10	1	526	10.67	10.67	5612.42	12.317	74.65
HEM5	1	306	0	0	0	0	0
HEA10	1	512	0	0	0	0	0
HEA5	1	292	0	0	0	0	0
MeOH	1	32	0	0	0	0	0
HEM15	1	732	0	0	0	0	0
H2O	4	4.50	0	2.74	12.35	0	0
HOC2H4OH	2	31	0	0	0	0	0
SR-444	.56	599.35	0	0	0	0	0

Equivalents after reaction .1800 % H2O = .22 %H2O: HEM .22  
 Total volume of reactants 6835.08 Final volume = 15  
 Total weight of reactants 7518.59 Final weight = 100  
 Total PEO content in % = 62.58 Cure speed = 2.00  
 Ratio of Des3200 to HMDI 10.00 additive 0.05% = .008 .050  
 additive 0.10% = .016 .100  
 INSTRUCTIONS: additive 20% = 3.294 19.96

Type the numbers of molecules in the recipe in column D  
 Type the % of water in HEM10 in F23  
 Type total volume required in G24 or total weight in H25  
 The weights to use are given in columns G and H  
 Check the sum of equivalents in D23. A positive number means excess OH.

#### 4 Water wipeability

The ease of dispersion in water of the four types of water-dispersible resins follows the percentage of PEO in the resin molecule. The urethanes contain the least PEO and are the least dispersible, although they do disperse in water on vigorous shaking or when aided by scrubbing. When the resins are compounded into inks, the pigment exerts a large effect on the dispersibility of the ink. This effect has not been studied because pigment selection for these inks is only beginning at BEP. The first three types of resin dispersed very well in water, but are much too low in viscosity and cured only slowly.

#### 5 Cure Speed

Urethane resins such as those based on the trifunctional isocyanate contain three methacrylate groups per molecule, which corresponds to three moles of methacrylate groups in about 2100 grams of material. A small molecule crosslinker such as trimethylol propane triacrylate contains three moles of acrylate groups in 338 grams of material. Since acrylate groups are between 3 and 10 times more reactive than methacrylate groups, and the crosslinker has effectively  $2100/338=6.2$  more polymerizing groups per unit weight than the urethane resin, it is clear that the crosslinker can exert an enormous influence on the cure speed as well as on the mechanical properties of the cured film. The function of the urethane is to act as a highly viscous, curable surfactant. It renders the crosslinker water dispersible and wets the pigment well. Because the urethane resin is highly viscous, the pigment can be dispersed well in it on a three roll mill. Also, the urethane resin can be diluted with at least 30% of crosslinkers and less viscous surfactants and the ink will still be suitable for the intaglio process.

Our assessments of cure were qualitative and were made by indenting the cured film with a pencil. These assessments were sufficient for our purposes. Our initial efforts were geared toward making a resin which was sufficiently water dispersible and sufficiently viscous. Relating the cure rate to the structure and viscosity of the resin was complicated by the variable amounts of BHT we placed in the resins to act as stabilizers. Subsequent efforts concentrated on using the water in the HEM material to increase viscosity by forming urea links. The spreadsheet approach was developed at this time and allowed us to estimate the PEO content of various recipes quickly and easily. Work then concentrated on mixing the di- and tri-functional isocyanates to give more viscous urethane resins. The trifunctional isocyanate pulled into long strands and conferred this desirable property to the urethane resin. Crosslinkers were then added to make the resin cure more quickly and to make the cured films stronger. At this point, we were equally concerned about film strength, resistance to premature



gelling, and cure speed. Several materials were tried to increase the stability of the uncured resin without unduly poisoning the cure. Eventually, a satisfactory film was obtained with a fast enough cure and with the expectation that the toxicity of the uncured resin would be reasonably low. The final cure criterion used was no transfer of color from ink cured with two megarads when wiped under pressure with rough paper.

## 6 Conclusions

Several types of non-ionic resins which cure under the action of radiation such as UV or electron beam have been synthesized. These resins disperse in neutral water when uncured. The water dispersibility is conferred by incorporating polyethylene oxide sequences in the resin molecules. The polymerizing action is conferred by methacrylate groups. Typically, one end of each polyethylene sequence is attached to a methacrylate group, and the other end is chemically linked in various ways to produce resins varying from 2 to 4 in methacrylate functionality. The linking moieties used are (1) a phosphazene ring, (2) a siloxane center, (3) a poly (methyl methacrylate backbone, and (4) a mixture of difunctional and trifunctional isocyanates.

When the resins containing the urethane linkages were used with low viscosity crosslinkers, the mixtures were of appropriate viscosity for use in intaglio inks and cured with less than two megarads exposure to give reasonably flexible scuff-free films. The other resins were not viscous enough for use in intaglio inks and in some cases cured too slowly.

A patent application based on the urethane resins has been filed.

## References

1. Disclaimer: Identification of commercial materials in this report serves to illustrate procedures, materials and equipment and must not be taken as endorsement of said materials.
2. R.A.Shaw, B.W.Fitzsimmons, and B.C.Smith, "The phosphazenes (phosponitrilic compounds)", Chem. Rev. 62, 247-281 (1962).
3. R.A.Shaw, R.Keat, and C.Hewlett, "Phosphazene compounds", Chapter 1 in Preparative Inorganic Reactions, Vol. 2, W.L.Jolly, ed., Interscience, (1965).
4. H.R.Allcock "Recent advances in phosphazene (phosponitrilic) chemistry", Chem. Rev. 72, 315-356, (1972).

5. M.Anzai and M.Ohashi, "Studies on the reaction product of hexachlorocyclotriphosphazene and 2-hydroxyethyl methacrylate and on the physical properties of its polymer", J. Nihon Univ. Sch. Dentistry 26, 109-118, (1984).
6. M.Anzai and M.Ohashi, "Studies on composite resins with hexa(methacryloylethylene-dioxy)cyclotriphosphazene used as a monomer. Filers and physical properties", J. Nihon Univ. Sch. Dentistry 26, 238-242, (1984).
7. B.A.Dombrow, "Polyurethanes", Reinhold Publishing Corporation, New York (1957).
8. "DABCO, Properties, Reactions and Applications", Air Products and Chemicals, Inc., Performance Chemicals Division, Box 538, Allentown, PA 18105 (1978).

## Appendix 1: Synthesis of urethane PEO methacrylates

### A) HMDI/HEM10 recipe for low viscosity resins based on urethane methacrylates

This resin is the addition product of hexamethylene isocyanate with HEM10. The HEM10 is used in 97% of the stoichiometric quantity. The remaining isocyanate groups are consumed by the water in the HEM10. The reaction is carried out as follows. The HEM10 is placed in a bottle of sufficient size that the final reaction mixture will be less than half the volume of the bottle. Tertiary butyl hydroxytoluene is added in 0.05% by weight quantity based on the weight of the urethane product (i.e., the combined weights of the isocyanate and the HEM10). The same weight (0.05 wt%) of benzoquinone is added to act as a post reaction stabilizer.

The resin as used at BEP contains at least 20 wt% of a trifunctional or higher functional crosslinking comonomer to confer appropriate film properties. If the comonomer does not contain hydroxyl groups, it also may be added at this stage. Trimethylol propane triacrylate has been used and is satisfactory.

The isocyanate is then added to the bottle, and the mixture shaken well for a few seconds. Reaction does not begin at any significant rate until the catalyst is added. Dibutyl tin dilaurate catalyst is added as one drop per 10 mLs of reaction mixture at these small volumes of reactants.

The mixture is shaken, and cooled (an air stream may suffice) to keep it under 30°C. If the comonomer is present, the thermal capacity of the mixture in 10g to 100g quantities is such that not much cooling is needed. After 30 minutes, the reaction can be left unattended. The bottle is rotated in a horizontal position at a slow rate for at least 16 hours and preferably more if time is not important. The rotation speed is such that the resin is able to flow over the surface of the bottle even when the reaction is complete. The final viscosity when no comonomer is used is about 4 Pa.s (40 poises) and is 1.5 Pa.s (15 poises) when 20% of trimethylolpropane is present. Reaction is complete within 24 hours, during which time the reaction mixture should be kept in the dark or in subdued light. The resultant resin should be stored in dark bottles. The resin is stable in clear half-filled bottles for several weeks in normal laboratory fluorescent lighting.

For 100 grams of urethane methacrylate resin, one would use

14.11 g HMDI  
85.70 g HEM10  
0.050 g BHT  
0.050 g benzoquinone  
10 tin catalyst.

B) High viscosity resins based on Mobay 3200 trifunctional isocyanate and HEM10 hydroxy polyethylene oxide methacrylate stars

All ingredients are mixed as in the preparation of the HMDI/HEM10 resin, tertiary butyl hydroxy toluene and benzoquinone are added in 0.05% amount by weight as stabilizers, and tin catalyst is added in one drop per 10 mls. The reaction mixture is kept below 30°C. Reaction is complete after 24 hours, during which time the reaction mixture should be rolled or stirred and kept in subdued light or in the dark. The final viscosity is in the region of 100 Pa.s (1000 poises) if no comonomer is present, and is about 40 Pa.s (400 poises) in the presence of 20 wt% trimethylolpropane.

The following quantities are used to make 100 grams of the 3200/HEM10 resin:

26.64 g 3200  
73.69 g HEM10  
0.050 g BHT  
0.050 g benzoquinone  
10 drops tin catalyst.

#### INGREDIENTS

The raw materials include but are not limited to:

- 0% to 30% Poly ethylene oxide,  $\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ ,  $n=5$  to 100.
- 40% to 90% Hydroxy ethylene oxide acrylate or methacrylate,  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n-\text{C}(\text{O})\text{C}(\text{R})=\text{CH}_2$ ,  $n=3$  to 50,  $\text{R}=\text{H}$  or  $\text{CH}_3$ .
- 5% to 30% Isocyanate, known types such as hexamethylene diisocyanate,  $\text{OCN}-(\text{CH}_2)_6-\text{NCO}$ , and Mobay 3200,  $\text{R}-(\text{NCO})_3$ .
- 0% to 50% Comonomer, known types, see below.
- 0% to 1% Catalyst, known types such as dibutyl tin dilaurate
- 0% to 0.5% Stabilizer, known types such as BHT and benzoquinone.

#### COMONOMERS

Blending the resins described here with comonomers such as crosslinkers is desirable to produce a more resistant film. The comonomers may be selected from commercially available

crosslinkers such as PEG400 diacrylate, trimethylolpropane triacrylate and pentaerythritol triacrylate, pentaerythritol tetraacrylate, and dipentaerythritol pentaacrylate.

#### SOURCES OF MATERIALS

The isocyanates HMDI and Desmadour 3200 were obtained from  
Mobay Chemical Corporation  
Mobay Road  
Pittsburgh PA 15205-9741  
(412) 777-2000.

The hydroxyl ethylene oxide methacrylates and acrylates (HEM5 and HEM10) were obtained<sup>1</sup> from

Alcolac  
3440 Fairfield Road  
Baltimore, MD 21226  
(301) 355-2600.

The crosslinkers trimethylolpropane triacrylate and pentaerythritol triacrylate were obtained<sup>1</sup> from

Sartomer Company  
Marshall Building  
West Chester Pike  
West Chester, PA 19382  
(215) 430-2200.



NIST-114A  
(REV. 3-90)

U.S. DEPARTMENT OF COMMERCE  
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY

**BIBLIOGRAPHIC DATA SHEET**

1. PUBLICATION OR REPORT NUMBER

NISTIR 4564

2. PERFORMING ORGANIZATION REPORT NUMBER

3. PUBLICATION DATE

MAY 1991

4. TITLE AND SUBTITLE

Synthesis of Non-Ionic Water-Dispersible Resins for Use in Intaglio Inks Curing by Electron Beam Radiation

5. AUTHOR(S)

Brian Dickens, Barry J. Bauer, and Walter J. Pummer

6. PERFORMING ORGANIZATION (IF JOINT OR OTHER THAN NIST, SEE INSTRUCTIONS)

U.S. DEPARTMENT OF COMMERCE  
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY  
GAITHERSBURG, MD 20899

7. CONTRACT/GRANT NUMBER

8. TYPE OF REPORT AND PERIOD COVERED

Annual Report, Sept. 30, 1987

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS (STREET, CITY, STATE, ZIP)

Office of Research and Technical Services  
Bureau of Engraving and Printing  
14 & C Sts. S.W.  
Washington, D.C. 20226

10. SUPPLEMENTARY NOTES

11. ABSTRACT (A 200-WORD OR LESS FACTUAL SUMMARY OF MOST SIGNIFICANT INFORMATION. IF DOCUMENT INCLUDES A SIGNIFICANT BIBLIOGRAPHY OR LITERATURE SURVEY, MENTION IT HERE.)

Several types of non-ionic resins which cure under the action of radiation such as UV or electron beam have been synthesized. These resins disperse in neutral water when uncured. The water dispersibility is conferred by incorporating polyethylene oxide sequences in the resin molecules. The polymerizing action is conferred by methacrylate groups. Typically, one end of each polyethylene sequence is attached to a methacrylate group, and the other end is chemically linked in various ways to produce resins varying from 2 to 4 methacrylate functionality. The linking moieties used are (1) a phosphazene ring, (2) a siloxane center, (3) a poly (methyl methacrylate backbone, and (4) a mixture of difunctional and trifunctional isocyanates.

When the resins containing the urethane linkages were used with low viscosity crosslinkers, the mixtures were of appropriate viscosity for use in intaglio inks and cured with less than two megarads exposure to give reasonably flexible scuff-free films. The other resins were not viscous enough for use in intaglio inks and in some cases cured too slowly.

12. KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)

electron beam; intaglio ink resin; methacrylate; non-ionic; radiation curing; polyethylene oxide

13. AVAILABILITY

UNLIMITED

FOR OFFICIAL DISTRIBUTION. DO NOT RELEASE TO NATIONAL TECHNICAL INFORMATION SERVICE (NTIS).

ORDER FROM SUPERINTENDENT OF DOCUMENTS, U.S. GOVERNMENT PRINTING OFFICE,  
WASHINGTON, DC 20402.

ORDER FROM NATIONAL TECHNICAL INFORMATION SERVICE (NTIS), SPRINGFIELD, VA 22161.

14. NUMBER OF PRINTED PAGES

26

15. PRICE

A03

ELECTRONIC FORM







