Synthesis of Non-Ionic and Ionic Resins for BEP Intaglio Inks Curing by Electron Beam Radiation

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Executive Summary

    In FY87 and FY88, syntheses were devised and carried out to
produce resins which are water dispersible and which cure under
the action of UV radiation or electron beams. These resins
include (1) FY87 work on urethane/polyethylene oxide/methacrylate
nonionic resins, (2) FY88 work on polymethacrylate
backbone/polyethylene oxide methacrylate graft nonionic resins,
and (3) FY88 work on methacrylate resins containing carboxylic
acid functionality. Resins of types 1 and 2 wash in neutral
water. Resins of type 3 wash in neutral water if used as salts
and in caustic water solutions if not used as salts. All the
resins disperse pigments used in intaglio inks.

    FY87 work on polyurethane resins which wash in neutral water
was concluded. Intaglio inks were made from these resins at BEP.
Small scale laboratory tests at BEP showed that these inks had
acceptable cure rate, viscosity and washability. This technology
was transferred to BEP for scaleup.

    Work on polymethacrylate backbone/polyethylene oxide
methacrylate graft nonionic water-soluble polymers was continued
from FY87. Water dispersible resins of appropriate viscosity
were produced.

    A new effort was undertaken to produce resins that contain
carboxylic acid functionality. These resins wash in caustic
water solutions. An intaglio ink was formulated at BEP from the
reaction product of an aliphatic dianhydride and glycerol
dimethacrylate. When the ink formulation included lithium
carbonate and poly ethylene glycol diacrylate, acceptable cure
speed, washability, viscosity and stability resulted. A second
good candidate for an intaglio ink resin was obtained by reaction
of the aliphatic monoanhydride succinic anhydride and glycerol
dimethacrylate.

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1: Introduction

The inks currently used to print US postage stamps on web presses are dried by heat evaporation of solvents. Emission of solvents into the atmosphere is governed by Local and Federal Government Regulations. Reduction of these emissions to acceptable levels can be accomplished by either of two methods available to the BEP. 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 removed using catalytic after-burners. This type of ink is known as a heat-set ink. Evaporation of solvent using IR ovens suffers from the drawback that light colors absorb heat less readily than dark colors and thus dry more slowly.

Heat-set inks are not acceptable for currency printing because heat-dried ink can later be removed from the substrate by solvents, negating the safeguard in currency printing that blank printing paper is difficult to obtain.

The second option is to use ink resins which themselves are liquids but which can be transformed into crosslinked solids by chemical reaction. Much less solvent, if any, is needed in these inks. Web inks must dry very quickly, so the chemical curing reactions must be initiated by radiation. Crosslinked inks can not be removed satisfactorily using solvents. This report is concerned with radiation-curable resins and inks which form crosslinks on curing.

Among the advantages of the electron beam are that it cures all colors equally well and cures thicker layers of ink than do heat-set and conventional UV curing. The prototype resins in our approach have been designed to cure in 2 megarads or less exposure to a 165 KV electron beam.

It should be noted that recent advances have produced a commercially available (Fusion Systems) mercury lamp which has double (600 watts per 2.54 cm) the previous output (300 watts per 2.54 cm). 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 of E-beam curing and UV curing are very similar, so resins can be developed simultaneously for both systems.

Inks for intaglio presses must be compatible with an aqueous cylinder-wipe system. Thus, the inks must wash off a wiping blade which cleans a wiping cylinder and must remain in aqueous 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, and ether groups.

This work was part of a continuing effort to produce resins for use in formulation of intaglio inks for the printing of postage stamps and security documents. The inks are to be cured by exposure to an electron beam. The uncured inks are cleaned from the roller and wiping blade by washing the wiping blade with neutral water or with caustic water. Our previous efforts involved polyethylene oxide-containing materials as non-ionic water-soluble groups and methacrylate groups as the E-beam polymerizable groups. Laboratory scale work on these urethane/polyethylene oxide/methacrylate resins has now been concluded and information on the synthesis has been provided to BEP for patenting and scaleup. Some effort on nonionic resins continued into FY88.

Work on ionic resins was also performed to make resins that would wash with caustic water solutions. This requires different synthetic methods and monomer types. Several monomer systems have been designed, synthesized and tested.

2: Review of Required Resin Properties

2.1: Curing Reaction

E-beam irradiation of organic materials results in bond cleavage. The free radicals thus formed can initiate polymerization. Acrylates and methacrylates are the groups most commonly used in free radical polymerization.[1] Although methacrylates polymerize more slowly than acrylates, methacrylates generally have lower toxicity and are preferred in cases where cure speed is not a problem. If the resin molecules have only one polymerizable group, polymerization produces linear polymers. These are molecules with a linear backbone and no crosslinks to other molecules. Linear polymers form a solid film, but since this film is not crosslinked it is susceptible to dissolution in solvents.

Crosslinking is necessary for resistance to chemical and mechanical attack. For appreciable crosslinking, the resins must contain monomers with functionality of two or greater. The higher the functionality, the more rapid the cure and the more densely crosslinked the film. A side effect to be considered is that as the proportion of highly functional molecules in the material is increased, more and more reactive and potentially polymerizable groups will remain unreacted in the final film. This is because the film becomes stiffer (more viscous) as it cures and eventually becomes so stiff that the growing chains can no longer move at the temperature of the polymerization. If high temperatures are used to force the cure reaction to go to higher extents, the film may be brittle at normal temperatures.

Another type of curing mechanism involves cationic polymerization.[2] Initiators are added that form cations upon exposure to the E-beam. The polymerizable groups are generally

vinyl ethers instead of acrylates or methacrylates. While these resins have the disadvantage that they require strict conditions of preparation (for example, rigid exclusion of water), they are probably less toxic than acrylates and possibly methacrylates and have a very high cure rate. A proposal for research on this type of resin was rejected by BEP on the grounds that the technology was too unproven.

2.2: Water Washability

For satisfactory printing, the printing cylinder has to be cleaned by a series of wiping rollers, which are themselves cleaned by a wiping blade. Thus, the uncured intaglio inks have to be efficiently and continuously removed from the wiping blade during the printing process. Because the monomers constitute the greatest part of the liquid part of the inks, this requires that the monomers be dispersible in a solvent system. Due to environmental reasons, the solvent of choice is based on water. Non-ionic intaglio ink resins disperse in water. In some cases, a small amount (about 1%) of surfactant is required.

The ionic type of resin contains acid groups that make these resins washable by forming salts in basic water. The standard aqueous washing solvent is water containing 1% NaOH and 1% surfactant and is known as Dalmar solution. Good washability requires that the resin have an acid number of 50 mg KOH/g resin or greater. Viscosity is also important; typically, a viscosity of about 10 to 15 Pa s (100 to 150 Poises) gives an ink which performs well in laboratory tests. Addition of basic materials to the ink increases its ease of washing by pre-converting the carboxylic acid group into a salt. Volatile amines are commonly added to paints and inks for this purpose.

Non-ionic materials such as those containing polyethylene oxide do not require basic water for washing because they are soluble in neutral water. This is in principle a big advantage in the printing process because the washing solution does not have to be formulated and sodium hydroxide is not present as a pollutant. Also, neutral water is preferred for non-ionic monomers because some non-ionic monomers disperse more poorly in Dalmar solution than in neutral water because of the ionic strength of the Dalmar solution.

Nonionic moieties are much less efficient than ionized carboxylate groups at solubilizing resins in water-based washing solutions. To achieve the same washability as ionic resins, a much larger fraction of the non-ionic resin molecule must be devoted to the dispersion properties and hence less is available to devote to the film-forming properties. Non-ionic resins are expected to form much less densely crosslinked films than do ionic resins. Also, because of the flexibility of the polyethylene oxide parts of the molecules, those non-ionic

monomers based on polyethylene oxide will produce flexible and perhaps rubbery films. Thus, the water dispersibility is obtained at the expense of curability and film hardness.

2.3: Resin Viscosity

An intaglio ink can easily be made from a resin with viscosity in the range of 5 to 30 Pa s (50 to 300 poises). The most desirable situation is to have two resins that form a compatible mixture, one resin being of higher viscosity and the other of lower viscosity. These can then be mixed in various ratios to produce a series of composite resins with viscosities in the desired range. Several commercial resins, such as polyethylene glycol diacrylate, have high solubility in water and low viscosity. It was therefore necessary to produce a resin of high viscosity to blend with the low viscosity commercial resins to obtain the appropriate viscosity range.

2.4: Resin Stability

E-beam resins must be stabilized against premature polymerization. Butylated hydroxy toluene (BHT) and methyl ether of hydroquinone (MEHQ) are commonly used as stabilizers in commercial acrylate and methacrylate resins. The stabilizers function by trapping free radicals that have become oxygenated by reaction with atmospheric oxygen. In the E-beam printing process, the ink is blanketed by nitrogen, keeping the radicals formed from reacting with oxygen. Under these conditions the stabilizer does not effect the curing reaction.

Because the resins must be reactive enough to cure during a brief exposure to the electron beam, they are naturally susceptible to gelling by heat, light and oxidation. This tendency is exacerbated when the resin is made into an ink, because other free radical-producing reactions, such as decomposition of the traces of hydroperoxides present in nearly all organic materials, can readily occur by the action of transition metal ions dissolved from the pigments. Therefore, the pigments have to be chosen with care.

3: Non-ionic Water-Soluble Resins

3.1: Introduction

All of the efforts in FY87 were on non-ionic resins that disperse in neutral water. Poly ethylene oxide (PEO) was chosen to confer the water-dispersibility and a variety of materials containing PEO were produced.[3] All of the structures contained ethylene oxide sequences terminated at one end with methacrylate groups. The PEO methacrylate monomers were available from Alcolac of Baltimore, Maryland and are now available from Interez of Jeffersontown, Kentucky.[4] (Note that PEO is sometimes

referred to as polyethylene glycol, PEG. The distinction between PEO and PEG is small. PEG is a polyethylene oxide sequence which terminates in hydroxyl groups. PEO is a polyethylene oxide sequence where the end groups are not specified but are presumably not hydroxyl groups.)

Multifunctional star-shape molecules were made by reaction of the terminal hydroxyl group of the polyethylene glycol monomethacrylate with polyfunctional molecules containing isocyanate or chlorosilane or chlorophosphazene groups. These multifunctional star-shape resins crosslink when the electron beam polymerizes the attached methacrylate groups.

Urethane-based methacrylate resins containing ethylene oxide sequences were made from the reaction of difunctional and trifunctional isocyanates with hydroxyethyl methacrylate derivatives. E-beam inks made from these resins washed in neutral water in an acceptable manner and cured to a hard film upon exposure to 2 Mrads of a 165 KV electron beam. A wide range of viscosities could be attained. A patent application has been filed on behalf of BEP.

3.2: PMMA Homopolymer and Copolymer Backbone Resins

Ethoxylated methacrylic acid was polymerized to form a multifunctional graft-like structure of a methacrylate backbone with side chains containing 1, 5 or 10 units of ethylene oxide (the commercial designation of these monomers is HEM-D, HEM-5, and HEM-10 respectively).[4] The terminal -OH groups on the side chains were then esterified with acryloyl chloride or methacryloyl chloride to give a polymerizable resin (Figure 1). Under the influence of an electron beam, the acrylate groups polymerize and crosslink the resin.

If the commercial HEM monomers are polymerized without transfer agent, an insoluble, infusible gel results. HPLC studies indicated that difunctional methacrylates are present in the commercial monomer. When no transfer agent is present, the kinetic chain length of the polymerization reaction is sufficiently long to allow these difunctional units to cause crosslinking. Preparative HPLC could be used to remove these impurities to prove the point in small scale laboratory testing, but this technique would be far too costly for commercial resin production. The addition of a transfer agent causes the kinetic chain length to be short enough to prevent crosslinking during preparation of the resin. However, this results in very short chains of both the kinetic and macro molecular varieties, which causes the resin to be of low viscosity. These resins cured when exposed to an electron beam, but inks made from them did not have the proper rheological properties.
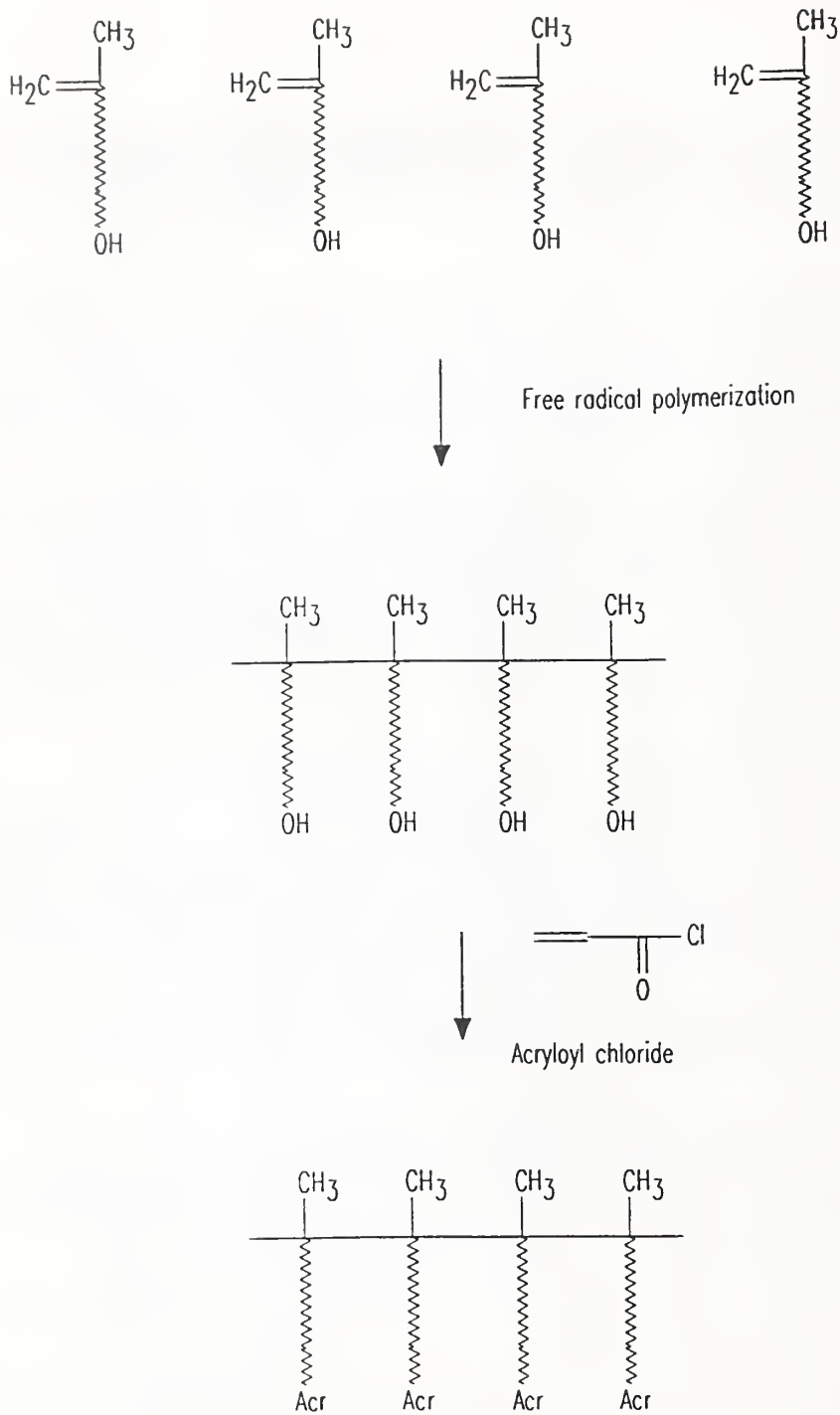
Figure 1: Polymerization of HEM-10 to give polymethyl methacrylate backbone with PEO side arms subsequently terminated with acrylate groups.

Because the major part of the structure of HEM-5 and HEM-10[4] is ethylene oxide, the glass transition temperatures of polymers derived from these monomers are quite low (literature values range from -115 to -40°C), causing films based on these polymers to be rubbery and perhaps sticky. The viscosity of small oligomers is low, but changes very rapidly with molecular chain length, going from a few poises to infinity (crosslinked). It is not practical to try to stop the reaction at an appropriate viscosity just prior to the crosslinking.

The viscosity of an unpolymerized resin is approximately correlated with the glass transition temperature of the polymer obtained from the resin. This relationship exists because both phenomena are to a first approximation dependent on the ease with which segments of the molecule can rotate. To increase the viscosity of the resultant resins, the HEM monomers were copolymerized with monomers that increase the glass transition temperature of the resulting polymer. Table 1 gives a list of the copolymerizations that were carried out. A small amount of the appropriate comonomer raises the glass transition of the subsequent copolymer by a large amount. Oligomers of these copolymers have greatly increased viscosities even though the oligomer molecules are still small. Therefore, the viscosity can be increased to a useful level with the polymerization stopping well short of the gel point. Samples can be made ranging from low viscosity (less than 1 Pa s = 10 poises) to nonflowing solids by the appropriate choice of comonomer.

Many of the combinations listed in Table 1 remained compatible during the polymerization so no solvent was necessary. The acrylamide copolymerizations separated into two phases during the co-polymerization. A solvent was necessary to make a uniform sample in that case. Water dissolves both the monomers and the polymers but is difficult to remove and its presence in the second stage of the synthesis would cause undesired side reactions. Methacrylamide was used instead of acrylamide as comonomer since methacrylamide did not require a cosolvent to maintain a single phase.

These copolymerizations also lead to gelation if no chain transfer agents are used. With the proper amount of transfer agent (between 5 and 20 wt % depending on transfer agent and monomer types) gelation could be avoided. Although some of the copolymers were solids at room temperature, they were freely soluble in neutral water. Even after the addition of the hydrophobic acrylate groups to the ends of the side arms of the copolymers, the resins remained very hydrophilic in comparison to the urethane resins.

4: Ionic Water-Soluble Resins

4.1: Introduction

The inks currently used in the printing of security documents are washed from the wiping blade of the press by use of Dalmar solution, an aqueous solution of 1% sodium hydroxide and 1% surfactant. The resins contain carboxylic acid groups which cause the resins to form salts and hence be dispersible in the basic aqueous solution.

Although non-ionic water-soluble groups confer water-dispersibility to resins and have the advantage of washing with neutral water, they are relatively inefficient. The polyethylene oxide resins required approximately 70% of the weight of the resin to be water-soluble polymer. Carboxylic acid-containing resins can be made water washable by having an acid number of between 50 and 100 mg KOH/g resin. This represents an acid content of between 4% and 8% of the total weight. Therefore a much larger fraction of the molecule can be made of polymerizable groups, enhancing the cure rate and the crosslink density.

Currency inks must pass resistance tests, including resistance to solvent and aqueous NaOH. Although we produced resins with higher acid numbers than is normally considered acceptable for currency applications, some acid numbers being as high as 200 mg KOH/g resin, the extensive cure obtained in E-beam inks makes even such highly acidic resins resistant to alkali when cured.

Parenthetically, we note that this type of acidic polymerizable resin is useful in photo-resists, where the unexposed part can readily be dissolved in aqueous alkali, leaving a layer of polymer where photo-initiated polymerization took place.

4.2: Types of Starting Monomers

A few commercially available monomers containing acrylate or methacrylate groups and carboxylic acid functionality have one acid group and one polymerizable group per molecule. Upon exposure to an electron beam, the (meth)acrylate groups polymerize, forming a solid polymer. Since there is no difunctional (meth)acrylate present, the polymer will not be crosslinked and will still be soluble. Also, the viscosities of these monomers are too low to allow them to be used in intaglio inks by themselves. In much of our work, we designed viscous monomers that give structures containing two or more polymerizable groups per molecule so that densely crosslinked networks would form upon irradiation.

A common way of introducing carboxylic acid groups into a molecule is to react an acid anhydride with a molecule containing a hydroxyl group. One part of the anhydride group forms an ester linkage with the -OH group and the other remains as the free acid. If a dianhydride is used, a molecule with two ester groups and two acid groups is formed. For E-beam resins, this doubles the number of polymerizable groups per molecule and thus increases the cure rate and crosslink density of the ink. The temperature is held below that required to esterify the new free acid group with the remaining alcohol groups.

Some of the commercially available materials appear to be severe skin irritants. Therefore, an important advantage of a larger molecule is that it is expected to be less toxic, other things being equal. Methacrylates rather than acrylates were used where feasible to make the toxicity lower.

The general reaction scheme is to react an acid anhydride with a polyhydric alcohol partially esterified with acrylate or methacrylate groups. When reacted with multifunctional polymerizable molecules such as glycerol dimethacrylate, even a mono-functional acid anhydride gives a molecule two polymerizable groups and is therefore capable of crosslinking.

Five different anhydrides were used, three of which are monoanhydrides and two of which are dianhydrides. The monoanhydrides are succinic, maleic, and phthalic anhydrides. The two dianhydrides are the aromatic dianhydride, pyromellitic dianhydride (PMDA, 1,2,4,5-benzenetetracarboxylic anhydride) and the aliphatic dianhydride, Epiclon B-4400[4].

The anhydrides were reacted with several radiation-curable alcohols: pentaerythritol partially esterified with acrylic acid, dipentaerythritol partially esterified with acrylic acid, and glycerol dimethacrylate (Rohm-Tech D-1108[4]). These alcohols are available commercially. They polymerize well in the E-beam but are too hydrophobic and, in the case of the acrylates, probably too toxic for use in washable intaglio inks. Because of toxicity considerations, attention was concentrated on glycerol dimethacrylate. Glycerol dimethacrylate contains a secondary alcohol group and is less reactive than the other alcohols used, but nonetheless reacts satisfactorily with the various anhydrides. Reaction of an anhydride group with glycerol dimethacrylate produces one acid group and adds two polymerizable groups to the molecule and produces a resin capable of crosslinking. Reaction schemes for the five acid anhydrides with glycerol dimethacrylate are given in Figures 2 to 6.
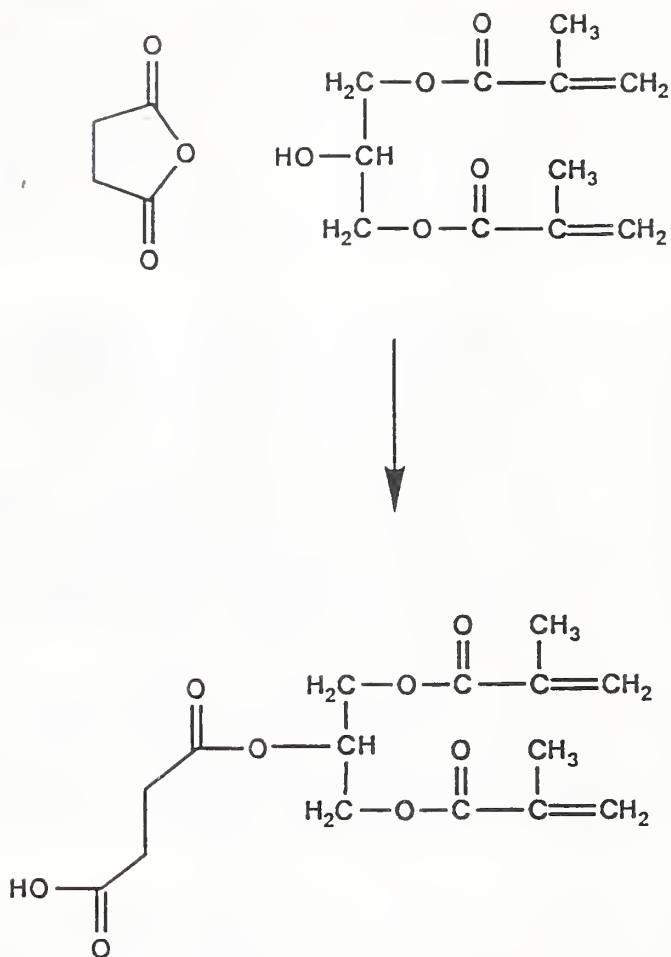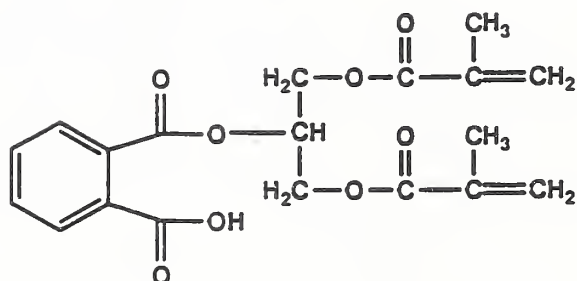
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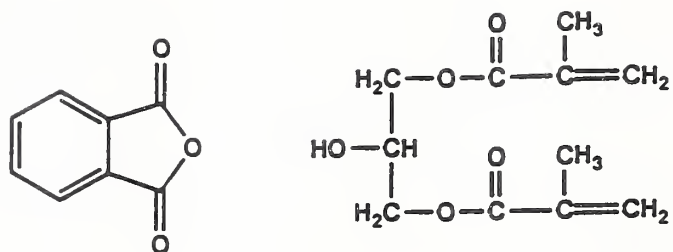
Figure 2: Synthesis of carboxylic acid/methacrylate resin based on succinic anhydride and glycerol dimethylmethacrylate.
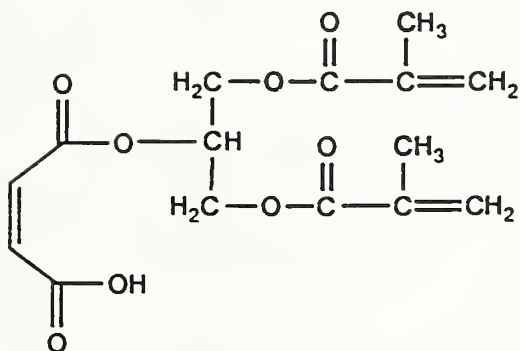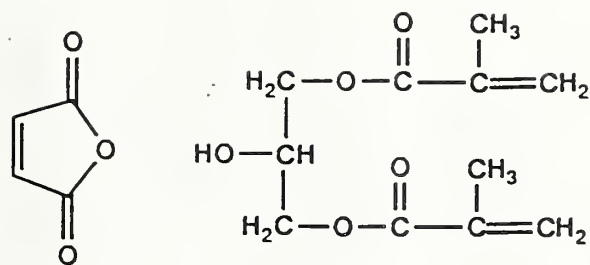
Maleic-GDM

Figure 3: Synthesis of carboxylic acid/methacrylate resin based on maleic anhydride and glycerol dimethylmethacrylate.

Phthalic-GDM

Figure 4: Synthesis of carboxylic acid/methacrylate resin based on phthalic anhydride and glycerol dimethylmethacrylate.
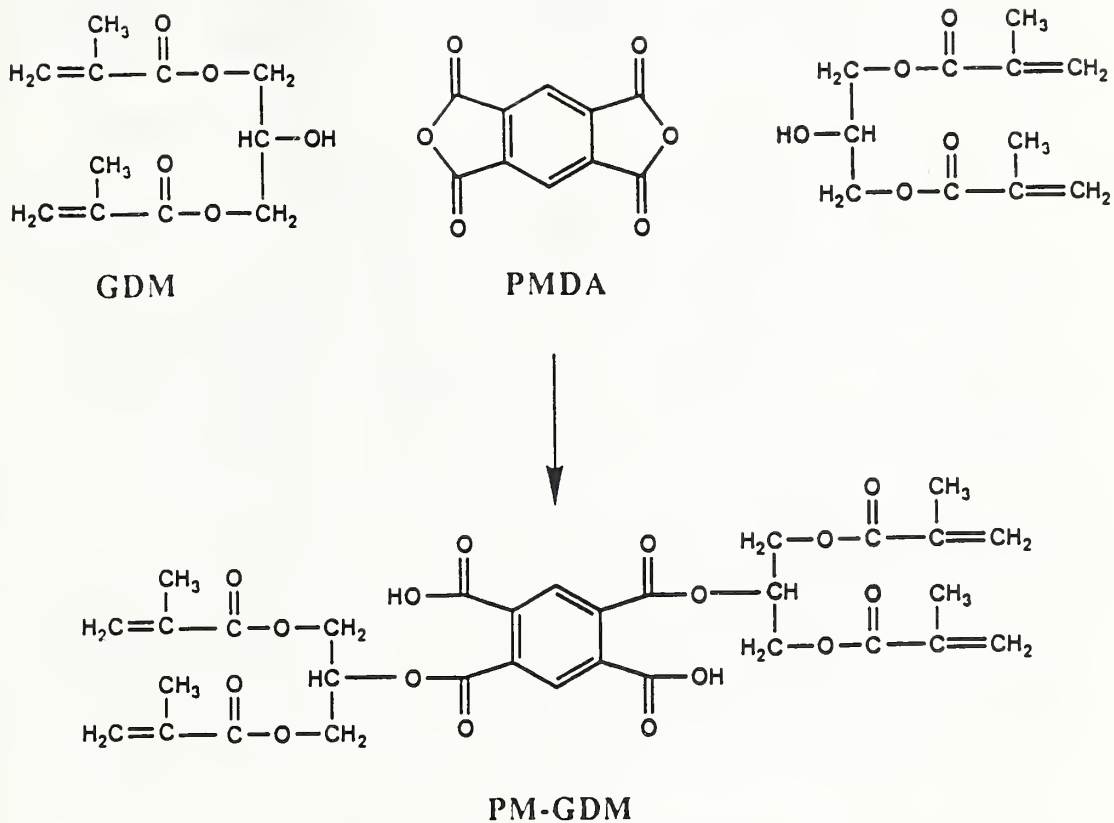
Figure 5: Synthesis of carboxylic acid/methacrylate resin based on pyromelletic dianhydride and glycerol dimethylmethacrylate.
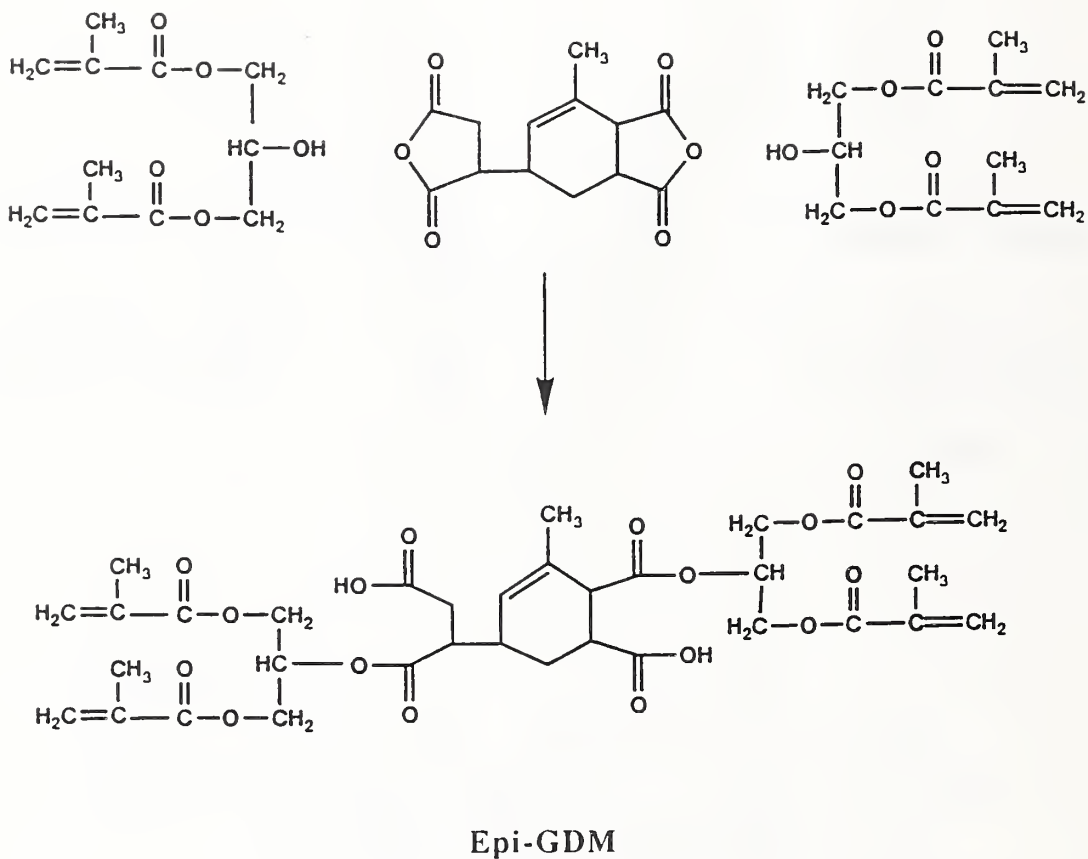
Epi-GDM

Figure 6: Synthesis of carboxylic acid/methacrylate resin based on B-4400 dianhydride and glycerol dimethylmethacrylate.

Because of the relatively low viscosity of the resins based on the monoanhydrides, the resins based on the dianhydrides were studied more extensively. Of the two dianhydrides used, the aromatic dianhydride PMDA reacted faster with the secondary alcohol group in glycerol dimethacrylate. This is as expected because aromatic acids are stronger acids than aliphatic acids. In all cases, the reaction could be speeded up by the addition of amines as catalysts. Use of poly 4-vinyl pyridine allowed complete removal of the catalyst by filtration at the end of the reaction. Use of soluble amines as catalysts tended to destabilize inks made from these resins, causing them to gel with time.

The resins were formulated into intaglio inks and were also cured neat in the E-beam. The resin based on PMDA gave more brittle films. Films derived from Epiclon B-4400 seemed tougher and the cure rate seemed to be marginally faster. The manufacturer's literature[4] on this compound claims that the hydrolysis rate of its esters is slow, which is expected to give longer than average shelf life as a stored ink and service life as a printed ink film. Low toxicity is also claimed. These properties give the Epiclon dianhydride several advantages over pyromellitic dianhydride.

4.3: Synthetic Methods.

The first reactions were catalyzed esterifications carried out in solution. Stoichiometric amounts of monohydroxy monomer and anhydride were used. The monohydroxy monomers are low viscosity liquids, but the anhydrides are high melting solids. If mixtures of the alcohol and anhydride are heated much above 55°C, polymerization of the methacrylate groups gels the mixture long before a homogeneous mixture is formed. Therefore, a solvent was used to make a homogeneous mixture at ambient temperature.

Initially, approximately 20 wt% stoichiometric solutions were made in THF and N,N-dimethyl benzylamine was used as a catalyst (1% by weight of the alcohol component). The THF solution was refluxed for 3.5 hours, then the solvent was stripped off in a rotary evaporator under partial vacuum with a stream of air being bled into the flask so that any free radicals would be converted to peroxyl radicals and would be trapped by the BHT. Most of the solvent was removed this way. The final step was to blow a stream of air over the surface of the resin to remove more of the solvent. The product was a viscous liquid with a faint smell of solvent. When placed in a 120°C oven, the resin cured forming a glassy material. Between 5% and 15% volatile material was removed by the heating.

These resins were taken to BEP and formulated into inks. While the ink was being milled, it became much more viscous due to the evaporation of residual solvent in the resin. To maintain

an appropriate viscosity, a low viscosity monomer, diacrylated polyethylene glycol 400, was added. The resulting film cured by exposure to 2 Mrads or less of 165 KV electrons.

THF is a good solvent for the resin components but has a tendency to form peroxides when unstabilized. Peroxides will cause gelation, resulting in unacceptably low shelf life. The decomposition of peroxides will be catalyzed by traces of the amine catalyst used in the anhydride/alcohol reaction. If stabilized THF is used in the synthesis, large amounts of stabilizer (usually BHT) remain in the resin. It is well known that excess BHT poisons the cure of acrylates and methacrylates.[1] Therefore acetone was used extensively in later work when a solvent was required because it forms no peroxides and does not contain inhibitors.

Because of the difficulty of removal of residual solvent from the resin, attempts were made to synthesize the resins without the use of solvent. Both pyromellitic dianhydride and Epiclon B-4400 are fine powders. When mixed with hydroxy-containing polymerizable monomers, they form a opaque slurry of relatively low viscosity. The bottles containing such slurries were rotated slowly for a period of up to two weeks. The surface of the anhydride powder reacted with the liquid monomer in contact with it and the reaction slowly proceeded. The contents became semi-transparent and the viscosity increased dramatically. The very high final viscosity inhibited the reaction from going to completion.

Both uncatalyzed reactions and reactions catalyzed with N,N-dimethyl benzylamine were then carried out in acetone. The reaction with pyromellitic dianhydride was allowed to react for 3 to 5 hours when 1 wt% catalyst was added. The uncatalyzed reaction was allowed to react for two days or more. The reaction rate of Epiclon B-4400 was slower than that of the pyromellitic dianhydride so a 7 day reaction time was used. The amine catalyst had a destabilizing effect - inks formulated from these resins gelled in a short period of time. Inks made from uncatalyzed resins did not gel after several weeks, even if no additional inhibitor over that originally in the glycerol dimethacrylate was added. Reactions were then catalyzed successfully using 1 wt% poly 4-vinyl pyridine and heating to 45°C. The poly 4-vinyl pyridine catalyst was filtered off at the end of the reaction. The reaction mixture was thinned with acetone before filtering and later concentrated using rotary evaporation. The resulting resin was stable.

Table 2 lists some of the ionic resins that were synthesized. They cover a wide range of ingredients and polymerization conditions. Most were small-scale syntheses with the neat resins being cured in the E beam without being made into inks. Some, such as 112-1, were made in much larger quantities

and taken to BEP for formulation into inks to better test stability, cure rate, and effect of different formulations on the ultimate ink properties.

4.4: Curing Rates

Table 2 gives a qualitative list of properties of the resins and inks made from them. Resins containing large amounts of PEG400 DA also did not form hard films, probably because of the low glass transition of the cured film. The best films were obtained from resins based on reacting pyromellitic dianhydride or Epiclon B-4400 with the polymerizable alcohols D-1108[4], SR-444[4], and SR-399[4]. All these reaction products gave hard, durable films. Films obtained from resins cured on glass slides were removed from the slides by soaking in water and found to be strong and tear-resistant. An ink made from resin 112-1 was drawn down on stamp paper and cured with 2 Mrad irradiation. The cured film could not be removed from the paper, even after very long soaking in water.

4.5: Washability of uncured resins and inks

Samples prepared at NIST are tested for washability by shaking a small amount of resin in a glass tube with a 20-fold excess of Dalmar solution. When non-acidified resins such as D-1108 are tested this way, very little of the resin seems to disperse, as expected. All of the acidified resins show much more affinity for the Dalmar solution and become suspended in the liquid.

Carboxylic acid groups in the acid form are not particularly hydrophilic. They require the sodium ions present in the Dalmar solution so that a soluble or water-dispersible ionic salt can be formed. However, this process takes time. If the resin is viscous, the ink made from it is inhibited from associating with the sodium ions in the aqueous solution, increasing the number of wipes necessary to wash the resin in the standard laboratory tests. A common way of causing acidified resins to disperse more rapidly is to make some of the needed salt before or during manufacture of the ink. This is conveniently and routinely carried out in air-dry ink systems and water-dispersible paint systems by adding basic materials such as amines. The amines abstract a proton from the carboxylic acid group to form an ionic pair that is very hydrophilic. In the case of paints, which are only lightly crosslinked if at all, a volatile amine is used that later evaporates from the curing film and the resin reverts to the non-ionized and hence less soluble form. In the case of E-beam cured materials, the degree of crosslinking in typically very large so it is not necessary that the cationic species be volatile. In particular, alkali metal ions can be used just as well. As pointed out above, soluble amines tend to destabilize inks containing acrylates and methacrylates and therefore cannot be used as solubilizing agents.

To illustrate the point, various amines were mixed with resin 112-1 to measure the change in Dalmar solution washability. The hydrophilicity of the resins improved dramatically. Inks made from them washed very well in Dalmar solution but seemed much more prone to gelation, as had been found from the amine-catalyzed reactions. Some ink formulations gelled to a hard solid mass in a matter of hours. Amines are known to catalyze the decomposition of peroxides and their presence in E-beam inks will probably cause unacceptable shelf life. Alkaline metal salts were then used to increase the solubility and dispersibility of the inks without affecting their stability. Inks have been formulated at BEP that have contained stoichiometric amounts of Li_2CO_3 (one Li per -COOH). These have excellent washability in Dalmar solution and also wash in neutral water containing no surfactant.

4.6: Resin Stability

Previous work on urethane E-beam resins (1) demonstrated the importance of the proper combination of stabilizers. Acrylate and methacrylate monomers are prone to gelation when unstabilized. Initial results indicate that 0.05 to 0.1 wt% butylated hydroxy toluene (BHT) and 0.05 to 0.1% methyl ether of hydroquinone (MEHQ) is an appropriate choice for the ionic E-beam resins.

Samples of neat resins remained ungelled after a period of months even without added stabilizers. When blended into inks, however, some formulations rapidly gelled. As remarked above, the presence of amines as solubilizers or as catalyst seem to promote gelation. When resins are synthesized without the amine catalyst and are solubilized with alkali metals by addition of salts such as lithium carbonate, the resins and the inks made from them seem to be much more stable. An ink stored in a clear glass vial and exposed intermittently to fluorescent light was stable for over two years, whereas similar inks gelled within days in a metal can. Storage in metal containers is to be avoided because any un-neutralized acid groups will tend to dissolve transition metal ions from the container. The metal ions are expected to act as peroxide decomposers, just as driers for air-dry resins do, and set off a free radical polymerization reaction that gels the ink. Clearly it is best to keep the resins and inks in glass-lined storage containers.

Alkali metal carbonates are preferred over the hydroxides since the reaction is much less exothermal. The heat generated from rapid addition of finely divided potassium hydroxide powder gels a resin in minutes. The preferred alkali metal is lithium because its small coordination sphere is expected to produce the least increase in viscosity of the neutralized resin by coordination of acid groups in more than one molecule to the

lithium ion. A beneficial effect of reducing the number of un-ionized carboxylic acid groups is that the ink is much less likely to dissolve metal ions from metal containers.

4.7: Toxicity tests

BEP commissioned an outside laboratory to perform Draize tests on two resins, one made from PMDA and GDM and the other from Epiclon B-4400 and GDM. The mean primary dermal irritation scores were estimated to be 2.8 and 2.4, respectively. According to the testing laboratory, a material must score 5 or more to be considered a primary dermal irritant.

5. Conclusions

Work on the urethane E-beam resins has been concluded. A patent description has been written and submitted for legal action. A synthesis of a high viscosity and a low viscosity resin has been developed and this technology was transferred to industry for scaleup to quantities suitable for press trials.

Homopolymers of the HEM[4] type of monomers are too low in viscosity for ink formulations. The viscosity can be increased while retaining the water solubility by copolymerization of various comonomers. Methacrylamide copolymerizes well with the HEM monomers and can control the viscosity of the resin anywhere from the low viscosity poly-HEM material to nonflowing solids. The free -OH groups are then reacted to attach pendant acrylate groups or methacrylate groups.

Several carboxylated resins have been synthesized for use in E-beam intaglio inks that wash in Dalmar solution. The resins cure to hard durable films by exposure to between 1 to 2 Mrads of 165 KV E-beam irradiation. To achieve high viscosity, a resin based on a dianhydride is a necessary component. The aliphatic dianhydride Epiclon B-4400[4] was used because of its low reported toxicity and the good quality of cured films made from resin based on this anhydride. Polymerizable components can be glycerol dimethacrylate or dipentaerythritol pentaacrylate, both being commercially available and producing resins with a good overall set of properties.

Very good Dalmar solution washability and even water washability results when Li_2CO_3 is added to carboxylated resins and inks. The viscosity can be adjusted by addition of polyethylene glycol diacrylate which itself has good washability and cure rate but is too low in viscosity to be used alone. Because of the high cure rate of these resins when unstabilized, it is probable that a fair amount of stabilizer can be added without increasing the necessary cure dose beyond acceptable limits. Inks based on these resins were stable for years in glass containers.

6: References

1.   "Radiation Curing of Polymers", D.R. Randell, Ed., Royal Society of Chemistry, London, 1987.

2.   Lapin, S. C., "Vinyl Ether Functionalized Urethane Oligomers: an Alternative to Acrylate Based Systems", Radtech '88-North America Conference Papers, 1988, p. 395.

3.   Dickens, B., Bauer, B. J., and Pummer, W. J., "Synthesis of Prototype Resins for Use as BEP Intaglio Ink Vehicles Curing by Electron Beam Radiation", Annual report of September 30, 1987.

4.   Trade names of certain commercial materials and equipment are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are the best available for the purpose.

Table 1. Copolymerizations of HEM monomers with other
water-soluble monomers.

	HEM-10	HEM-5	HEM-D
Acrylamide	–	–	–
Methacrylamide	+	+	+
N,N-dimethyl acrylamide	+	0	0
N,N-dimethyl aminoethyl acrylate	+	0	0
Carboxyethyl acrylate	+	0	0
Methyl methacrylate	0	+	0

Two phases (water required as solvent), – ; single phase, + ; not
tried, 0.

Table 2. Preparation of Ionic E-Beam resins
Ingredients by wt%

Sample	Acid Anhydride	wt %	Polymerizable Alcohol	wt %	Peg-400 DA Comonomer/Solvent wt %	Cure
BD-1	Phthalic	50.0	HEM-A	50.0	----	good
KK-1	Succinic	17.6	SR-444	82.4	----	good
KK-2*	PMDA	32.4	D-1108	67.6	----	good
KK-3**	PMDA	32.3	D-1108	67.7	----	good
104-1	PMDA	23.9	D-1108	25.0	51.1	poor
104-2	PMDA	17.6	HEM-10	82.4	----	
104-4	PMDA	25.3	D-1108	28.3	46.4	poor
105-1	PMDA	24.2	SR-444	38.0	37.8	poor
105-2	PMDA	33.6	D-1108	35.4	31.0	poor
105-3	PMDA	32.3	D-1108	38.1	29.6	poor
107-1	B-4400	37.1	D-1108	35.0	27.9	poor
107-2	B-4400	38.1	D-1108	32.9	29.0	poor
107-3	PMDA	32.6	D-1108	34.1	----	good
			SR-344	33.3	----	
111-1*	B-4400	36.6	D-1108	63.4	----	excellent
112-1*	B-4400	36.2	D-1108	63.8	----	excellent
121-1*	B-4400	18.6	SR-399	81.4	----	excellent
BD-2	Succinic	100	D-1108		----	excellent

* = reaction carried out in THF
** = reaction carried out in acetone

PMDA, pyromellitic dianhydride
THF, tetrahydrofuran
PEG-400 DA, 400 molecular weight polyethylene glycol diacrylate

Commercial Trade Names[4]

Alcolac, HEM-A, HEM-10
Rohm Tech, D-1108
Sartomer, SR-399, SR-344, SR-444
Dainippon, B-4400

HEM-A, Polyethylene glycol monomethacrylate, MW=526
HEM-10, Polyethylene glycol monomethacrylate, MW=526
D-1108, Glycerol dimethylmethacrylate
SR-344, Sartomer polyethylene glycol (400) diacrylate
SR-399, Sartomer dipentaerythritol pentaacrylate
SR-444, Sartomer pentaerythritol triacrylate
B-4400, Dainippon 5-(2,5-dioxotetrahydrofuryl)-
        3-cyclohexene-1,2-dicarboxylic anhydride

Appendix 1: Synthesis of acid methacrylate resins

The general form of the preparation is to esterify acid
anhydrides with alcohols already partially esterified with
methacrylic acid or acrylic acid. Temperatures up to at least
60°C can be used if the reaction times are kept short (hours). A
di-anhydride is typically used. A solvent such as acetone is
used to dissolve the acid anhydride. A low-viscosity
free-radical curing oligomer such as polyethylene glycol
diacrylate can also be used as solvent. Poly 4-vinyl pyridine
can be used as a solid catalyst and BHT or a similar inhibitor of
free radical polymerization can be used as stabilizer to prevent
polymerization during the preparation. The reaction is followed
by measuring the acid number of the reaction mixture or the IR
carbonyl absorbance of the anhydride group. When essentially all
the anhydride has reacted, the catalyst is filtered off and the
solvent is evaporated off either by bubbling air through the
resin or by heating the reaction mixture to about 40°C in a
rotary evaporator in an atmosphere of oxygen (or air) at about
100 to 600 Pa (1 to 5 mm Hg) pressure.

Example of typical synthesis

110 grams of glycerol dimethacrylate and 52.57 grams of
pyromellitic anhydride were combined in a 1000 mL flask equipped
with a stirrer and a water-cooled condenser. 1.10 grams of poly
4-vinyl pyridine catalyst, 0.11 grams of butylated hydroxy
toluene stabilizer and 150 mL of dry acetone solvent were added.
The contents of the flask were heated to 60°C with continuous
stirring. The reaction of the di-anhydride with the secondary
alcohol group of the glycerol di-methacrylate was followed by
monitoring the acid number of aliquots of resin. The aliquot was
dissolved in isopropanol and titrated with potassium hydroxide
dissolved in isopropanol. When an acid number (milligrams KOH
per gram resin) of less than 170 was obtained, the reaction
mixture was filtered under suction and then introduced into a
pear-shaped flask and the solvent evaporated off on a rotary
evaporator. The flask was held at 40°C. Air was bled into the
flask at a pressure of about 600 Pa (5 mm Hg).

4. TITLE AND SUBTITLE

SYNTHESIS OF NON-IONIC AND IONIC RESINS FOR BEP INTAGLIO INKS CURING BY ELECTRON BEAM RADIATION

5. AUTHOR(S)

Barry J. Bauer and Brian Dickens

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.)

In FY 87 and FY 88, syntheses were devised and carried out to produce resins which are water dispersible and which cure under the action of UV radiation or electron beams. These resins include (1) FY 87 work on urethane/polyethylene oxide/methacrylate non-ionic resins, (2) FY 88 work on polymethacrylate backbone/polyethylene oxide methacrylate graft non-ionic resins, and (3) FY 88 work on methacrylate resins containing carboxylic acid functionality. Resins of types 1 and 2 wash in neutral water. Resins of type 3 wash in neutral water if used as salts and in caustic water solutions in not used as salts. All the resins disperse pigments used in intaglio inks.

FY 87 work on polyurethane resins which wash in neutral water was concluded. Intaglio inks were made from these resins at BEP. Small scale laboratory tests at BEP showed that these inks had acceptable cure rate, viscosity and washability. This technology was transferred to BEP for scaleup.

A new effort was undertaken to produce resins that contain carboxylic acid functionality. These resins wash in caustic water solutions. An intaglio ink was formulated at BEP from the reaction product of an aliphatic dianhydride and glycerol dimethacrylate. When the ink formulation included lithium carbonate and polyethylene glycol diacrylate, acceptable cure speed, washability, viscosity and stability resulted. A second good candidate for an intaglio ink resin was obtained by reaction of the aliphatic monoanhydride succinic anhydride and glycerol dimethacrylate.

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

intaglio ink resin; electron beam resin; free radical curing; synthesis; water dispersibility