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Review

Tris-3-(1-aziridino)propionates and their use in formulated products☆

R.R. Roesler[a,*], K. Danielmeier[b]

[a] *Bayer Polymers LLC, Innovation Department, 100 Bayer Road, Pittsburgh, PA 15205, USA*
[b] *Bayer Polymers LLC, Global Operations Department, Building Q21, Leverkusen, Germany*

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Abstract

An overview concerning tris-3-(1-aziridino)propionate chemistry and their uses are given. The overview is based on an exhaustive literature search, which covers the chemical literature up to March 2002, and concentrates on the three most commercially significant tris-3-(1-aziridino)propionate crosslinkers: trimethylolpropane tris-(1-(2-methyl)aziridino)propionate (TTMAP), trimethylolpropane tris-3-(1-aziridinopropionate) (TTAP) and pentaerythritol tris-3-(1-aziridinopropionate) (PTAP). A bibliometric analysis showed that publication of articles and patents has been increasing, which demonstrates an increasing interest in this technology. Two hundred and sixty articles and patents have been published since 1952; half of the them, since 1993. One hundred and twenty-eight corporations and organizations have published articles and patents. Minnesota Mining and Mfg. Co. (17), Konica Co. (15), Eastman Kodak (13) and DuPont (12) are the companies with the most patents.

Applications that use tris-1-aziridinopropionate crosslinkers include adhesives, formulated coatings—primers, intermediate coats and topcoats, unformulated primers using a tris-3-(1-aziridino)propionate crosslinker as the sole ingredient, photographic film coatings, inks, thermal imaging and fabric coatings.

Polymer coreactants that have been used with tris-3-(1-aziridino)propionate crosslinkers include polyacrylate copolymers—solutions and dispersions, maleic acid–styrene copolymers, polyvinyl copolymers, polyolefins, polyurethane polymers—solutions and dispersions and biopolymers including polysaccharides and proteinacious gelatins.

Keywords: Polyaziridine; Crosslinking; Bibliometrics; Coatings; Adhesives

1. Introduction

This paper reviews publications concerning commercial tris-1-aziridinopropionate chemicals of the generic structure shown in Fig. 1. Other polyazirine crosslinkers are on the United States TSCA list, but the tris-1-aziridinopropionates are the most used commercial aziridine crosslinkers.

The specific materials evaluated were trimethylolpropane tris(3-2-methylaziridino)propionate (TTMAP), trimethylolpropane tris(3-aziridinopropionate) (TTAP) and pentaerythritol tris-(3-aziridinopropionate) (PTAP). Their chemical structures are given in Fig. 2.

The principle functional group of these materials is the aziridine ring. (PTAP has in addition hydroxyl functionality, which could be used to tie PTAP into molecules—with an isocyanate group for example.) The chief difference between the unsubstituted aziridine and the methyl substituted aziridine is that the unsubstituted ring has less steric hindrance and so is more prone to nucleophilic attack. Both aziridines react very quickly with nucleophilic materials such as car-

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* Corresponding author.

E-mail address: richard.roesler@bayerpolymers.com (R.R. Roesler).

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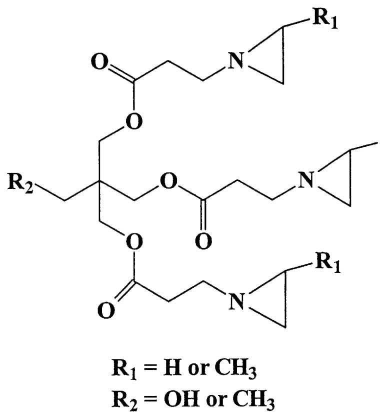

Fig. 1. Generic structure.

boxy groups (Fig. 3), amines, alcohols, mercaptans, etc. The nucleophile attacks and opens the ring to form a secondary amine. This reaction can be catalyzed by acidic conditions.

Strong acid conditions will lead to self polymerization, especially in the absence of other nucleophiles. This process is used for the synthesis of polyethyleneamines (Fig. 4). A good review about activation and reactivity of the aziridine ring has been published, although this paper covers no polymeric applications [1].

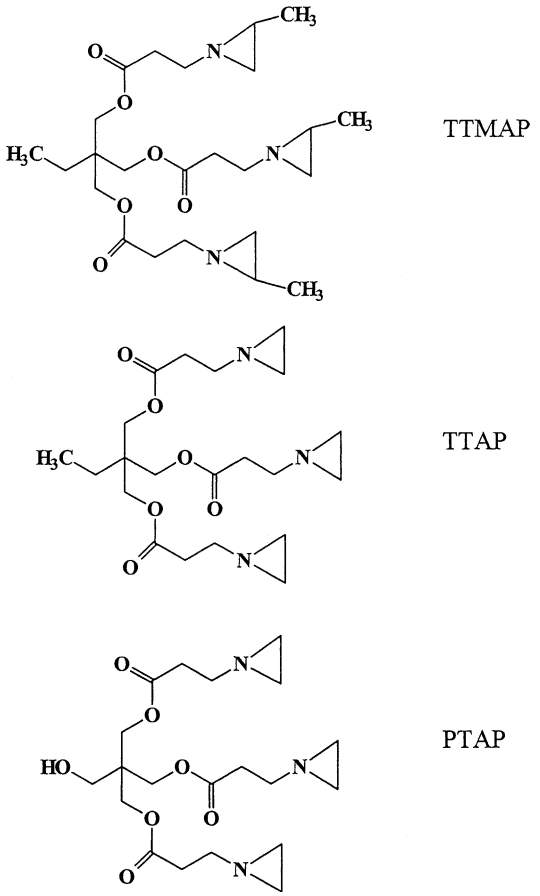

Fig. 2. Tris-3-(1-aziridino)propionate chemicals.

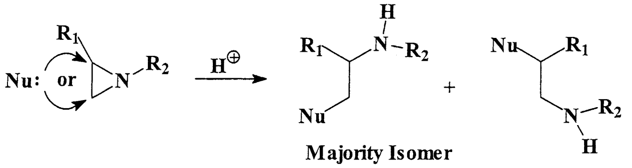

Fig. 3. Reaction of a nucleophile with aziridine.

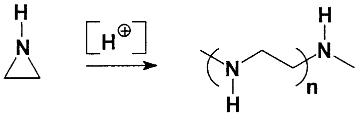

Fig. 4. Preparation of polyethyleneimine.

Since acrylic emulsions and polyurethane dispersions utilize nucleophilic carboxy groups for stabilization, polyfunctional aziridines can be and are being used to crosslink these resins.

The literature search was done using the CAS number for each of the three polyaziridine chemicals. The CAS number was used as the search term in the CAPLUS, CAOLD and MEDLINE databases using the SciFinder search engine. These databases include articles since 1957. In addition a search was done in the hardbound Chemical Abstracts journals prior to 1957. This literature summary includes articles in the abstract databases through March 2002.

The outline of this review includes a bibliometric analysis of the products followed by a summary of the articles on the chemistry and the uses of these tris-3-(1-aziridino)propionate crosslinkers. Articles that reported the use of tris-aziridine as comparative examples were excluded from the analysis. A summary and an individual analysis was included for the three tris-3-(1-aziridino)propionate crosslinkers. The graphs maintained the same axis dimensions to ease comparisons, even though publications may not have occurred for the comparative years, technologies, etc.

Note. In the following review, in order to make for easier reading and understanding, the terms TTMAP, TTAP and PTAP are used as synonyms for the CAS numbers and all the other trade products. In most cases the trade names are not specifically mentioned in the patent or article.

2. Product bibliometrics

2.1. Totals for tris-3-(1-aziridino)propionate crosslinkers

Since 1952, 260 patents and articles have been published on tris-3-(1-aziridino)propionate crosslinkers.[1] The number of articles indicate the great interest in the technology. The fact that the trend for publications is increasing demonstrates

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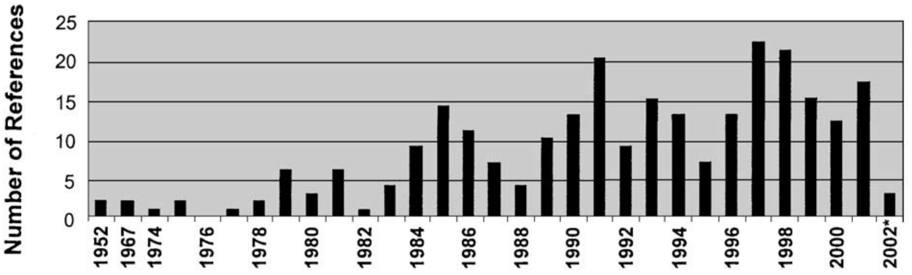
[1] This number does not include the duplication of publication, when the same patent is filed in more than one country. If this is done, the number of patents more than doubles.



*Includes publications January through March

Fig. 5. Publication history: tris-3-(1-aziridino)propionate.

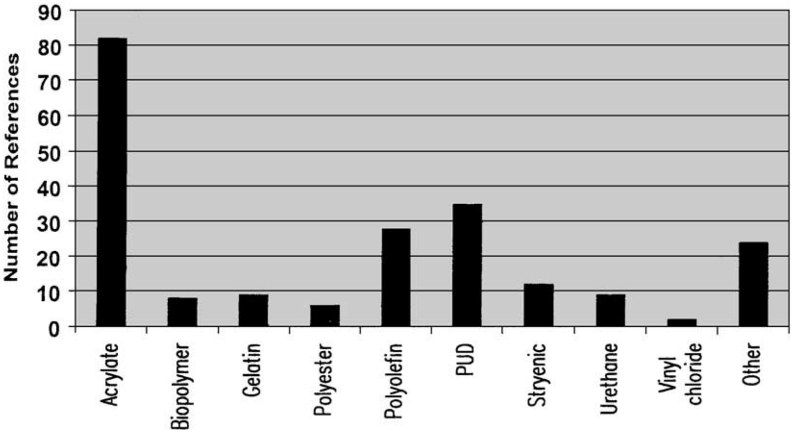


Fig. 6. Technologies: tris-3-(1-aziridino)propionate.

that interest in tris-3-(1-aziridino)propionate crosslinkers remains strong (see Fig. 5).

The articles were categorized as to type of resins used with the tris-3-(1-aziridino)propionate crosslinkers (see Fig. 6). The term “acrylate” included pure acrylates and copolymers with methacrylates, vinyls, etc.; “biopolymers” included proteins, polysaccharides, etc.; “gelatin” included only proteinacious materials; “polyolefin” included non-acrylate vinyls, e.g., polypropylene, rubber copolymers, etc.; “styrenic” included styrene–maleic anhydride copolymers; urethane included 100% solids or solvent solutions.

The applications of the tris-3-(1-aziridino)propionate crosslinkers are categorized in Fig. 7. The single most important use is in photography. The next important applications are coatings and adhesives. Key properties of the tris-3-(1-aziridino)propionate crosslinkers are their water-white color and their ability to crosslink resins.

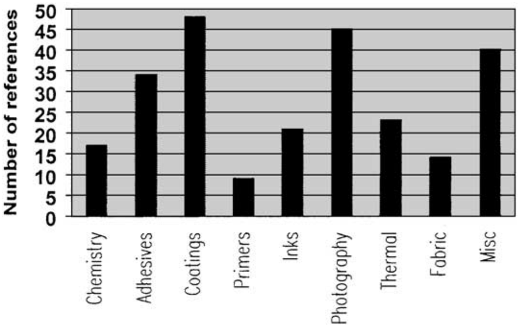


Fig. 7. Applications: tris-3-(1-aziridino)propionate.

Categories of technology were collected together: chemistry applications included mechanistic studies; adhesives are pressure-sensitive and laminating types; coatings are the general areas of primer, intermediate coat and topcoat formulations; the primers are applications in which the polyfunctional aziridine is used alone to treat a substrate; inks included toners, thermal printing media and ink receptive layers; photography summarized antistatic photographic coatings, primers, which are called subbing layers, and imaging layers; thermal are thermal transfer material and electrostatic receptive layers; fabric includes textile and fiber treatments; miscellaneous describe a range of applications from rocket propellants’ to chromatography media. An examination of application versus year did not show that any specific technology was growing or waning. All showed similar trends to the total publications as shown in Fig. 5.

One hundred and twenty-eight corporations have published patents or articles (see Table 1): 8 corporations with 6 or more publications; 20 corporations with 4 or more publications; 12 corporations with 3; 19 corporations with 2; 76 corporations with 1. (A complete list of the corporations including their interest in specific tris-3-(1-aziridino)propionate crosslinkers is given in Appendix A.)

Table 1
Corporations with four or more publications

Corporation	Total
Minnesota Mining and Mfg. Co.	17
Konica Co.	15
Eastman Kodak Company	13
E.I. DuPont de Nemours and Co.	12
Nippon Shokubai Kagaku Kogyo Co.	8
Ricoh Co. Ltd.	7
Mitsubishi Paper Mills Ltd.	6
Toyo Ink Mfg. Co. Ltd.	6
Kanzaki Paper Mfg. Co. Ltd.	5
Konishiroku Photo Ind	5
Mitsubishi Kasei Vinyl	5
Mitsui Toatsu Chemicals Inc.	5
Nippon Sanmo Sensyoku Co.	5
Nitto Denko Corporation	5
Bayer (Sybron)	4
Aventis Research and Technologies GmbH	4
Mitsui Chemicals Incorporated	4
Nippon Polyurethane Industry Co.	4
Rexam Graphics Inc.	4
Tomoegawa Paper Co. Ltd.	4

2.2. *Trimethylolpropane tris(3-2-methylaziridino) propionate (TTMAP)*

The following section describes the bibliometrics of TTMAP. Table 2 describes the typical properties of TTMAP.

Since 1978 there have been 90 patents and articles published. The number of articles indicate the strong interest in this product. The fact that the trend for publications is increasing demonstrates that interest in TTMAP remains strong. (See Fig. 8. The recent years are in numeric order, but the first two bars are for years 1952 and 1967.)

These articles were categorized as to the type of resins used (see Fig. 9).

The applications of the tris-3-(1-aziridino)propionate crosslinkers for TTMAP are categorized in Fig. 10. The most important uses are in photography and coatings.

Eighty-three corporations have published patents or articles concerning TTMAP (see Table 3): 7 corporations with 3 or more publications; 6 corporations with 2; 41 corporations with 1.

Table 2
Description of TTMAP

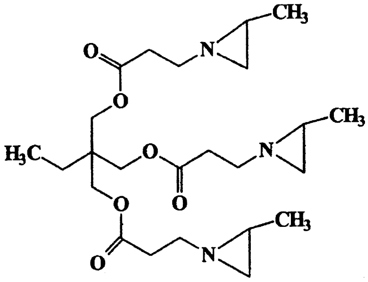
Chemical name	Trimethylolpropane tris(3-(2-methylaziridino)propionate)
Structure	
CAS number	64265-57-2
Synonyms	PFAZ-322—Bayer Corporation CX 100—Avecia
Typical properties	
Aziridine content (meq/g)	6.0
Aziridine functionality	2.8
Appearance	Clear, amber liquid
Density	1.07
Viscosity (mPa s at 25 °C)	500
Color, Gardner	2

Table 3
Corporations with three or more publications

Corporation	Total
Minnesota Mining and Mfg. Co.	9
E.I. DuPont de Nemours and Co.	6
Aventis Research and Technologies GmbH	4
Eastman Kodak Company	3
PPG Industries Inc.	3
Scitex Corporation Ltd.	3
Avecia Resins	3

2.3. *Trimethylolpropane tris(3-aziridinopropionate) (TTAP)*

The following section describes the bibliometrics of TTAP. Table 4 describes the typical properties of TTAP.

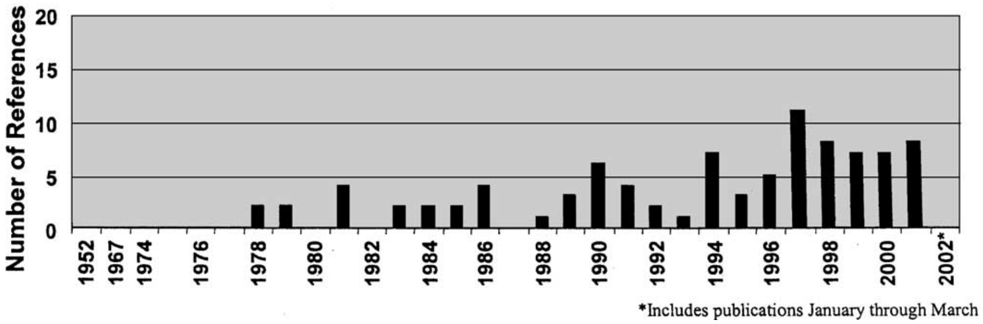


Fig. 8. Publication history: TTMAP.

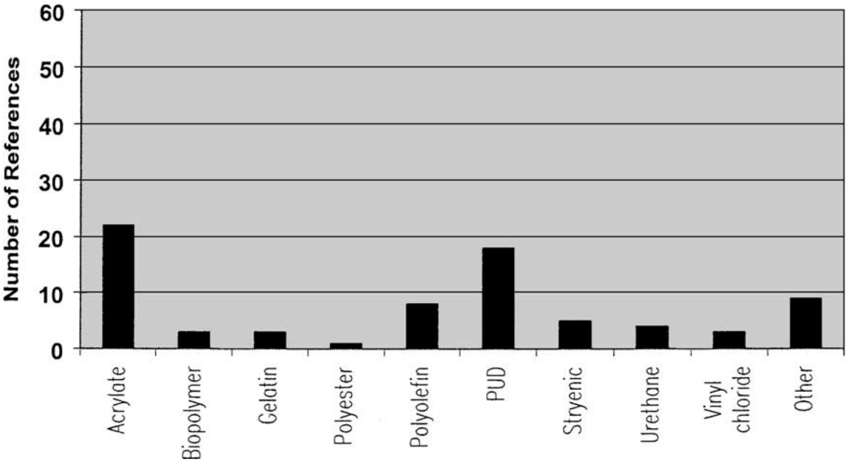


Fig. 9. Technologies: TTMAP.

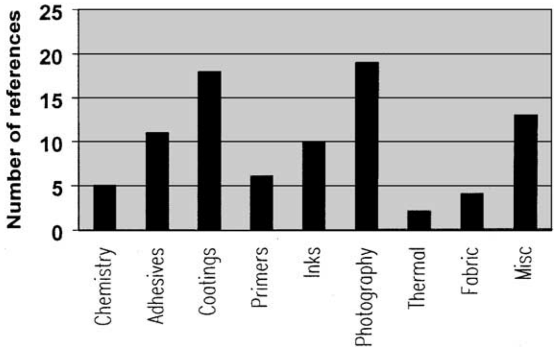


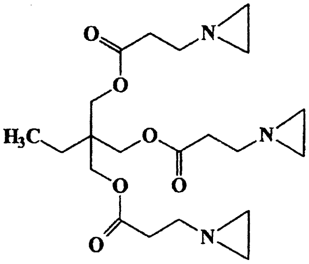
Fig. 10. Applications: TTMAP.

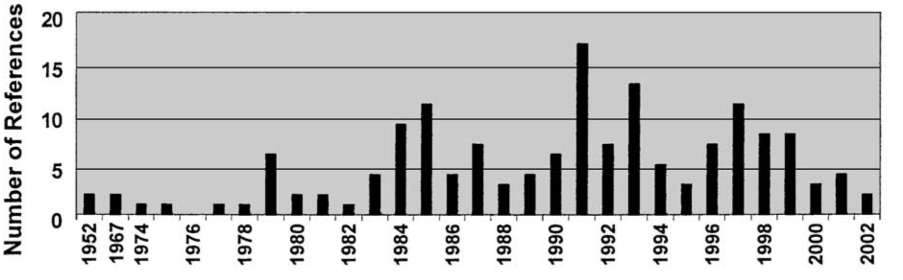
Since 1974 there have been 145 patents and articles published. The number of articles indicate the interest in this product. Although 1991 had the most articles published, the fact that half of the publications have been written since then demonstrates that interest in TTAP remains strong. (See Fig. 11. The recent years are in numeric order, but the first two bars are for years 1952 and 1967.)

These articles were categorized as to the type of resins used (see Fig. 12).

The applications of the tris-3-(1-aziridino)propionate crosslinkers for TTAP are categorized in Fig. 13. The most

Table 4
Description of TTAP

Chemical name	Trimethylolpropane tris(3-aziridinopropionate)
Structure	
CAS number	52234-82-9
Synonym	XAMA-2—Bayer corporation TAZ TAZM—Sogo Pharmaceuticals Chemitite PZ 32—Nippon Shokubai Kagaku Kogyo Co. Ltd. Chemitite PZ 33—Nippon Shokubai Kagaku Kogyo Co. Ltd.
Typical properties	
Aziridine content (meq/g)	6.5
Aziridine functionality	2.8
Appearance	Clear, amber liquid
Density	1.09
Viscosity (mPa s at 25 °C)	300
Color, Gardner	2



*Includes publications January through March

Fig. 11. Publication history: TTAP.

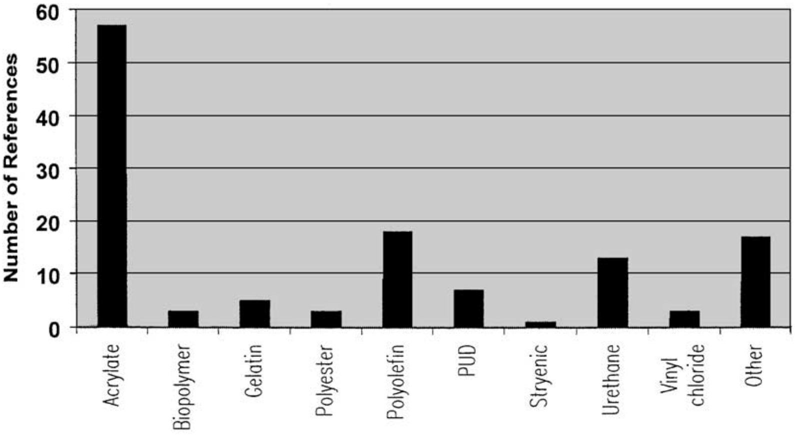


Fig. 12. Technologies: TTAP.

important uses are coatings, photography, thermal and adhesives.

Sixty-nine corporations have published patents or articles concerning TTAP (see Table 5): 19 corporations with 3 or more publications; 11 corporations with 2; 42 corporations with 1.

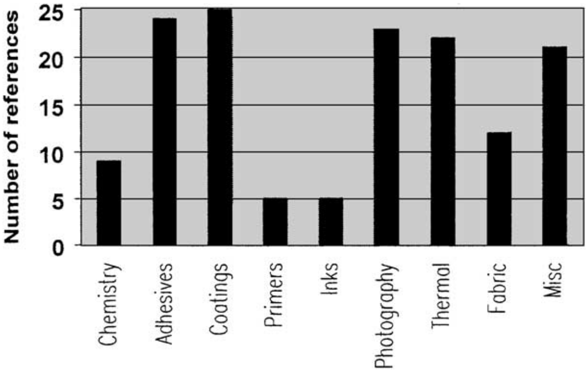


Fig. 13. Applications: TTAP.

Table 5
Corporations with three or more publications

Corporation	Total
Konica Co.	13
Minnesota Mining and Mfg. Co.	8
Nippon Shokubai Kagaku Kogyo Co.	7
Ricoh Co. Ltd.	7
Mitsubishi Kasei Vinyl	5
Nippon Sanmo Sensyoku Co.	5
Nitto Denko Corporation	5
E.I. DuPont de Nemours and Co.	4
Kanzaki Paper Mfg. Co. Ltd.	4
Mitsubishi Paper Mills Ltd.	4
Nippon Polyurethane Industry Co.	4
Tomoegawa Paper Co. Ltd.	4
Toyo Ink Mfg. Co. Ltd.	4
Dainippon Ink and Chemicals Inc.	3
Konishiroku Photo Ind	3
Mitsubishi Kagaku Emu Kee	3
Mitsui Chemicals Incorporated	3
Nippon Urethane Service Co.	3
Tamkang University, Taiwan	3

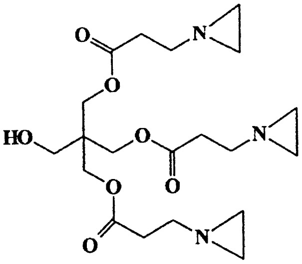
2.4. *Pentaerythritol tris(3-aziridinopropionate) (PTAP)*

The following section describes the bibliometrics of PTAP. Table 6 describes the background of PTAP.

Since 1975, there have been 75 patents and articles published. The number of articles indicate the interest in the technology. Although 1991 had the most articles published, the fact that half of the publications have been written since then demonstrates that interest in PTAP remains strong (see Fig. 14).

These articles were categorized as to the type of resins used (see Fig. 15).

Table 6
Description of PTAP

Chemical name	Pentaerythritol tris(3-aziridinopropionate)
Structure	
CAS number	57116-45-7
Synonym	XAMA-7—Bayer corporation TAZO—Sogo pharmaceuticals
Typical properties	
Aziridine content (meq/g)	6.7
Aziridine functionality	3.3
Appearance	Clear, amber liquid
Density	1.19
Viscosity (mPa s at 25 °C)	>1000
Color, Gardner	2

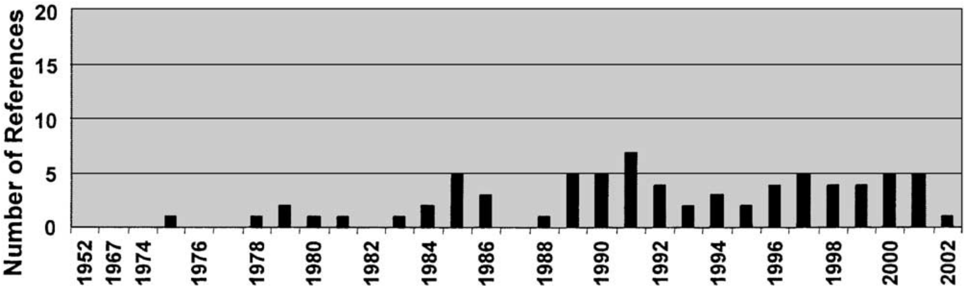


Fig. 14. Publication history: PTAP.

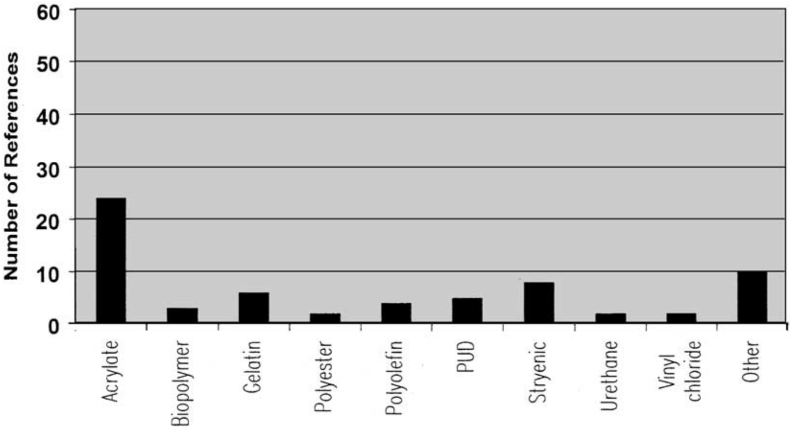


Fig. 15. Technologies: PTAP.

The applications of the tris-3-(1-aziridino)propionate crosslinkers for PTAP are categorized in Fig. 16. The most important use is in photography.

Forty-three corporations have published patents or articles concerning PTAP (see Table 7): 8 corporations with 3 or more publications; 8 corporations with 2; 28 corporations with 1.

2.5. Addendum

There were a total of 260 patents and articles identified in the literature search: 8 of these patents and articles referred to the CAS number of all three compounds; 5 of these referred to the CAS number of both TTMAP and TTAP; 6 referred to the CAS number of both TTMAP and PTAP; 21 articles referred to the CAS number of both TTAP and PTAP. All the remaining patents and articles referred to only one of the products. These redundancies will be highlighted in the applications review.

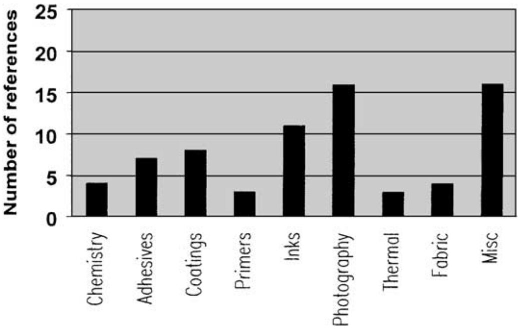


Fig. 16. Applications: PTAP.

Table 7
Corporations with three or more publications

Corporation	PTAP
Minnesota Mining and Mfg. Co.	9
E.I. DuPont de Nemours and Co.	8
Konica Co.	4
Rexam Graphics Inc.	4
Bayer (Sybron)	3
Halliburton Co.	3
Mitsubishi Paper Mills Ltd.	3
Mitsui Toatsu Chemicals Inc.	3

As can be seen in the Publication Categories, all three compounds found uses in most categories. No obvious, specific reason was apparent why one compound was chosen versus the others for use in a given patent.

3. Health and safety of polyfunctional aziridine crosslinkers

Polyfunctional aziridines are reactive chemicals. Like all reactive chemicals, they have the potential for adverse health effects if not carefully handled. Actual risk of adverse health effects from working with polyfunctional aziridines does not depend only on the toxicity of the neat material. Some factors, which mitigate risk, are as follows:

- low vapor pressure of polyfunctional aziridines;
- low percentage of use of polyfunctional aziridines in the finished formulation;
- non-spray/non-heated application methods;
- use of good personal protective equipment.

The following summary is a brief overview of Bayer's current understanding with regard to the toxicology of polyfunctional aziridine crosslinkers. (For a more detailed discussion of potential health effects and worker protection guidelines, the reader is urged to consult the Material Safety Data Sheet (MSDS) and the label information of each specific product before beginning work.)

3.1. *Acute toxicity*

Short-term oral and dermal toxicity of these compounds range from slight for NeoCryl CX-100 ($LD_{50} = 3038\,mg/kg$) [2] to moderate ($LD_{50} \sim 1000\,mg/kg$) [3]. Recently developed acute inhalation data for a 100% respirable spray mist of two polyfunctional aziridines places them in the moderate (for XAMA 7) to high toxicity (for XAMA 220) range ($LC_{50} = 338–252\,mg/m^3$) [4]. In this regard it should be noted that typical, ready to apply formulations, contain from 0.5 to 2% of the polyfunctional aziridine crosslinkers. No inhalation toxicity data is available for these formulated products.

3.2. *Primary irritation/corrosivity*

Skin irritation tests for this class of materials have given results ranging from mild irritation to severe irritation with scarring (corrosion). In some tests of for NeoCryl CX-100, mild irritation was seen with unabraded skin but severe irritation with abraded skin [2].

Eye irritation tests for XAMA 220 have shown polyfunctional aziridines to cause moderate irritation up to corrosion (severe irritation with permanent damage) [5]. This is one of the key hazards of working with these materials. Workers should be very careful to avoid eye contact.

3.3. *Sensitization*

The results from animal and human skin exposure tests, taken as a whole, do not indicate a consistent pattern of sensitization behavior. Reports have been published of both positive and negative animal tests for skin sensitization, depending on the method. There are several published human case studies claiming both skin and respiratory sensitization. In one report, the test material was identified only as polyfunctional aziridine [6]. In another report, the test material was called "polyfunctional aziridine crosslinker CX-100" [7]. As a practical matter, workers, who have been medically determined to be sensitized (skin rash, reddening or swelling or asthmatic symptoms such as cough, shortness of breath or chest tightness), should no longer work with these materials.

3.4. *Mutagenicity/carcinogenicity*

At lease one aziridine monomer (ethyleneimine) used as a raw material for the production of polyfunctional aziridines has been found to cause cancer in laboratory animals [8]. In addition, polyfunctional aziridines have consistently shown genotoxic potential in all systems tested so far: XAMA 220 was tested in vitro [9] and XAMA 7 was tested in vivo [10]. This suggests a pattern of reactivity at least qualitatively comparable with that of the aziridine monomers. Therefore, care must be taken to minimize worker exposure to polyfunctional aziridine crosslinkers.

4. Applications of tris-3-(1-aziridino)propionate crosslinkers[2]

4.1. *Chemistry*

The tris(aziridinylpropionates) has been prepared by two different procedures. The first method used the Michael-addition of aziridine to acrylic esters of trimethyol propane (Fig. 17 [11–14]). Although a triaziridine material has been the goal, the functionality is often not exactly 3, because of the difficulty of getting a triacrylate. When trimethyol propane is used, the esterification to the acrylate is incomplete resulting in functionalities of less than 3; and when pentaerythritol with a functionality of 4 is used, the esterification to the acrylate is more than the desired 3.

The second method of preparation used the transesterification of methyl (1-aziridinyl) propionates with polyols with the aid of tertiary amine catalysts (Fig. 18 [15]). For example, a mixture of trimethylol propane, methyl 3-(1-aziridinyl) propionate and fatty amine was heated in nitrogen for ∼11 h at 118–134 °C; the methanol was distilled; and the product was distilled under vacuum to give TTAP. An improved method used titanium(IV) or tin(IV) compounds as catalysts, which improved the aziridine ring content to 97% of theory [16].

Another catalytic method with less cleavage of the aziridine ring in the transesterification of methyl (1-aziridinyl) propionates to TTAP or PTAP was seen when the more effi-

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[2] Within each application area the patents and articles are grouped as much as possible by use. The order is by publication date—oldest first. The bibliography includes the first author, corporate or university affiliation and patent family references, i.e., all the patents corresponding to US, EP, WO and DE. Where none of these countries are included in the patent family, one relevant country is given. Japanese references are given only when no other countries are part of the patent family.

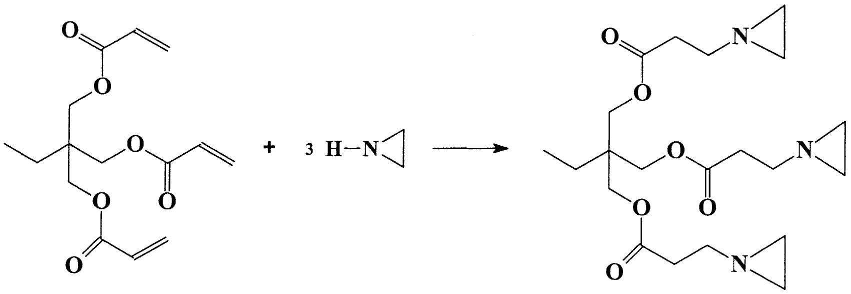

Fig. 17. Preparation of TTAP.

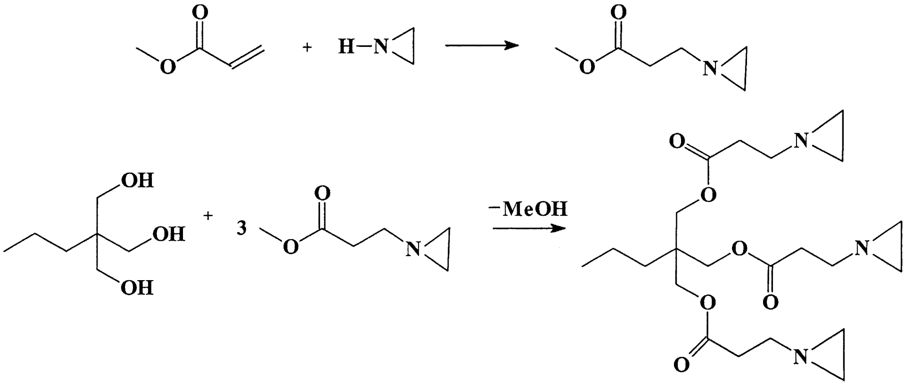

Fig. 18. Preparation of TTAP from (1-aziridinyl) propionates.

cient transesterification catalysts Ti(IV) or Sn(IV) catalysts were used [2].

The tris-1-aziridinopropionates are soluble in many aromatic and polar solvents [2]. In addition, the tris-1-aziridinopropionates are miscible with water. Because of this the tris-1-aziridinopropionates are used in both solvent-borne and water-borne formulations. Although the solvent solutions are stable, the tris-1-aziridinopropionates slowly react with water to form an aminoalcohol, Fig. 19, and lose their effectiveness for crosslinking.

However, the presence of the aminoalcohol in the resin film does not have any adverse consequences on performance. In addition, if the aziridine becomes inactive through hydrolysis, more aziridine can be added to the formulation to get the desired crosslinking.

4.2. Crosslinking reactions

The crosslinking mechanism of TTMAP was studied. The crosslinking reaction was dependent on the availability of an active hydrogen to protonate the aziridine ring [2,17]. In most cases a carboxylic group is used. The generic mechanism is shown in Fig. 20. In this case the product of the reaction is a β-aminoester.

The crosslinking reaction of aziridine and carboxylate occurs at a reasonable rate at ambient conditions, so no heat or catalyst is needed to complete the cure. The reaction is relatively slow, compared to carbodiimide, for example, so that film formation (and particle coalescence in the case of water-borne latexes) can occur before the crosslinking reaction leading to a more completely crosslinked system [Fig. 3]. In any case, the degree of crosslinking affects the ultimate performance of the polymer.

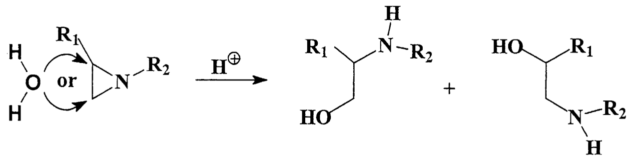

Fig. 19. Reaction of water with aziridine.

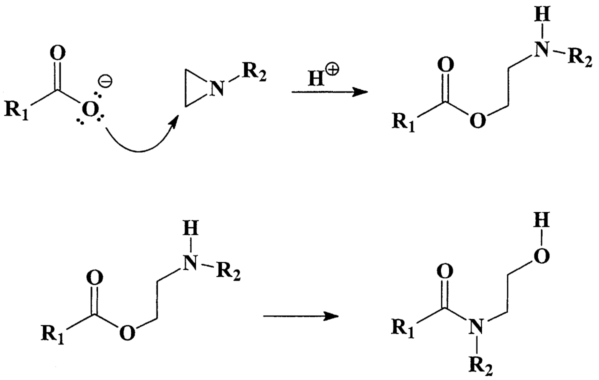

Fig. 20. Reaction of aziridine with carboxy group.

Cr(III) carboxylate (e.g., octoate) catalysts were used to accelerate the reaction of carboxylic acids with aziridine. For example, the reaction of PTAP with dimer (C_{36}) diacid was accelerated by Cr(III) carboxylate which gelled to a hard rubbery polymer in 1 min at 32 °C, versus a gooey mass after 24 h without catalyst [18].

The self-curing behaviors of a single-pack, water-borne polyurethane containing TTMAP or TTAP were evaluated. The system was shown to be stable at high pH, but cured when the pH was lowered. The reaction took place via a ring opening of the aziridine ring with the carboxy group on the urethane. The amino ester bond of the ambient cured polyurethane was transformed into the more stable amide linkage upon heat treatment [19] (see Fig. 20).

Polyurethane dispersions were crosslinked with a combination of difunctional epoxy and TTAP. The mechanical, physical and thermal properties of the dual-cured rubbers were evaluated [20,21].

An oxirane–aziridine copolymer was prepared that included an epoxy resin, TTMAP as a coreactant and a BF_3·amine complex as polymerization catalyst. Epoxy resins included bis-phenol A epoxy, bis-phenol F epoxy, novolak epoxy, cycloaliphatic epoxy and triglycidyl isocyanurate. Compounds with active H, such as phenols, alcohols, carboxylic acids or anhydrides may be included in the anionic polymerization [22].

The performance properties of crosslinked polyurethane dispersions in the production of abrasion resistant and chemical resistant coatings were evaluated. Crosslinkers included TTMAP, water-dispersible polyisocyanate, carbodiimides, epoxy silanes and methoxymethyl melamine. For carboxy-functional polyurethane dispersions, crosslinking with TTMAP gave the best overall performance [23].

4.3. Adhesives

As was pointed out earlier, the third largest use of tris-3-(1-aziridino)propionate crosslinkers is to improve the performance of adhesives. The addition of tris-3-(1-aziridino)propionate crosslinkers improves the mechanical properties of traditional adhesive resins, e.g., polyacrylates, polyurethanes and maleic anhydride copolymers, both in solvent-borne and water-borne systems. This section gives examples of these applications.

The effect of the amount of wax in an acrylic–urethane film crosslinked with TTMAP on the adhesion strength between the acrylic–urethane film and steel sheet was investigated by varying the amount of wax using a pull-off test [24]. Increasing the amount of wax decreased the adhesion.

PTAP was part of a catalyst system for the polymerization of acrylic monomers. The catalyst was composed of an organoborane–amine complex and PTAP. The catalyst was especially useful in formation of acrylic adhesives that had especially good adhesion to low surface energy polymers [25].

Polytetramethylene glycol, 4,4′-diaminodiphenylmethane and diphenylmethane-4,4′-diisocyanate polyurea/urethane crosslinked with TTAP was used to prepare a solvent-borne flocking adhesive. This binding agent for pile fabrics had superior pile fallout resistance during processing and during a wet friction test [26].

A solvent-borne pressure-sensitive adhesive was prepared from an acrylic based tackifying resin and PTAP. The acrylic resin with 0.5% PTAP was applied to a corona-treated polyethylene terephthalate film, dried at 170 °C and cured for 48 h at 60 °C to give an adhesive film. This adhesive film had good adhesion to stainless steel and was removable even after 50 h under UV light [27].

A solvent-borne, pressure-sensitive adhesive was prepared from a carboxy-functional acrylic copolymer, based on methacrylate esters and acids and other vinyl polymers, a liquid epoxy resin and TTMAP or TTAP. This formulation was stable even when heated at 40 °C for 8 h and could be cured in 3 days, even at 0 °C to give good adhesion to stainless steel [28].

A solvent-borne, pressure-sensitive adhesive was prepared from a mixture of a carboxy-functional polyacrylate, an isoprene–styrene block copolymer and TTAP and coated onto a polyester film to give an adhesive tape with good adhesion. The key to improve the adhesion in this process was the modification of the surface of the adhesive resin with functional groups [29].

A solvent-borne, pressure-sensitive adhesive was prepared from an acrylic copolymer, a rubber resin, aluminum acetylacetate and TTAP [30].

Pressure-sensitive tape was prepared from a water-borne, polyacrylate and TTAP crosslinker [31,32].

A water-borne adhesive suitable bonding plywood was prepared from an olefin–maleic anhydride copolymer, a carboxy-terminated SBR rubber and TTAP. The adhesive gave superior properties compared to a similar composition where an epoxy resin replaced the tris-3-(1-aziridino) propionate crosslinker [33].

A water-borne, pressure-sensitive adhesive was prepared from an acrylic copolymer and PTAP. The adhesive composition was applied to a corona discharge-treated ethylene–vinyl acetate (EVA) surface of an EVA-laminated polypropylene film to give a product useful in protecting the backside of semiconductor wafers during grinding [34].

Film for a semiconductor wafer with good adhesion in protection and releaseability after protection has a radiation-curable adhesive layer and an additional adhesive layer based on polyethylene glycol propenylnonylphenyl ether sulfate salt, polyacrylate graft copolymer ammonium salt and TTAP. The film is bonded to the circuit formation side of the wafer and is used in place while the reverse side is machined or chemically treated [35].

A water-borne, pressure-sensitive adhesive was prepared from an acrylic copolymer and TTAP. The adhesive composition was roll-coated onto a polypropylene releasing film and transferred to an EVA copolymer film to give a product useful for protecting wafers while grinding [36].

A water-borne, pressure-sensitive adhesive was prepared from conductive polyacrylate micro-particles based on polyethylene oxide acrylate, an acrylic emulsion and TTMAP, TTAP or PTAP. This film was coated onto a polyester film to yield an antistatic, removable pressure-sensitive film [37].

A water-borne, pressure-sensitive adhesive was prepared from a low Tg acrylic copolymer, a carboxy-functional acrylic copolymer and TTAP. This material was coated onto a polyester film and covered with a release paper to give an adhesive tape suitable for bonding dewy or wet surfaces [38].

A water-borne, pressure-sensitive adhesive was prepared from a low Tg, carboxy-functional acrylic copolymer, a carboxy-functional rosin and TTAP. The composition was applied to a release sheet, dried and transferred to a polyester tape. The adhesive tape had good adhesion to steel and polyethylene with little whitening in water and with no crawling, shrinking, streaking or pinholes [39].

A heat-sealable coating was composed of an ethylene–methacrylic acid copolymer and TTAP. The composition was coated onto a polypropylene substrate and dried at 120 °C for 2 min to give a heat-sealable system that gave much improved adhesion [40].

A heat-activatable adhesive was prepared from crystalline, acrylic polymers, e.g., a copolymer of acrylic acid, ethyl acrylate and hexadecyl acrylate, and TTMAP. The mixture was heated at 80 °C for 2 days, dissolved in toluene and applied to a PVC film. The film was non-tacky at room temperature, but adhered well to skin at body temperature and was easily removed with a damp towel [41].

A pressure-sensitive adhesive for medical applications was prepared from a mixture of a tertiary amine functional hydrophilic polyacrylate, a carboxy-functional polyacrylate, mono- and di-carboxylic acids (e.g., lauric and adipic acids), optionally a polyol and TTMAP crosslinker. This adhesive was applied to siliconized polyester film and dried at 80 °C for 30 min to give an adhesive compress that adhered well to either wet or dry skin and had high permeability to water vapor [42].

A water-activatable adhesive was prepared from an solution of a maleic anhydride–methyl vinyl ether carboxy-functional copolymer and TTMAP in ethanol–toluene. A layer of this adhesive on polyester film could be activated with water to form a laminate with glass. The laminate exhibited strong adhesion and good moisture resistance [43].

A solvent-activatable adhesive was prepared from a polyurethane and TTAP or PTAP. The adhesive was applied to the lead end on one side and the trailing end on the opposite side of a polyolefin label. The adhesive was activated by solvent and the label wrapped around a container to complete the bonding process [44].

A water-borne, laminating adhesive was prepared from a vinyl plastisol, plasticizer (e.g., dioctyl phthalate) and TTMAP or TTAP. The composition had good heat stability, low setting temperatures, strong bonding strength and good resistance to water and oil. The composition was useful as an adhesive, coating or sealant for metal, glass and plastics [45].

A water-borne, laminating adhesive was prepared from a carboxy-functional polyurethane dispersion and TTAP. A laminate comprising a steel plate coated with the adhesive formulation, a non-woven cloth and a birch wood panel withstood water immersion, thermal shock and flexing without delamination or crack formation [46].

A water-borne, laminating adhesive was prepared from an EVA copolymer and TTAP. This adhesive could be used to laminate PVC sheets to lauan plywood [47].

A solvent-borne adhesive composition for PVC surfaces was prepared from polyacrylate and TTMAP [48].

A water-borne, heat-activatable laminating adhesive was prepared from a vinyl acetate polymer, a polyurethane dispersion and TTMAP and was stable for up to 90 days. The adhesive was applied to a thermoplastic sheet and dried. The adhesive layer was heated and contacted to a rigid substrate to form a strong bond [49].

A water-borne, dry-bonded laminating adhesive was prepared from a carboxy- and sulfo-functional polyurethane dispersion and TTMAP. This adhesive was useful in forming laminates of flexible films such as polyolefins, polyesters and polyamides as well as metals [50]. The laminate has improved bonded properties especially after immersion in boiling water.

A water-borne, laminating adhesive was prepared from a urethane/acrylate copolymer with a $T_g > 50\,^{\circ}\mathrm{C}$ and TTAP or PTAP. The composition was useful as an edge sealer or as a binder for holding frictional particles to antislip products such as friction surface sheet materials and non-skid or antislip sheet materials [51].

A water-borne, heat-activatable laminating adhesive was prepared from a polyurethane dispersion and TTMAP. The polyurethane dispersion was characterized as having a high polydispersity index, which gave a good combination of adhesion and thermal stability [52].

A water-borne, laminating adhesive was prepared from a polyacrylate resin and either TTAP or PTAP. This adhesive could be used to laminate polyethylene terephthalate to aluminum foil and polypropylene [53].

A water-borne, heat-activatable adhesive was prepared from a styrene–butadiene latex, melamine resin and TTAP. This adhesive could be used to laminate oak veneer to a lauan plywood [54].

Composites useful as recording disks with good adhesion consist of rigid layers bonded by a mixture of TTMAP and a copolymer of dimethyl sodium sulfoisophthalate–dimethyl terephthalate–ethylene glycol copolymer. The composite was useful in bonding a magnetic coating to a polyester film [55].

A solvent-borne laminating adhesive was prepared from a solution of a carboxy-functional polyacrylate resin and

TTAP. This adhesive could be used to laminate PVC sheets to steel plate [56].

A solvent-borne laminating adhesive was prepared by reaction of a polyester resin with PTAP and subsequently epoxy novalac or bis-phenol A epoxy resins. The composition was useful in bonding polyimide resin to copper foil with good peel resistance before and after soldering, after exposure to organic solvents or after aging at 257 °C for 96 h. The adhesive composition was useful for bonding film to film, film to foil, foil to foil, and hardboard to hardboard [57].

A solvent-borne laminating adhesive was prepared from a mixture of polyester, solid epoxy resin, polyurethane and TTAP. The adhesive could be used to prepare a laminate of polyester film and copper foil without bubbling. The laminate had good solder heat resistance [58].

A solvent-borne laminating adhesive was prepared from an ethylene–methacrylic acid copolymer zinc salt and TTAP. The adhesive was used to bond polypropylene fabric to a layer of 1-butene copolymer film to give a product with excellent peel strength that would be suitable for outdoor uses, e.g., tents or sheets [59].

A solvent-borne laminating adhesive was prepared from a chloroprene–methacrylic acid copolymer and TTAP. The composition was useful for bonding rubber sponge to a nylon jersey [60].

4.4. *Coatings*

The single biggest use of tris-3-(1-aziridino)propionate chemicals is in the formulation of high performance coatings and primers. The excellent solubility of tris-3-(1-aziridino)propionate crosslinkers in both water and solvent makes the crosslinkers a versatile coreactant for water-borne or solvent-borne systems. Tris-3-(1-aziridino)propionate crosslinkers are used in conjunction with all polymer types, including polyacrylates, polyesters, polyurethanes, and vinyl copolymers. Among the reported advantages are improved adhesion, hardness, mechanical properties and solvent and water resistance. Coating applications vary from general coatings for magnetic recording material, wood, anti-graffiti substrates, paper, and ophthalmic lenses and primers for improved adhesion to plastics.

4.4.1. *General*

Organotin polyesters based on aziridine were prepared from maleic anhydride–styrene copolymers that had been hydrolyzed and esterified with bis(tributyltin) oxide and mixed with TTMAP. The compositions were useful as matrix materials for fouling-resistant fiber-reinforced composites. These composites underwent no apparent change when subjected to Soxhlet extraction with benzene/2-butanone mixtures [61].

A solvent-borne coating composition was prepared from a carboxy-functional acrylic resin and TTAP. A cured film had higher hardness and better resistance to solvents, water and gasoline than an acrylic/urethane coating [62].

A water-borne coating suitable as a floor coating was prepared from a mixture of a carboxy-functional acrylic resin, a carboxy-functional urethane resin, a carboxy-functional resin (e.g., an acid modified rosin or a styrene–maleic anhydride copolymer) and TTMAP [63].

A water-borne coating composition was prepared from a carboxy-functional acrylic emulsion and TTAP. The cured composition was useful for automotive repair and had good resistance to methyl ethyl ketone, water and gasoline [64].

Water-borne coating compositions were prepared from acrylic and styrene–butadiene resins and were cured with TTMAP to give room-temperature cured coatings with good water spotting and MEK rub resistance, gloss enhancement and good Sward and pencil hardness [65].

A water resistant aqueous coating with good soil release properties was prepared from a fluoropolyolefin, a macromonomer having hydrophilic groups (e.g., polyethylene glycol mono(vinyloxybutyl) ether) and TTAP [66].

Magnetic recording tapes with a magnetizable layer was prepared from a dispersion of inorganic particles, a carboxy-functional acrylic copolymer dispersion and TTMAP or TTAP. A magnetic recording tape was prepared by coating the binder on plasma-treated polyethylene terephthalate, orienting the pigment magnetically in the longitudinal direction and drying at 90 °C for 2 min. The tape had excellent blocking and wear resistance [67].

Non-agglomerating magnetic recording ink was prepared from Cr_2O_2, a polyester based polyurethane dispersion and TTMAP or TTAP [68].

A coating for a magnetic disk was prepared by coating Krytox M157 carboxy-functional fluorocarbon lubricant onto the disk and then treating with TTAP. The coating had low static and sliding friction and good wear resistance [69].

Magnetic recording material consisted of a non-magnetic support and a magnetic recording layer comprising a ferromagnetic powder and a binder prepared from a polyisocyanate and TTAP. The recording material had high recording density and reliable replay properties [70].

Magnetic recording material consisted of a non-magnetic support and a magnetic recording layer comprising a ferromagnetic powder, an abrasive, carbon black and a binder prepared from a polyisocyanate and TTAP. The recording material had high recording density and reliable replay properties [71].

A water-borne coating for metal or plastic consisted of a polyurethane dispersion and PTAP. The cured composition was suitable for protecting metalized plastic parts for head lamps or metal wheel covers [72].

A paper coating was prepared from a copolymer of maleic anhydride and isobutene was reacted with butanol and glycidyl versatate and blended with TTAP. The coating had better gloss and adhesion than an aqueous acrylic coating [73].

Sized paper was coated with low density polyethylene and then with a mixture of poly(vinyl acetate) and TTMAP to yield a laminate with adhesion to polyvinyl chloride [74].

A coating for ceramic tile consisted of a polyurethane dispersion and TTMAP. The coating had high gloss and adhesion and good resistance to citrate, alcohol and yellowing from UV exposure [75].

A thermochromic coating was prepared from polyurethane dispersion or polyacrylate latex, a fusible polyester or polyamide powder, TTMAP and an encapsulated thermochromic liquid crystal dispersion. The thermochromic coating was screen-printed onto a black polyester/cotton textile, air-dried and hot-pressed at 120 °C to give a thermochromic coating with good color brightness and soft feel [76].

An anticorrosive composition was prepared from a polyurethane dispersion and TTAP. A zinc coated sheet was first treated with chromate and then coated with the composition to give a sheet that showed no formation of rust after 1000 h of salt-spray [77].

An anticorrosive composition was prepared from copolymers with ionic linkage (e.g., ionomers of ethylene or styrene crosslinked with methacrylic acid), silica, powdered polyethylene wax and TTAP. Metal strips that had been coated with the anticorrosive composition showed good corrosion resistance, good printability and improved workability [78].

An anti-chipping composition was prepared from a polyurethane dispersion and TTAP. A coating system for zinc phosphate treated galvanized steel consisted of an e-coat, the composition as primer and topcoated. The coated article showed good resistant to chipping, impact and moisture resistance [79].

Aircraft coatings were prepared from polyurethane dispersions and TTMAP that had 80 in lb Gardner impact resistance when applied to an epoxy primer-coated aluminum alloy [80].

A coating for aluminum substrate was prepared from poly(vinyl chloride) and PTAP. The coating formulation that included the PTAP gave adhesion to aluminum, whereas without the tris-3-(1-aziridino)propionate there was no adhesion [81].

A two-component coating for sheet molding compound was prepared from a combination of a polyester polyol with acid value >1, PTAP and a polyisocyanate. The coating had good adhesion with water and solvent resistance [82].

A plastic coating was prepared from a hydroxy substituted resin, a polyisocyanate and TTMAP. The hydroxy substituted resin was a copolymer of vinyl pivalate, vinyl versatate, hydroxyethyl allyl ether undecylenic acid and chlorotrifluoroetheylene. The composition could be used to coat polyethyl terephthalate or polycarbonate moldings or for repair of poly(vinylidene fluoride) coated materials [83].

A primer for an ophthalmic lens was prepared from a latex rubber (e.g., carboxy styryl–butyl rubber) and TTMAP. The ophthalmic lens was primed with the above composition and topcoated with an acrylic–styrene copolymer. The primer improved the shock resistance [84].

A golf ball primer composition was prepared from a mixture of acrylic or polyurethane dispersion and TTMAP. A coating system for the golf ball made with the above primer and a polyurethane topcoat showed good adhesion [85,86].

Films with good mechanical strength, weather and light resistance and resistance to haze formation was prepared by coating a polyester sheet with a combination of acrylate copolymer emulsion, colloidal silica and TTAP. The protected sheet was suitable for agricultural uses [87–89].

In the preparation of gas-barrier packaging films, an anchor coating on polyethylene terephthalate with good moisture resistance was prepared from polyvinyl alcohol and TTAP [90].

An antifogging composition was prepared from an inorganic colloidal sol (e.g., alumina), a silyl containing polyacrylate resin and TTAP. The cured composition had good adhesion to plastic or glass and formed films with good transparency and antifogging when first formed and after 1 year [91].

An antifogging coating layer in a lamination was prepared from an acrylic polymer emulsion and TTAP [92].

Films with good water resistance and bleeding prevention were prepared from a polyvinyl chloride support and a coating based on carboxy-functional polyacrylate, monoisopropyl phosphate and TTAP [93].

Glossy coatings with good hardness were prepared from a fluoropolymer, e.g., butyl acrylate–methacrylic acid–chlorotrifluoroethylene–Me methacrylate–tetrafluoroethylene–vinylidene fluoride graft copolymer dispersion, and PTAP [94].

A plywood primer was prepared from a carboxy-functional styryl–butyl rubber and TTAP. The primer was applied in two coats with curing at 50 °C after each coat. The primer was topcoated with a two-pack acrylic urethane to give material suitable for framing concrete forms [95].

A plywood primer was prepared from a latex resin, polyisocyanate and TTAP. The primer was applied in two coats with baking after each coat. The primer was topcoated with a 100% solids, two-pack acrylic urethane to give material suitable for framing concrete forms that would give smooth, glossy concrete surfaces [96].

A plywood primer was prepared from a melamine–urea condensate, a polyurethane dispersion and TTAP. A topcoat was prepared from the polyurethane dispersion and TTAP. A plywood panel was primed and topcoated to give good surface smoothness. The composition could be cured at low temperatures [97].

A plywood coating was prepared from an acrylic acid–methyl methacryl–styrene copolymer and TTAP. The coating was applied to plywood and stored at 80 °C for 24 h to give a coating with good alcohol, methyl ethyl ketone, heat and soil resistance [98].

A wood coating was prepared from a polyester based polyurethane dispersion, trimethylol triacrylate, polyethylene glycol diacrylate and TTMAP that showed good sealing and adhesion [99].

Antigraffiti additives were prepared from a fluorocarbondiol and a polyisocyanate. The fluorocarbon was prepared by reacting a mixture of a fluorocarbon alcohol or acid and a glycol with TTMAP. The additives were useful for the preparation of coating compositions with increased soiling resistance and stain release properties [100].

An electrically conductive coating on quarry tile was composed of a polyurethane dispersion, carbon black and TTAP or PTAP. A 25 mil coating had 1600 Ω resistance with good adhesion and abrasion resistance [101].

A graft coating system for polyethylene consisted of an aliphatic moisture curing polyurethane and TTMAP [102].

A hybrid coating for a medical device is prepared from a polyester based polyurethane dispersion and TTMAP in the first layer. The first layer also includes a therapeutic agent. The second layer had a cobonded anticoagulant. Together these layers provide a hybrid coating with controlled release bioactive materials [103].

A primer for a current collector (the combination of the elements that function as anode or cathode, generically known as electrodes, together with the elements for collecting or distributing the current accumulated on the electrodes) was prepared from a ethylene–acrylic acid copolymer, PTAP and a conductive pigment. The electrode layer was adhered to the primer layer [104].

A composition that contained maleimide–styrene copolymer and PTAP with a *p*-toluenesulfonic acid catalyst was cured at 110 °C to give a product with good solvent and water resistance [105].

A photocurable coating was prepared from a mixture of nitrobenzyl functional acrylate and TTAP. The mixture was subjected to 2 min exposure to a high pressure Hg vapor lamp to give a coating with good adhesion to a decreased steel panel and which was insoluble in esters, ketones, alcohols and aromatic solvents [106].

A photocurable composition was prepared from a mixture of crosslinkable neutral and carboxy-functional acrylic monomers and TTAP. The composition was coated onto polyethylene, bonded to stainless steel and cured with a Hg lamp. When the polyethylene was peeled away, the stainless steel was protected with an acrylic coating with good adhesion and hardness [107].

A radiation-curable coating was prepared from liquid bis-phenol A epoxy resin and PTAP using a UV catalyst ($PH_3S{\cdot}SbF_6$) that generated a Lewis acid upon irradiation. Adhesion of the epoxy was dramatically improved with the inclusion of the tris-3-(1-aziridino)propionate resin [108].

4.4.2. Aziridine as primer vehicle

Coating aramide fibers with a 1% aqueous solution of TTMAP, TTAP or PTAP increased the shear strength of unsaturated polyester matrix composites [109].

The adhesion of a magnetic coating to biaxially oriented polyester was increased when the polyester was first treated with a solution of TTMAP in acetone [110].

A Surlyn A sheet was treated with a 1% TTAP solution in isopropanol as a primer solution. The tris-3-(1-aziridino)propionate improved the adhesion of two-pack epoxy, two-pack urethane, vinyl chloride polymer or phthalic acid resin coatings [111].

The delamination resistance of a composite film consisting of layers of poly(ethylene terephthalate) and an acrylic acid–ethylene copolymer was improved when the polyester film was treated with a mixture of TTMAP and Triton® TX-100 wetting agent before lamination with a polyacrylic extrusion [112].

An ice releasing film used TTMAP as a primer on poly(ethylene terephthalate). The poly(ethylene terephthalate) film was first treated with the tris-3-(1-aziridino)propionate and then with a polysiloxane topcoat to form an article capable of repeatedly releasing ice [113].

Polyester fibers were first treated with a primer made from TTAP or PTAP, made into cords and then coated with adhesives (e.g., a resorcinol–formaldehyde copolymer latex with vinylpyridine latex). When the cords were embedded into a rubber stock, the cords exhibited improved adhesion [114].

A polypropylene surface that had been modified with maleic anhydride graft was treated with TTAP as a primer. The tris-3-(1-aziridino)propionate primer was topcoated with a two-pack polyurethane. The topcoat had excellent adhesion to the polypropylene [115].

The adhesion between a flexographic printing plate and the photosensitive layer was improved by the use of a TTMAP as a primer on the printing plate before application of the polyacrylate layer [116].

A bowling pin had the Surlyn ionomer of the undercoat bonded to the polyurethane topcoat by use of TTMAP, TTAP or PTAP as a primer or tie coat. The use of the tris-3-(1-aziridino)propionate *crosslinker* improves the shock resistance of the lamination [117].

4.5. Inks and printing

Although the number of publications for the use of tris-3-(1-aziridino)propionate crosslinkers in inks is lower than other applications, the references report many, varied resin combinations, including polyacrylates, polyurethane dispersions, polyvinyl chloride and shellac. Both water-borne and solvent-borne formulations are reported.

A thermal printing composition useful for the preparation of food packaging labels was prepared from a water-stable phenol–amine complex, a furan–styrene copolymer and TTMAP [118].

A paper coating for print stock (labels, magnetic cards, etc.) with good resistance to the migration of adhesive or vegetable oil was prepared from a mixture of butylamine salt of dihydoxydiphenyl sulfone, a silicone defoamer, behemic acid amide, styrene–maleic anhydride copolymer and TTMAP or PTAP [119].

An image-receptive coating was prepared from a mixture of a carboxy-functional polyacrylate emulsion, a water-soluble polymer (e.g., polyvinyl alcohol) and TTMAP, TTAP or PTAP. The mixtures formed a transparent coating which did not change in integrity after absorption of solvents. The composition was useful in ink-jet printing to form non-tacky ink-absorbing coatings for graphic art [120].

An image-receptive coating was prepared from a water-soluble, amphoteric polymer and TTAP or PTAP. The coating was used on a polyester film or a resin-coated paper. The coating prevented damage from water and could produce images with photograph picture-like gloss [121].

A image-receptive sheet with a colloidal silica anchor layer was prepared with colloidal silica and an acrylic resin binder with PTAP crosslinker and topcoated with a polyacrylamide polymer ink-receiving layer. The sheet shows rapid ink absorption and a lustered surface that gives clear images [122].

An image-receptive sheet was prepared from a coating based a polyurethane dispersion and TTMAP. The coating was applied to at least one side of the sheet. The sheet was useful for multiple applications including manual drafting, ink-jet recording and electrophotographic printing and copying [123].

A coating receptive to water-borne ink-jet printing ink was prepared from a carboxy-functional acrylic copolymer and PTAP. The ink-jet printing sheet prepared with the above coating showed a good printed image, ink absorbance, ink fixing, surface gloss, water resistance, light resistance and little color change in the non-printed area over time [124].

A coating receptive to ink-jet recording was prepared from a terpolymer of vinyl lactam, acrylic acid and 2-carboxyethyl methacrylate and TTMAP crosslinker. This crosslinked terpolymer formed water-insoluble coatings on supports such as paper or polyester and were particularly receptive to water-based ink-jet printing inks [125].

A water-borne coating for the receptive layer of an ink-jet recording medium was comprised of a mixture of a polyvinyl colloidal suspension (e.g., polyvinyl acetate), a water-soluble polymer (e.g., polyvinyl pyrrolidone), a radiation-curable monomer and PTAP. When both the water-soluble and the water-insoluble prepolymers were cured, a coating was created which had a cage structure with the radiation cured, water-insoluble material existing as a micelle within the water-soluble polymer matrix. The medium exhibits excellent water resistance and extremely high gloss [126].

A water-borne coating for the receptive layer of an ink-jet recording medium was comprised of a mixture of a polypeptide gelatin, a plasticizer based on 2-pyrrolidone, a polyurethane dispersion and PTAP. The ink-jet receiving medium had fast ink dry time, good dye-fade resistance, dimensional stability and durability [127].

A coating for a thermal stencil sheet was made with a mixture of polyurethane dispersion, melamine crosslinker and TTMAP. The coating also contains a dispersed IR absorbing material. This thermal stencil sheet was used with a printing system [128].

Recording film for producing printing plates consisted of a coating composed of a polyester based polyurethane and TTMAP. The important feature was the weakening of chemical bonds upon impact with IR radiation, such that the resin portion with weakened bonds could be washed away [129].

A coating for security paper was prepared from a mixture of polyurethane dispersion, vinyl copolymer (e.g., styrene/acrylic copolymers, acrylated vinyl acetate, vinyl chloride/ethylene copolymers, or vinyl acetate copolymers) and TTMAP. The coating does not increase the opacity of the paper [130].

A solvent-borne printing ink was prepared from a resin made with an amine terminated polyurethane resin and PTAP. The ink was suitable for printing on polyester film, which was used in a lamination with polyethylene [131].

A water-borne printing ink was prepared from a shellac resin and TTAP. This ink was suitable for use in a printed lamination, where the ink was printed onto a sheet and the sheet was laminated on both sides with a polyolefin coating. The laminate was suitable for photographic processing for the prevention of edge-permeation of the processing solution [132].

Water-borne printing inks suitable for corona-treated polypropylene were prepared from acrylic resin emulsions and TTAP or PTAP. The ink was readily transferred gave easy of plate cleaning and produced markings with good resistance to abrasion, water, alcohol and alkali [133].

A water-borne printing ink was prepared from a polyurethane resin that had been reacted with PTAP and a polyurethane resin that contained carboxy groups. The two resins were prepared independently in acetone and then combined. The addition of water and subsequent azeotropic distillation to remove acetone gave the desired ink, which had good storage stability and adhesion to various plastics [134].

An oil based varnish suitable for lithographic inks was produced from a rosin modified phenolic resin, linseed oil and TTAP. The varnish had good printability and drying properties [135].

A two step ink-jet ink system consisted of first applying TTMAP to a substrate and subsequently applying a polymer solution having a functional group reactive with the aziridine (e.g., carboxy, thiocarboxy, sulfo, phosphono, epoxy and isocyanato). Printed images with excellent wet rub resistance and accent marker resistance were obtained. The system can be used to produce images directly or develop lithographic printing plates [136].

An ink-jet recording sheet comprised an ink-jet receptive layer on a substrate. The ink-jet receptive layer consists of a water-soluble polymer, (poly)vinyl pyrrolidone/

dimethylaminoethyl methacrylate copolymer, crosslinked with PTAP. The resulting ink-jet medium exhibits excellent water resistance and high gloss [137].

4.6. Photography

A photographic sheet is a complicated laminate of many coatings on both sides of a carrier film (usually polyester) including pigmented and non-pigmented backing layers, subbing (primer) layers, antistatic layers, silver or color imaging layers and abrasion resistant layers. Tris-3-(1-aziridino)propionate crosslinkers have been used in all these layers as coreactants for film forming resins, e.g., polyacrylate or sodium sulfostyrene copolymers, to improve the performance.

An antistatic backing layer consisted of a copolymer of sodium styrenesulfonate and maleic acid, a hydrophobic polyacrylate copolymer and PTAP. The surface resistance and clarity of this antistatic layer was much better than an antistatic layer consisting solely of poly sodium styrenesulfonate [138].

An antistatic backing layer consisted of a polyacrylate and TTAP. The coating had good adhesion to a flame treated polyester film without the need for a subbing (primer) layer and exhibited good antistatic characteristics [139].

An antistatic backing was prepared in a two-coating process. The first coating consisted of an electrical conductive sodium styrenesulfonate–maleic anhydride copolymer and, optionally, a carboxy-functional hydrophobic polymer. The second coating consisted of PTAP. The backing from the two-coating process gave improved water resistance and surface resistivity compared to a single layer coating of the sulfonate copolymer and PTAP [140,141].

An antistatic backing was prepared in a two-coating process. The first coating consisted of an electrical conductive sodium styrenesulfonate–maleic anhydride copolymer. The second coating consisted of gelatin and PTAP. When wet, the crosslinking agent will migrate into the conductive polymer-containing layer effectively serving to crosslink gelatin and conductive copolymer. The presence of the gelatin layer improves the adhesion of subsequent layers [142].

An antistatic layer consisted of a maleic acid–sodium sulfostyrene copolymer, a styrene–aziridine functional acrylic ester copolymer and TTAP. The aziridine functional copolymer exists as hydrophobic, insoluble particles in the antistatic layer. The antistatic layer was applied to an acrylic primer on a polyester film and topcoated with a backing, protective layer. The antistatic layer was transparent without haze [143–152].

An antistatic backing layer consisted of a carboxy-functional, crosslinkable, conductive polymer (e.g., poly(sodium styrene sulfonate–maleic anhydride)), hexadecyl betaine, alkyldimethyl betaines, carboxylated imidazolines and coco amido betaines TTMAP or PTAP. The photographic film had a silver halide emulsion layer coated on one side of a polyester film, and an antistatic layer and the above backing layer on the other side. The backing coatings contributed antistatic properties and antihalation effects to the film [153].

An antistatic layer consisted of a water-soluble conductive polymer, a water-soluble polymer polyacrylate resin and TTAP. The photographic material shows good antistatic ability even after being developed [154].

An antistatic backing layer consisted of a water-soluble, electrical conductive, carboxy-functional acrylic polymer, TTMAP, an antihalation dye and a matting agent. The coating was applied to the back of a polyester film exhibited excellent antistatic and antihalation parameters as well as low dye-stain and improved dimensional stability [155].

A backcoat for a photographic recording material was prepared with a conductive organic polymer, colloidal silica, sodium magnesium silicate, a surfactant, a polyacrylate resin and PTAP crosslinker. The photographic recording material showed good condition before and after processing, good printability, smear-resistant characteristics and improved adhesion [156].

An antistatic coating consisted of a water-soluble, electroconductive polymer with sodium sulfonate functionality, a hydrophobic polymer with methylol functionality and TTMAP, TTAP or PTAP. The coating composition was applied to a polyester film base and subjected to thermal treatment to form an antistatic layer without appreciable haze useful for photographic film [157].

An antistatic coating consisted of an electrical conductive polymer which was crosslinked with TTMAP or TTAP [158].

An antistatic coating consisted of an electrical conductive polymer, a hydrophobic polymer and TTAP. The antistatic layer could be coated on the same side as the photographic emulsion layer [159].

An antistatic coating consisted of an electrical conductive sodium sulfoisophthalate copolyester which was crosslinked with PTAP [160].

An antistatic coating consisted of an electrical conductive polymer, e.g., poly(sodium styrenesulfonate), and TTMAP or PTAP. When applied to a polyester support, the tris-3-(1-aziridino)propionate immobilizes the conductive polymer to form a distinct and permanent antistatic layer, that gives antistatic protection to the photographic element [161,162].

An antistatic coating consisted of a mixture of smectic clay or zinc antimonate particles, polyurethane or gelatin dispersion and TTMAP [163].

Subbing (primer) layer coating compositions contained gelatin, a water-soluble polyester and TTMAP, TTAP or PTAP. Use of this subbing layer resulted in less waste and improved recycling of biaxially oriented polyester film supports [164,165].

A white reflective subbing (primer) layer consisted of a carboxy-functional acrylic resin, fluorocarbon surfactant and TTMAP, TTAP or PTAP. The coating was applied to a flame treated opaque polyester film support and topcoated with a gelatin–acrylic layer. The white reflective subbing layer showed good anchorage to the polyester when tested both under dry and wet conditions [166].

A subbing (primer) layer consisted of an acrylic resin and TTAP. The subbing layer was applied to a polyester support and overcoated with a photosensitive composition. The system was useful in an ammonia-type process diazo machine [167].

A subbing (primer) layer consisted of an aqueous latex resin (e.g., butadiene–acrylic ester copolymer or polystyrene), a water-soluble resin (e.g., casein or gelatin, cellulose derivatives, polysaccharides, vegetable gums or synthetic polymers such as polyvinyl alcohol or ethylene–maleic acid copolymer) and TTAP. When a corona-treated polypropylene paper was treated with the subbing coating, the adhesion of a gelatin–Ag emulsion was satisfactory [168,169].

A subbing (primer) layer consisted of a gelatin-grafted polyurethane. The coating was prepared from gelatin, polyurethane dispersion and TTMAP. The subbing layer was an adhesion promoting underlayer for photographic film [170].

Overlay color-proving film was prepared with a protective coating consisting of a carboxy-functional methacrylate copolymer and TTAP or PTAP. A polyester film was coated on one or both sides with the above coating. A photosensitive coating was then applied to the treated film [171].

Photographic recording material with a printable backside was prepared from a silver halide emulsion layer on one side and a back coating layer consisting of a conductive organic polymer, colloidal silica, a carboxylic functional acrylic resin and PTAP [172].

An imaging element in a photographic diffusion-transfer material of the “peel-apart” type consisted of several layers. An intermediate layer consisted of polyacrylamide and PTAP. An image-receiving layer consisted of a graft copolymer comprising 4-vinylpyridine and vinylbenzyl trimethylammonium chloride grafted onto hydroxyethyl cellulose and PTAP [173].

Photographic film had a coating based on a protein gelatin and TTAP or PTAP. The tris-3-(1-aziridino)propionate was necessary to obtain the desired adhesion of the coating to the primer coat, which consisted of a water-dispersible copolyester. This layer acted either as the subbing underlayer layer to tie the gelatin topcoat to the primer or as the photographic coating [174].

An imaging element had a topcoat composed of a polyurethane dispersion, a fluoropolyether and TTMAP. The flourocarbon imparted improved water repellency to the element [175].

An imaging element consisted of a support film and a coating layer made from a film forming, acrylic copolymer and non-film forming polymeric particles. The non-film forming particles were prepared from an acrylic copolymer crosslinked with TTMAP. The non-film-forming polymer particles were glassy polymers that provided resistance to blocking, ferrotyping, abrasion, and scratches [176–178].

An imaging element consisted of a support film and a coating layer made from a film forming, acrylic copolymer, non-film forming polymeric particles and a fluoropolyether. The non-film forming particles were prepared from an acrylic copolymer crosslinked with TTMAP. The non-film-forming polymer particles were glassy polymers that provided resistance to blocking, ferrotyping, abrasion, and scratches. The flourocarbon imparted improved water repellency to the element [179].

An imaging element had a topcoat composed of a fluoroacrylate copolymer and TTMAP. The fluoroacrylate copolymer had two different segments, one of which was fluorinated and oleophobic and the other of which was hydrophilic. The overcoat imparted stain resistance to the element [180].

An imaging element had a topcoat composed of a urethane–acrylic copolymer, a water-soluble polymer (e.g., polyvinyl alcohols, cellulose ethers, *n*-vinyl amides, functionalized polyesters, poly(ethylene oxide), starch, proteins including gelatin, whey and albumin, alginates and gums) and TTMAP. Initially the topcoat was permeable to processing solutions, but became fused when treated to a developer solution with pH greater than 7. The topcoat imparted excellent resistance to water permeability, fingerprinting, fading and yellowing, exceptional transparency and toughness necessary for providing resistance to scratches, abrasion, blocking, and ferrotyping [181].

An imaging element had a protective coat that consisted of a stain resistant interpolymer (e.g., a fluoromethacrylate copolymer), a polyurethane dispersion and TTMAP. Use of this protective coat on a standard imaging element with silver halide gelatin and antistatic layer produced a product with improved tar adsorption and stain [182].

Motion picture film prepared from a matting agent, a polyacrylate resin and TTMAP had excellent protection from ferro-typing, improved resistance to abrasion and excellent image quality and soundtrack reproduction [183].

4.7. *Thermal and electrostatic imaging*

Tris-3-(1-aziridino)propionate crosslinkers have been used in thermal and electrostatic imaging formulations to reduce blocking of the sheets and to improve recording sensitivity. Coreactants included styrene–maleic acid and vinyl copolymers and polyacrylate resins.

Thermal transfer material was prepared by forming a thermal transfer ink layer on the front of a polyester base film and a hardened film on the back. The hardened film was prepared from a styrene–maleic acid copolymer and TTAP. The ink layer was prepared from carnauba wax and carbon black. This composition showed good antisticking properties and high sensitivity [184].

Thermal transfer material was prepared by forming a thermal transfer ink layer on the front of a polyester base film and a hardened film on the back. The hardened film was prepared from a carboxy-functional polyacrylate resin, a carboxy-functional silicone resin and TTAP. Without the TTAP the backcoat showed sticking with the thermal head [185].

A thermal transfer receptor sheet had a protective layer that consisted of a water-borne carboxy-functional vinyl copolymer and TTAP. The recording material had good antisticking properties, and provided high density images with excellent storage stability [186].

A thermal transfer receptor sheet consisted of paper with a coating layer containing a water-soluble or water-dispersible dye, a carboxy-functional silicone, vinyl polymer particles and TTAP. The sheets had a matte surface, which prevented melt-adhesion to the transfer sheets and provided high quality images with high density [187,188].

A water-borne coating, receptive to thermal transfer, was prepared from a dyeable resin, a release agent, TTAP and core–shell resin grains having a rubber core. The coating enables the control of glossiness of images without impairing their quality and recording sensitivity [189].

A water-borne mold-release coating for a thermal transfer sheet was prepared from a sulfo-functional polyester resin, a mold-release agent, TTAP and, optionally, thermoplastic resin particles. The image receptor sheet showed superior recording sensitivity and produced sharp and high density images [190,191].

A thermal transfer receptor sheet for preparing electrostatic transparencies was prepared by coating a polyester film with a coating layer containing an EVA copolymer, an amine modified silicone oil and TTAP. The media showed good storage stability and provided clear images without greasing on rough paper [192].

A thermal transfer sheet consisted of a peeling layer, an interlayer containing a thermosetting resin and an image formation layer containing gelatin and TTAP. The material showed good image recording and the support was able to be recycled after image formation [193].

A thermal transfer printing ribbon was prepared with an internal layer with good adhesion to a support layer was prepared from a polyamide resin and TTAP [194].

A thermal recording material with durable image was prepared from a heat sensitive layer and a protective layer containing a copolymer of acrylamide, acrylate esters and polyvinyl alcohol and TTAP. The material provided high and low density images with good resistance to plasticizers, oils and water [195].

Thermal recording material was prepared consisting of a paper support with a thermally sensitive layer and a backcoat layer that consisted of polyvinyl alcohol, aluminum hydroxide, zinc stearate and TTAP [196].

Thermal recording material was prepared consisting of a paper support with a heat sensitive layer and a protective layer. The heat sensitive layer contained leuco dyes and color developers and the protective layer consisted of a maleic anhydride copolymer and TTAP [197].

Thermal recording material was prepared from a thermal color-forming layer containing leuco dyes and developer and a protective layer containing polyvinyl alcohol and TTAP. The images of the recording material were easily read by laser image readers [198].

Thermal recording material consisted of a thermal recording layer, an interlayer and a protective layer. The interlayer and protective layers were prepared from UV curable resins. The thermal recording layer consisted of leuco dyes and developer, a crosslinkable acrylic resin and TTAP [199].

Thermal recording material consisted of a thermal recording layer, an interlayer and a protective layer. The protective layer was prepared from a UV curable resin. The interlayer consisted of a polyester resin and TTAP and colloidal silica. The thermal recording layer consisted of leuco dyes and developer and a polyester polyurethane resin [200].

Thermal recording material consisted of a thermal recording layer and a protective layer. The protective layer was prepared from an isoprene–phenylacrylamide–maleic anhydride copolymer, TTAP and organic or inorganic pigment. The thermal recording layer consisted of leuco dyes and developer and a polyester polyurethane resin. The material showed improved water resistance and was suitable for outdoor use [201].

Thermal recording paper sheet of improved strength was prepared from layers of recycled paper and used pulp which was crosslinked with TTAP [202].

An abrasion resistant antistatic layer for an imaging element (electrostatic, thermographic or photographic) was prepared from an aqueous mixture of an electronically conductive polymer, a polyurethane dispersion and TTMAP [203].

A negative photoresist was prepared by coating a polyester support with polyacrylate, a partially esterified styrene–maleic anhydride copolymer, a carboxylic acid substituted polyacrylic, carboxy-functional urethane oligomer and TTAP or PTAP [204].

An element suitable for preparing electrostatic transparencies was prepared from a polyester support, a subbing (primer) layer and a toner receptive layer. The toner receptive layer consisted of a sodium styrenesulfonate–maleic copolymer, a water-soluble, carboxy-functional, polyacrylate resin, inert beads made from polyacrylate, either polyethylene or Teflon and TTMAP or PTAP [205].

An element suitable for preparing electrostatic transparencies was prepared from a clear plastic support and a toner receptive layer. The toner receptive layer consisted of a carboxy-functional, polyacrylate core/shell latex polymer, an antistatic agent and TTMAP, TTAP or PTAP [206].

Toner particles were prepared by polymerizing aziridine functional polyacrylate monomers, carbon black treated with TTAP, polyvinyl alcohol and sodium sulfate in the presence of AIBN and water [207,208].

A coating receptive to recording with ink-jet printing ink was prepared from gelatin, which may optionally have been grafted with *N*-vinylpyrrolidone, and TTAP. The coating was especially suitable for overhead projection sheets [209].

4.8. Fiber and fabric treatment

Tris-3-(1-aziridino)propionate crosslinkers have been added to fiber and fabric treatment formulations to improve resistance to dry cleaning and laundering and provide special effect coatings, like water repellency. A variety of coreactant resins have been used including polyurethane dispersions, polyacrylate and melamine resins. Among the textiles that have been used are cotton, wool, silk, polyester and nylon.

A fabric treatment composition was prepared from a flourocarbon functional polyacrylate and TTAP. Cotton fabric treated with a solution of the above composition and dried at 120 °C for 3 min gave a water- and oil-resistant fabric with good wash fastness and good resistance to dry-cleaning solvents [210].

Silk and other fabrics are water- and oil-proofed with a combination of a fluorocarbon, a metal alcoholate or ester and TTMAP, TTAP or PTAP [211,212].

A finishing agent composition consisted of a mixture of *N*-β-(aminoethyl)aminopropyltrimethoxysilane and TTAP or PTAP, which had been hydrolyzed, and mixed with a silicone water repellent and a hardener in methyl ethyl ketone. Scoured and dyed polyester fabric was soaked in the solution to 40% pickup, dried at 120 °C and heated at 180 °C for 1 min to give a fabric with excellent water repellence and good adhesion to a lining coated with polyamide hot-melt adhesive [213].

A textile coating composition was prepared from a polyurethane dispersion, an acrylic emulsion, a self-curing polysiloxane and TTAP. This composition was knife- or roll-coated on fabric and cured to give a hydrophobic coating that have improved resistance to dry cleaning and laundry compared to compositions without the tris-3-(1-aziridino)propionate crosslinker [214].

A textile or leather coating composition was prepared from a polyurethane dispersion with carboxy- and sulfo-functionality, a polymeric thickener without carboxy groups, TTMAP or PTAP and a hydrophilicly modified, hexamethylene biuret polyisocyanate. A polyamide was coated with the above composition to give a microporous, moisture permeable coating [215].

An aqueous fabric treatment composition was prepared from a fluoropolymer, a melamine resin and TTAP. Nylon taffeta was printed with the above paste and baked at 170 °C for 30 s to produce a fabric whose water repellency in the printed parts was greater than 90%. The fabric formed patterns that only appeared when wet and would be useful for swimwear, diaper covers, umbrellas and tents [216].

Textiles containing keratin fibers had increased shrink and felt resistance when treated with a mixture of Impranil DLN polyurethane dispersion and TTMAP [217].

Wool was shrink-proofed by first dipping into a solution of water-soluble organo-phosphine, then immersed in a second aqueous bath of TTAP and finally rinsed in water and dried [218].

Polyester fiber was grafted with a mixture of collagen, bactericides and TTAP to give a fabric showing lasting antimicrobial, antistatic and water absorption properties [219].

Odor absorbing, antibacterial organic fibers were prepared that contained metal carboxylates. Scoured cotton yarns were first treated with a solution containing methacrylic acid, a chelating agent, dilute sulfuric acid, hydrogen peroxide and ferrous sulfate. The fibers were then treated with sodium hydroxide and cuprous sulfate to give fibers containing 1.5% copper. The fibers were finally treated with TTAP to give fibers that exhibited odor absorption after 20 wash cycles [220].

Ink-jet printing of fabrics with print sharpness and retention of fabric handle (feel) was accomplished by first treating the fabric with a metal salt and then treating the fabric with an aqueous solution of polyesters or polyamides and TTAP. The printed fabric had a sharp pattern without ink oozing and had good fastness to washing and crocking [221].

Dyeability of hard to dye fabrics, e.g., Kevlar fiber or silk with anionic dyes, was improved by treatment with TTAP [222].

Weathering of silk was improved by treatment with TTAP [223].

A carpet back coating was prepared from a vinyl copolymer (prepared from ethylene, vinyl acetate and hydroxyethyl ethylene) and TTMAP or PTAP. The carpets treated with the carpet back coating exhibited increased wet strength [224].

Retroreflective textile ink was prepared from glass beads, a polyacrylate resin and TTMAP. Use of this ink form textiles having prints that are only noticeable at night [225].

Moisture absorptivity of a cloth made from hydrophobic synthetic fiber was improved by treatment with polyacrylate resins that had been crosslinked with TTAP [226].

4.9. Miscellaneous uses

This section covers a wide range of applications that makes use of the good solubility, the high functionality and the interesting reactivity of the tris-3-(1-aziridino)propionate crosslinkers. For example, tris-3-(1-aziridino)propionate crosslinkers have been used as a binder in rocket fuels, as the immobilizing agent for various biologicals and as an antioxidant.

A solid propellant was prepared from polybutadiene, aluminum powder–ammonium perchlorate mixture and TTAP. The propellant slurry had good moldability. The solid propellant had good rupture strength and elongation [227].

A chromatography column suitable for separating adenine nucleotides was prepared be depositing a mixture of poly(ethylene imine) and TTAP onto silica gel. This column was more effective than one prepared with poly(ethylene imine) and glutaraldehyde—the traditional medium for protein purification [228].

Spherical beads of κ-carrageenan containing entrapped Bacillus were prepared by treating a cell-κ-carrageenan suspension in stirring oil with TTMAP. The beads had superior resistance to heat and abrasion [229].

PTAP was used to from crosslinks between a copper cluster $[Cu(I)_8Cu(II)_6penicillamine_{12}Cl_5]$ and molecules with biological activity such as *d*-biotin and proteins. The biologically active cluster had potential for biomedical applications, e.g., delivery of ^{64}Cu for positron tomography [230].

Enzymes were immobilized using a low molecular weight prepolymer of TTAP or PTAP. The single-step immobilization can take place in either water or inert organic solvent at room temperature. The enzymes are immobilized on a solid support and retain their enzymatic activity [231].

PTAP was used to immobilize the enzyme D-aminoacid oxidase with good retention of enzymatic activity in a fixed bed reactor used continuous operation [232].

The hydrophilicity of polypropylene was improved by treatment of a chromic acid etched surface with TTMAP. Before treatment the water contact angle of the polypropylene was ~92°; after treatment with chromic acid, the contact angle was ~90°; and after treatment with chromic acid and TTMAP, the contact angle was ~70° [233].

Absorbent articles were prepared from powder resins comprised of a carboxy-functional acrylic copolymer, polyoxyethylene sorbitan monostearate and TTAP. The powdered resins absorbed 62% of its weight in water in 30 s [234].

An absorbent foam was prepared from polyacrylic acid in water and TTAP or PTAP. The crushed foam readily absorbed water and 1% saline solution [235–237].

An absorbent material was prepared from sodium polyaspartate that had been crosslinked with TTAP or PTAP. The product had absorbency of ~50 g 1% saline solution/g resin, similar to that of crosslinked polyacrylic acid [238].

A soil conditioner was prepared by crosslinking partially hydrolyzed acrylonitrile polymers with TTMAP. When ground into powder 1 kg of this material absorbed 250 g water [239].

A soil conditioner was prepared from core–shell particles containing crosslinked polyaminoacid. A solution of polysuccinimide was reacted with lysine and methyl lysine to give crosslinked polyasparaginic acid particles. These particles were treated with PTAP to give surface crosslinked particles with freedom from gel-blocking and gum-balling. The surface crosslinked particles had good water absorption and retention and biodegradability [240].

Hyaluronic acid, a carboxy-functional polysaccharide, was rendered insoluble by treatment with TTMAP. The isolated product was suitable as surgical implant material [241].

An aqueous dispersion of crosslinked gelatin particles was prepared by dispersing an aqueous solution of sodium alginate and PTAP in toluene in the presence of Span 60 surfactant at a pH of ~11, adjusting the particle size with agitation and dropping the pH to 7–8 with acetic acid to initiate crosslinking. The water-soluble polymer particles may be used as a vehicle to deliver encapsulated drugs and other medications in vivo. The polymer particles are injectable and are easily and inexpensively administered to a patient. The particles have other uses, such as in cements and adhesives, thickeners of latex paints, substitutes for microcrystalline cellulose, nutrient media, and substitutes for agar gels with better-defined gel sizes [242, 243].

A protein based coating was prepared from a mixture of protein (e.g., casein or gelatin) and TTMAP in water. The protein coating was water-resistant but could be removed and used to protect technical articles such as a car, a bicycle, a pipe, a frame, a ceramic, a stone, concrete, glass, wood, cork, wallpaper, cardboard, etc. [244,245].

A thermally stabilized sheet contained polyvinyl chloride, dioctyl phthalate, barium stearate, zinc stearate and TTMAP, TTAP or PTAP. The sheet resisted discoloration and blooming while retaining its transparency [246].

Heat and oxidation resistant polymeric articles were prepared using TTAP as an antioxidant [247].

Molding compositions were prepared from polybutylene terephthalate and TTAP was used as a thermal stabilizer [248].

An injection molding resin was prepared from liquid bisphenol A epoxy, MDI and TTAP. The resin composition was cured 30 min at 140 °C and 4 h at 180 °C to give a hardened resin [249,250].

A heat resistant, interpenetrating network was prepared from MDI, phenyl glycidyl ether, styrene, tertiary amine and TTAP by use of injection molding [251,252].

A polyisocyanurate foam was prepared from MDI, polyether polyols, glycols, diamines, laurolactone and TTAP [253–255].

A biodegradable sheet was prepared from a cellulosic web of softwood pulp fibers, which had been crosslinked with an EVA copolymer and PTAP. A sheet weighing $51\,g/m^2$ biodegraded in soil after 30 days to $9\,g/m^2$ [256].

A release sheet was prepared from an octadecyl isocyanate adduct of poly(ethylene imine) and TTMAP or TTAP. When coated onto polyethylene sheet the composition had a good parting force from Scotch tape [257,258].

Vermiculite foil was prepared by coating a flexible support with a mixture comprising a colloidal dispersion of delaminated vermiculite platelets, polyvinyl chloride and TTMAP. The vermiculite foils were useful as thermal insulators, printed circuits, fire resistant sheaths for tubes and optical and electrical cables and fire resistant cover for gypsum boards [259].

A membrane for an encapsulated breaker for aqueous fracturing fluids was prepared from a carboxy-functional vinylacrylic latex and PTAP. The membrane has pores through which the breaker can escape the capsule to contact and break a fracturing fluid used in treating subterranean formations [260].

A membrane for an encapsulated breaker for fracturing fluids was prepared from a partially hydrolyzed acrylic polymer and PTAP. The membrane was cured above 115 °C and is fractured during use to release the viscosity reducing fluid [261].

Masking tape was prepared by applying a styrene rubber adhesive on one side and a backing layer of a polyurethane resin and TTAP on the other side of a urethane coated polypropylene film. The masking tape showed good results in peel and flake resistance tests [262].

Sheet molding compound consisted of a carboxy-functional unsaturated polyester and TTAP or PTAP and had a controlled stable viscosity with an extended pot life [263].

Fluoropolymer compositions useful in polishes, formable paints and coatings, extrudable or injection moldable resins and adhesives was prepared from a latex dispersion of chorotrifluoroethylene–itaconic acid–vinylidene fluoride copolymer and TTMAP [264].

Sealing film was prepared by coating a mixture of carboxy-functional acrylic resin, triethyl amine and TTMAP, TTAP or PTAP onto a polyester film. The film was used to mask certain parts of an electronic circuit being built on a polyimide board [265].

A crosslinkable aqueous epoxy composition was prepared by reacting an epoxy resin with a dianhydride with subsequent addition of TTMAP. When cured the gel content was ≥90% and was suitable for use as an adhesive, coating, etc. [266].

A lithium battery was prepared from a binder based on a polyacrylate and TTMAP [267].

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Appendix A

The tables in Appendix A summarize the bibliometric information (see page 6 and following) for the three tris-3-(1-aziridino)propionate crosslinkers. The number recorded for each product corresponds to the number of patents and articles published that mentioned that product. The “Total” column may not be the same as adding the numbers for the three specific products, since one patent or article may mention two or three of the tris-3-(1-aziridino)propionate crosslinkers.

Publication by year between products

Years	TTMAP	TTAP	PTAP	Total
2002	0	2	1	3
2001	8	4	5	16
2000	7	3	5	12
1999	7	8	4	15
1998	8	8	4	21
1997	11	11	5	23
1996	5	7	4	13
1995	3	3	2	7
1994	7	5	3	13
1993	1	13	2	15
1992	2	7	4	9
1991	4	17	7	20
1990	6	6	5	13
1989	3	4	5	10
1988	1	3	1	4
1987	0	7	0	7
1986	4	4	3	11
1985	2	11	5	14
1984	2	9	2	9
1983	2	4	1	4
1982	0	1	0	1
1981	4	2	1	6
1980	0	2	1	3
1979	2	6	2	6
1978	2	1	1	2
1977	0	1	0	1
1976	0	0	0	0
1975	0	1	1	2
1974	0	1	0	1
1967	0	2	0	2
1952	0	2	0	2

Technology distribution between products

Technologies	TTMAP	TTAP	PTAP	Total
Acrylate	22	58	25	84
Biopolymer	3	3	3	8
Gelatin	3	5	6	9
Polyester	1	4	2	7
Polyolefin	8	18	4	28
PUD	18	7	5	35
Stryenic	5	1	8	12
Urethane	4	13	2	11
Vinyl chloride	3	3	2	2
Other	10	17	10	25
Total	77	129	67	221

Applications of the tris-3-(1-aziridino)propionate crosslinkers

Application	TTMAP	TTAP	PTAP	Total
Chemistry	5	9	4	16
Adhesives	11	24	7	35
Coatings	18	25	8	48
Primers	6	5	3	9
Inks	10	5	11	21
Photography	19	23	16	45
Thermal	2	22	3	23
Fabric	4	12	4	14
Misc	13	21	16	40

Totals do not necessarily agree with summation of column entries because one article or patent may mention more than one tris-3-(1-aziridino)propionate chemical.

Publications by corporation between products

Corporation	TTMAP	TTAP	PTAP	Total
ATG Inc.	1			1
Agfa Gevaert AG			2	2
Aica Kogyo Co. Ltd.		1		1
AlliedSignal Inc.	1	1		2
AM International Inc.		1		1
American Hoechst Corp.		1	1	1
Amoco Corp.	1			1
Arakawa Chemical Industries Ltd.		1	2	3
Articles for Personal Use Co.		1	1	1
Asahi Glass Co. Ltd.		1		1
Aventis Research and Technologies GmbH	4			4
BASF AG		2	1	3
Bayer AG		1	1	2
Belzona Molecular Ltd.		1	1	1
Biomatrix Inc.	1			1
Bolton James A	1			1
Boston Scientific Corp.	1			1
Bridgestone/Firestone Inc.		1	1	1
Central Glass Co. Ltd.	1			1
Chemische Fabrik Pfersee GmbH	1			1
China Petroleum Company	1			1
CMS Gilbreth Packaging Systems Inc.		1	1	1
Courtaulds Performance Films			1	1
Daikin Industries Ltd.			1	1
Dainippon Ink and Chemicals Inc.	1	3	2	3
Dainippon Toryo Co. Ltd.		1		1
Department of Physical Sciences, Southeastern Oklahoma State University		1		1
Dimension Technology Chemical Systems Inc.			1	1
E.I. DuPont de Nemours and Co.	6	4	8	12
Eastman Kodak Company	3			13
Essilor International Compagnie Generale d’Optique				1
Felix Schoeller Technical Papers Inc.	1			1
General Electric			1	1
General Tire and Rubber Company		1		1
Germany		1		1
Graphic Controls Corp.	2		1	2
H B Fuller Licensing and Financing Inc.	1	1	1	2
Halliburton Co.			3	3
Hillyard Enterprizes Inc.	1			1
Hiraoka and Co. Ltd.		1		1
Hoechst Celanese Corp.		1	1	1
Hoechst Celanese Corp.		1		1
Honen Corp. KK		2		2
Infant	1			1
International Business Machines Corp.	1			1
International Paper Company	2	1	1	3
Isamu Toryo KK		1		1
ISP Investments Inc.	1			1
Japan Defense Agency		1		1
Kanebo Ltd.		1		1

Corporation	TTMAP	TTAP	PTAP	Total
Kanzaki Paper Mfg. Co. Ltd.	1	4		5
Kimberly Clark Corp.			1	1
Kobe Steel Ltd.		2		2
Komatsu Seiren Co. Ltd.		2	1	2
Konica Co.	2	13	4	15
Konishi Co. Ltd.		2		2
Konishiroku photo Ind	1	3	2	5
Kyodo printing Co.		1		1
Landec Labs Inc.	1			1
Lehigh University			2	2
Lisco Inc.	1			1
Logstar Ror A/S	1			1
Lohmann GmbH + Co.	1			1
Magnetic Peripherals Inc.	1			1
Martin processing Inc.			1	1
Mellon Institute	1			1
Merck Patent GmbH	1			1
Minnesota Mining and Mfg. Co.	9	8	9	17
Mitsubishi Chemical Industries Ltd.		2		2
Mitsubishi Kagaku Emu Kee		3		3
Mitsubishi Kasei Vinyl		5		5
Mitsubishi Paper Mills Ltd.		4	3	6
Mitsubishi Pencil Co.		1		1
Mitsubishi Rayon Co. Ltd.		2	1	3
Mitsui Chemicals Incorporated		3	1	4
Mitsui Toatsu Chemicals			1	1
Mitsui Toatsu Chemicals Inc.		2	3	5
Moltedch Corp.	1			1
National Starch and Chemical Investment Holding Corporation	1		1	1
Nippon Oil and Fats		1		1
Nippon Polyurethane Industry Co.		4		4
Nippon Sanmo Sensyoku Co.		5		5
Nippon Shokubai Kagaku Kogyo Co.	1	7		8
Nippon Synthetic Chemical Industry		1		1
Nippon Tokushu Toryo Co. Ltd.	1			1
Nippon Urethane Service Co.		3		3
Nitto Denko Corporation		5		5
Nitto Electric Industrial Co.		1		1
Oce Usa Inc.	1			1
Ohio State University		1		1
Oji paper Co. Ltd.		1		1
Ouhai Donbao Chemical Co.		2		2
Panatsuku KK		1	1	1
Personal Products Co.		1	2	2
Pohang University Science Technology	1			1
Polaroid Corp.			1	1
Portals Limited	1			1
PP Polymer AB	1			1
PPG Industries Inc.	3			3
Premix Inc.	1	1	1	2
Rexam Graphics Inc.			4	4
Rhone Poulenc Res Cent		1	2	2
Ricoh Co. Ltd.		7		7
Rockwell International Corporation	1			1

Corporation	TTMAP	TTAP	PTAP	Total
Rohm and Haas Company		1	1	1
Sakata Inx Corp.		1		1
Schoeller Felix Jr GmbH und Co.	1		1	2
Scitex Corporation Ltd.	3			3
Showa Denko KK		2		2
Soko Seiren Co. Ltd.		1	1	1
Sony Chemicals Corporation		1		1
Southeast Oklahoma State University			1	1
Sybron Corp. (now Bayer Corp.)			2	2
Tamkang University, Taiwan	2	3		3
Tamura Shokai		1		1
Tomoegawa Paper Co. Ltd.		4		4
Toray Industries Inc.		2		2
Tosero Kagaku KK		1		1
Tosoh Corp.		1		1
Toyo Boseki Kabushiki Kaisha		1		1
Toyo Ink Mfg. Co. Ltd.	1	4	2	6
Union Carbide Marble Care Inc.	1			1
Visibility Enhancement Technologies	1			1
W R Grace and Co. Conn	1			1
Washington State University	2			2
Westvaco Corp.	2			2
Wolff Walsrode AG	1			1
Avecia Resins	3			3

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