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<b>(21) International Application Number:</b> PCT/AU89/00523 <b>(22) International Filing Date:</b> 4 December 1989 (04.12.89)  <b>(30) Priority data:</b> PJ 1806 5 December 1988 (05.12.88) AU PJ 1807 5 December 1988 (05.12.88) AU  <b>(71)(72) Applicant and Inventor:</b> WATSON, Mark, Raey [AU/AU]; 128 Freeman Street, Seven Hills, NSW 2147 (AU).  <b>(74) Agent:</b> SPRUSON & FERGUSON; G.P.O. Box 3898, Sydney, NSW 2001 (AU).  <b>(81) Designated States:</b> AT, AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CF (OAPI patent), CG (OAPI patent), CH, CM (OAPI patent), DE, DK, ES, FI, FR (European patent), GA (OAPI patent), GB, HU, IT (European patent), JP, KP, KR, LK, LU, MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NO, RO, SD, SE, SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US.		<b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> POLYELECTROLYTES MODIFIED BY REACTION WITH ANHYDRIDE GROUP CONTAINING COPOLYMERS AND THEIR USE AS FLOCCULENTS  <b>(57) Abstract</b>  The present invention relates to modified polyelectrolytes which are useful as flocculents in separation processes, to processes for preparing the modified polyelectrolytes, flocculent compositions incorporating the modified polyelectrolytes and to separation methods employing the modified polyelectrolytes and modified polyelectrolyte compositions of the invention.		

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POLYELECTROLYTES MODIFIED BY REACTION WITH ANHYDRIDE  
GROUP CONTAINING COPOLYMERS AND THEIR USE AS FLOCCULENTS

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TECHNICAL FIELD

The present invention relates to modified polyelectrolytes which are useful as flocculents in separation processes, to processes for preparing the modified polyelectrolytes, flocculent compositions incorporating the modified polyelectrolytes and to separation methods employing the modified polyelectrolytes and modified polyelectrolyte compositions of the invention.

The modified polyelectrolytes of the invention perform better than the prior art polyelectrolytes in that they are capable of achieving the same level of flocculation at lower concentrations and are capable of retaining a higher percentage of super fines.

BACKGROUND ART

Introduction of synthetic water-soluble polymers to the mining industry in 1951 represented a major development in solid-liquid separation by chemical reagents. They were the first of a wide range of flocculents tailored to meet many needs such as clarification of water (municipal and industrial), treatment of municipal sewerage and industrial waste (food processing, oil refining, metal finishing, pulp and paper mills etc.), mineral processing (benefication, recycle-water clarification, effluent treatment), and manufacturing processes (paper production, sugar refining, phosphoric acid production etc.).

Although there are a large number of commercially available synthetic flocculents the number of significantly different types of chemical structures is relatively limited. In the market place selection of a flocculant depends on optimizing the cost-to-performance ratio, that is, achieving desired performance at minimal cost. Although a systems point of view predominates (including flocculant availability, reproducibility, handling, storage, tolerance to fluctuations in treatment-plant loading while meeting output specifications, equipment-in-place and necessary modification etc), the delivered cost per unit weight of individual flocculants enter as one factor. Consequently, a relatively few monomers suitable for incorporation into water-soluble polymers and produced on a sufficiently large scale to have low cost, are the major building blocks of commercially important synthetic polymeric flocculants.

Practical synthetic organic flocculants are water soluble polymeric substances with weight average molecular weights ranging from about 1000 to greater than 5 million (reported values as high as 20 million).

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Polyelectrolytes used as flocculants include polymers and copolymers made from a number of monomers including maleic anhydride, maleic acid, acrylic acid, acrylamide, acrylonitrile, methacrylic acid, vinyl sulfonic acid, p-styrene sulfonic acid, styrene, vinyl methyl ether, metaphosphoric acid, vinylamine, ethyleneimine, vinyl pyridine and 4-vinyl-N-dodecylpyridinium chloride.

#### DISCLOSURE OF THE INVENTION

In a first embodiment of the invention there is provided a modified polyelectrolyte characterized in that a polyelectrolyte is reacted with a copolymer of at least two ethylenically unsaturated monomers, at least one of which contains anhydride groups.

In a second embodiment of the invention there is provided a process for manufacturing a modified polyelectrolyte, which process comprises reacting a polyelectrolyte with a copolymer of at least 2 ethylenically unsaturated monomers, at least one of which contains acid anhydride groups. The reaction can be initiated by heat and/or by an inorganic accelerator such as a metallic base. A suitable accelerator is potassium carbonate.

The types of known polyelectrolytes suitable for use in this invention are extremely numerous and diversified. No unsuitable commercially available or laboratory synthesized polyelectrolyte has been found. Common trade names defining such polyelectrolytes include: SANYOFLOC; ALFLOC; SUPERFLOC; MACROFLOC; MAGNAFLOC; MAXFLOC and ZETAG.

Other materials designed for the same or similar purposes to those described above may also be used.

Generally, the polyelectrolytes which can be modified according to the invention have molecular weights in the range  $2 \times 10^4$  to  $1 \times 10^8$ , especially  $1 \times 10^5$  to  $7 \times 10^6$  daltons. The preferred copolymers with which the polyelectrolytes are reacted have molecular weights in the range  $1 \times 10^4$  to  $1 \times 10^6$  daltons.

It is particularly preferred that a known polyelectrolyte flocculant is reacted with a copolymer of methyl vinyl ether and maleic anhydride.

A third embodiment of the invention provides a further modified polyelectrolyte characterized in that the modified polymer according to the first embodiment of the invention is further modified by reaction with vinyl pyrrolidone or polyvinyl pyrrolidone followed by further reaction with the copolymer.

A fourth embodiment of the invention provides a process for

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manufacturing a further modified polyelectrolyte which process comprises terminating the process according to the second embodiment of the invention by reducing the temperature, dispersing the reaction mixture with vinyl pyrrolidone or polyvinyl pyrrolidone and allowing the reaction to proceed. The further reaction can also be initiated by heat and/or by an inorganic accelerator.

A fifth embodiment of the invention provides a flocculating composition comprising a modified polyelectrolyte or a further modified polyelectrolyte according to the invention in association with the usual carriers and diluents employed in conventional flocculating compositions.

A sixth embodiment of the invention provides a method of flocculation which method comprises adding to a material to be flocculated a modified polyelectrolyte, a further modified electrolyte and/or a flocculating composition according to the invention.

#### BEST MODES OF CARRYING OUT THE INVENTION

Polymer solids at an amount of between 0 and 200%, preferably 10% by weight (on the basis of polyelectrolyte solids) may effectively be employed in this invention.

Generally, the reaction is carried out by simple mixing or homogenization of the polyelectrolyte and copolymer. Reaction times and reaction temperatures will depend on the nature of the polyelectrolyte and the copolymer but generally the reaction can be carried out at temperature of between 0° and 120°C for a time of between 5 minutes to 4 hours. It is preferred that the polyelectrolyte and copolymer be selected such that the reaction can be carried out at a temperature of between 40° and 80°C for a time of up to 50 minutes. Preferably, the reaction is carried out in solution.

In order to further modify the polyelectrolyte, the reaction is stopped, preferably by reducing the temperature to below 30°C, vinyl pyrrolidone or polyvinyl pyrrolidone is added, the mixture is agitated or stirred to disperse the vinyl pyrrolidone or polyvinyl pyrrolidone and the mixture is reheated to restart the reaction. If there is an excess of copolymer, the vinyl pyrrolidone or polyvinyl pyrrolidone reacts with the anhydride moiety of either reacted or unreacted copolymer resulting in a mixture of further modified polyelectrolyte and modified copolymer.

It is preferred that the ratio of vinyl pyrrolidone or polyvinyl pyrrolidone to copolymer is in the range 1:1 to 1:10 by weight, more preferably 1:5 by weight.

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The following examples illustrate preferred embodiments of the invention and should not be construed as limiting on the scope thereof.

## EXAMPLE 1

11 polyelectrolytes were reacted with various methyl vinyl ether/maleic anhydride copolymers. The types of base polymers are set out in Table 1.

Table 1

<u>Example</u>	<u>Type</u>	<u>Approx MW</u> (daltons)
0	Polyacrylamide	$5 \times 10^6$
1	Copolymer of Sodium Acrylate and Acrylamide	$6 \times 10^6$
2	"	$6 \times 10^6$
3	"	$6 \times 10^6$
4	"	$6 \times 10^6$
5	"	$5 \times 10^6$
6	"	$1 \times 10^6$
7	Terpolymer of Acrylamide, Sodium Acrylate and Maleic Anhydride	$1 \times 10^5$
8	Terpolymer of Acrylamide, Sodium Acrylate and Vinyl Pyridine	$1 \times 10^6$
9	Copolymer of Sodium Acrylate and Acylamide	$5 \times 10^6$
10	Polysodium Acrylate	$1 \times 10^6$

NOTE: It can be seen that samples 0 to 10 range from nonionic to 100% anionic.

The polymers in Table 1 were reacted with poly methyl vinyl ether/maleic anhydride copolymers of the following molecular weights: 20,000; 67,000 and 80,000.

All reactions were carried out by dispersing the poly methyl vinyl ether/maleic anhydride copolymers in the finished base polymer. This blend was then placed in a water bath at 80°C and the reaction occurred within 40 minutes. The end point of the reaction could be determined as a visible physical change in the base polymer.

The amounts of poly(methyl vinyl ether/maleic anhydride) were varied between 0 to 100% of the solids of base polyelectrolytes.

The results obtained demonstrated that maximum efficiency (as determined by maximum performance for lowest amount of material) was at 10% polymer solids (based on polyelectrolyte solids) with molecular weight of poly(methyl vinyl ether/maleic anhydride) at 67,000 daltons.

Example 2 is based on the above percentage and molecular weight. The

base polymer number refers to Table 1.

#### EXAMPLE 2

The polymers prepared in Example 1 were evaluated for efficiency by comparison with the polyelectrolytes from which they were derived. In all cases the performance of the new materials was superior to that of the polyelectrolytes from which they were derived. Comparisons conducted at mine sites were advantageously done by selecting a polyelectrolyte with correct charge density for the materials being separated and comparing these with modified polyelectrolytes comprising the same base polyelectrolyte and possessing the same or similar charge density.

Whilst these examples are based on coal flocculation, the same and/or similar benefits can be attained wherever polyelectrolyte technology is in use.

The following results were obtained in laboratory scale testing on site at the following coal washeries:

1.	Mount Thorley [R.W. Miller]			
2.	West Cliff [Kembla Coal & Coke]			
3.	Hunter Valley No.1 [Coal & Allied]			
1.	Mount Thorley			
A.	Base Polymer	No.6*		
	Settling Velocity	8.2m/h		
	Clarity	Good		
B.	New Polymer	No.6R*		
	Settling Velocity	18.0 m/h		
	Clarity	Good		
2.	West Cliff			
A.	Base Polymer	No.2*	No.3*	
	Settling Velocity	1.0 m/h	0.8 m/hz	
	Clarity	Good	Good	
B.	New Polymer	No.2R*	No.3R*	
	Settling Velocity	1.25 m/h	1.4 m/h	
	Clarity	Very Good	Very Good	
3.	Hunter Valley No.1			
A.	Base Polymer	No.4	No.5	No.6
	Settling Velocity	4.3 m/h	8.3 m/h	6.1 m/h
	Clarity	Very Poor	Very Poor	Very Poor
B.	Base Polymer	No.4R	No.5R*	No.6R

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Settling Velocity	9.9 m/h	20 m/h	20 m/h
Clarity	<Poor	<Poor	<Poor

\* Indicates the correct charge density on the base polymer

m/h Metres/hour

R Where a second reaction has been performed on the base polymer.

## EXAMPLE 3

A Latex polymer of the following characteristics was prepared.

Organic solids	32.0%	pH(1%)	6.0
Ratio Acrylamide:Dimethylaminoethyl			
Methacrylate 60:40		nominal mw	$2 \times 10^6$

This polymer was cooled to below 30°C then further reacted with 1.5% by weight poly(methyl vinyl ether/maleic anhydride) with a mw 80,000 (daltons). The reaction was carried out by dispersing the powder through the latex and placing into a water bath at 50°C for 50 minutes. On cooling the flocculent latex was packaged.

This following results were obtained from testing work on an undigested sewerage sludge obtained from a sewerage treatment plant.

A.	Base Polymer	dose	240 ppm
	Settling Velocity		2.6 m/h
	Shear resistance		pass
B.	New Polymer	dose	240 ppm
	Settling Velocity		4.7 m/h
	Shear resistance		pass

m/h Metres/hour

## EXAMPLE 4

A solution polymer of the following characteristics was cooked.

Organic polymer solids	6%	pH(neat)	8.0
Ratio Acrylamide:Acrylic Acid	60:100	nominal mw	$6 \times 10^6$

This polymer was reacted with 0.5% polymer (methyl vinyl ether/maleic anhydride) with a mw of 67 000 daltons(ex GAF). The reaction was carried out by dispersing the powder through the solution and placing into a water bath at 60°C for 4 hours. The resultant mixture was cooled to below 30°C and 1.0% of polyvinyl pyrrolidone was dispersed into the mixture. The mixture was replaced into the water bath for 2 hours. On cooling the flocculent solution was packaged.



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## EXAMPLE 5

A latex polymer of the following characteristics was prepared.

Organic solids	28.5%	pH(1%)	8.0
Ratio Acrylamide:Acrylic Acid	34:23	nominal mw	$12 \times 10^6$

This polymer was cooled to below 30°C then further reacted with 2.5% by weight of poly(methyl vinyl ether/maleic anhydride) mw 67,000 (daltons) dispersed in twice its weight of in aromatic solvent. This mixture was cooled to below 30°C and 0.5% of polyvinyl pyrrolidone was dispersed in the mixture. The mixture was replaced into the water bath for 30 min. On cooling the flocculent latex was packaged.

## EXAMPLE 6

A solution polymer of the following characteristics was prepared.

Organic polymer solids	6%	pH(neat)	8.0
Ratio of Acrylamide:Acrylic Acid	7:1	nominal mw	$5 \times 10^6$

This polymer was reacted with 0.5% poly(methyl vinyl ether/maleic anhydride) with a mw 80,000 daltons. The reaction was carried out by dispersing the powder through the solution and placing into a water bath at 60°C for 4 hours. The resultant mixture was cooled to below 30°C and 0.1% of polyvinyl pyrrolidone was dispersed in the mixture. The mixture was replaced into the water bath for 2 hours. On cooling the flocculent solution was packaged.

## EXAMPLE 7

A solution polymer of the following characteristics was prepared.

Organic solids	6%	pH(neat)	8.0
Ratio of Acrylamide:Acrylic Acid	50:50		

This base polymer was reacted with 0.5% w/w poly(methyl vinyl ether/maleic anhydride) with a mw of 67,000 daltons. The reaction was carried out by dispersing the powder through the solution and placing into a sealed container in a water bath for 4 hours at 60°C. The resultant mixture was cooled to below 30°C and 0.1% of polyvinyl pyrrolidone was dispersed in the mixture. The mixture was replaced into the water bath for 2 hours. On cooling the flocculent solution was packaged.

## EXAMPLE 8

A solution polymer of the following characteristics was prepared.

Organic solids (of acrylic acid)	6%	pH(neat)	8.0
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This base polymer was reacted with 0.5% poly(methyl vinyl ether/maleic anhydride) with a mw of 67,000 daltons. The reaction was carried out by

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dispersing the powder through the solution and placing it into a sealed container in a water bath for 4 hours at 60°C. The resultant mixture was cooled to below 30°C and 0.1% of polyvinyl pyrrolidone was dispersed in the mixture. The mixture was replaced into the water bath for 2 hours. On cooling the flocculent solution was packaged.

The following results were obtained in laboratory scale testing on site at the following coal washeries:

- I. Mount Thorley [R.W. Miller]
  - Hunter Valley CPP [Coal & Allied]
- II. Ravensworth Colliery [Elcom]
- III. West Cliff [Kembla Coal & Coke]
- IV. Hunter Valley CPP [Coal & Allied]
  - I. Mount Thorley
    - A. Base Polymer
      - Settling Velocity 8.2m/h
      - Clarity Good
    - B. New Polymer
      - Settling Velocity 29m/h
      - Clarity Very Good
  - I. Hunter Valley CPP
    - A. Base Polymer
      - Settling Velocity 6.1m/h
      - Clarity Very Poor
    - B. New Polymer
      - Settling Velocity 18.4m/h
      - Clarity poor
  - II. Ravensworth
    - A. Base Polymer
      - Dose 5ppm
      - Settling Velocity 4.0m/h
      - Clarity 65% at 400nm
    - B. New Polymer
      - Dose 5ppm
      - Settling Velocity 12.8m/h
      - Clarity >90% at 400nm
  - III. West Cliff
    - A. Base Polymer

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	Settling Velocity	0.8m/h
	Clarity	Good
B	New Polymer	
	Settling Velocity	2.9m/h
	Clarity	Very Good
IV.	Hunter Valley CPP	
A.	Base Polymer	
	Settling Velocity	8.3m/h
	Clarity	Very Poor
B.	New Polymer	
	Settling Velocity	27.1m/h
	Clarity	Good

m/h Metres/hour

It can be seen from the test data that not only are these compounds a more cost efficient base (on the reaction being done on the compound of ideal charge density in order to coincide with the material being separated), but they also allow for a far greater latitude in charge density whilst maintaining performance. This is of particular importance in the mining industry where frequent (and sometimes dramatic) changes in charge density requirements are experienced throughout the mining process [e.g. change in orebody, change within a coal seam, or changes from coal seam to coal seam, changes in climatic conditions affecting the treatment of sewerage. Many other examples can be quoted].

#### INDUSTRIAL APPLICATION

The present invention provides modified polyelectrolytes which are useful as flocculents and find use in separation processes from fields as diverse as water treatment, oil refining, metal finishing, food processing, paper milling, mineral processing and manufacturing processes.

## CLAIMS

1. A modified polyelectrolyte characterized in that a polyelectrolyte is reacted with a copolymer of at least two ethylenically unsaturated monomers, at least one of which contains anhydride groups.
2. A process for the manufacture of a modified polyelectrolyte, which process comprises reacting a polyelectrolyte with a copolymer of at least 2 ethylenically unsaturated monomers, at least one of which contains acid anhydride groups.
3. A process according to claim 2 wherein the polyelectrolyte has a molecular weight in the range  $2 \times 10^4$  to  $1 \times 10^8$  daltons.
4. A process according to claim 3 wherein the polyelectrolyte has a molecular weight in the range  $1 \times 10^5$  to  $7 \times 10^6$  daltons.
5. A process according to any one of claims 2 to 4 wherein the polyelectrolyte is present at an amount of from 0 to 200% on the basis of polyelectrolyte solids.
6. A process according to claim 5 wherein the polyelectrolyte is present at an amount of 10% on the basis of polyelectrolyte solids.
7. A process according to any one of claims 2 to 6 wherein the copolymer has a molecular weight in the range  $1 \times 10^4$  to  $1 \times 10^6$  daltons.
8. A process according to any one of claims 2 to 7 wherein the copolymer is a copolymer of methyl vinyl ether and maleic anhydride.
9. A process according to any one of claims 2 to 8 wherein the polyelectrolyte is reacted with the copolymer at a temperature of between  $0^\circ$  and  $120^\circ\text{C}$  for a time of between 5 minutes and 4 hours.
10. A process according to claim 9 wherein the reaction is carried out at a temperature of between  $40^\circ$  and  $80^\circ\text{C}$  for a time of up to 50 minutes.
11. A process according to any one of claims 2 to 10 wherein the polyelectrolyte and copolymer are reacted in solution.
12. A modified polyelectrolyte as defined in claim 1 manufactured according to a process as defined in any one of claims 2 to 11.
13. A further modified polyelectrolyte characterized in that the modified polyelectrolyte according to claim 1 is further modified by reaction with vinyl pyrrolidone or polyvinyl pyrrolidone followed by further reaction with the copolymer.
14. A process for the manufacture of a further modified polyelectrolyte which process comprises terminating the process according to claim 2 by reducing the temperature, dispersing the reaction mixture with vinyl pyrrolidone or polyvinyl pyrrolidone and allowing the reaction to proceed.
15. A process according to claim 14 wherein the temperature is reduced to

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below 30°C, the mixture is agitated or stirred to disperse the vinyl pyrrolidone or polyvinyl pyrrolidone and the mixture is reheated to restart the reaction.

16. A process according to claim 14 or claim 15 wherein the ratio of vinyl pyrrolidone or polyvinyl pyrrolidone to copolymer is in the range 1:1 to 1:10 by weight.

17. A process according to claim 16 wherein the ratio of vinyl pyrrolidone or polyvinyl pyrrolidone to copolymer is 1:5 by weight.

18. A further modified polyelectrolyte as defined in claim 13 manufactured according to a process as defined in any one of claims 14 to 17.

19. A flocculating composition comprising a modified polyelectrolyte as defined in claim 1 or claim 12 or a further modified polyelectrolyte as defined in claim 13 or claim 18 in association with the usual carriers and diluents employed in conventional flocculating compositions.

20. A method of flocculation which method comprises adding to a material to be flocculated a modified polyelectrolyte as defined in claim 1 or claim 12, a further modified polyelectrolyte as defined in claim 13 or claim 18 and/or a flocculating composition as defined in claim 19.

# INTERNATIONAL SEARCH REPORT

International Application No. **PCT/AU 89/00523**

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) 6		
According to International Patent Classification (IPC) or to both National Classification and IPC Int. Cl. <sup>4</sup> C08G 81/02, C02F 1/56, B01D 21/01		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched 7		
Classification System	Classification Symbols	
IPC	C08G 81/02	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched 8		
AU: IPC as above		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> 9		
Category*	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages 12	Relevant to Claim No 13
X	Patents Abstracts of Japan, C-523, page 93, JP,A,63-83150 (MITSUBISHI PETROCHEM CO LTD) 13 April 1988 (13.04.88)	1,2
X	GB,A, 1293464 (MOBIL OIL CORPORATION) 18 October 1972 (18.10.72) See page 2 lines 75-81 and examples 1-5, 10-11	1,2
A	GB,A, 1133910 (AMICON CORPORATION) 20 November 1968 (20.11.68) See page 1 lines 35-87	1,2
A	Patents Abstracts of Japan, C-79, page 24, JP,A,56-103203 (OTSUKA KAGAKU YAKUHIIN K.K.) 18 August 1981 (18.08.81)	1,2
* Special categories of cited documents: 10		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Z" document member of the same patent family	
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search 13 March 1990 (13.03.90)	Date of Mailing of this International Search Report <b>16 March 1990</b>	
International Searching Authority  <b>Australian Patent Office</b>	Signature of Authorized Officer <i>Grant McNeice</i> <b>GRANT McNEICE</b>	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON  
INTERNATIONAL APPLICATION NO. PCT/AU 89/00523

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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Patent Document  
Cited in Search  
Report

Patent Family Members

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GB 1293464

DE 2005133  
US 3729529

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END OF ANNEX