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(54) Title: ZINC PYRITHIONE PLUS CUPROUS OXIDE IN PAINT		
(57) Abstract <p>The present invention relates generally to paints and paint bases, and, more specifically to a process and composition for providing a stable gel-free dispersion of zinc pyrithione plus cuprous oxide biocide in paint. In accordance with the process of the present invention, the paint or paint base is essentially water-free, and preferably contains a desiccant in order to impart desired gelation-inhibition to the paint.</p>		

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ZINC PYRITHIONE PLUS CUPROUS OXIDE IN PAINT

The present invention relates generally to paints and paint bases, and, more specifically to a process for providing a stable, gel-free dispersion of zinc pyrithione plus cuprous oxide biocide in paint.

5 Combinations of zinc pyrithione and cuprous oxide are known to be excellent antifouling agents when formulated into paints and paint bases (i.e., the paint before pigment addition) also containing rosin, as disclosed, for example, in U.S. Patent No. 5,057,153.
10 Unfortunately, however, such paints have now been found to thicken or gel unacceptably within a few days, at best, or a few hours, at worst, when formulated with typical commercial grades of zinc pyrithione in combination with cuprous oxide.

15 Heretofore, various solutions to the problem of gellation of paints containing rosin and zinc pyrithione in combination with cuprous oxide, have been suggested. Illustrative solutions have been to use rigorously
20 purified zinc pyrithione, as disclosed in U.S. Patent 5,098,473, or to add amines or esterified rosin, as disclosed in U.S. Patent 5,112,397, or to use a metal salt of rosin, as disclosed in U.S. Patent 5,137,569. Since these solutions may have drawbacks such as
25 increased cost or lack of compatibility with some paints, a new, economical solution to the problem would be highly desired by the paint manufacturing community in order to maximize flexibility in using this

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combination of biocides in view of its excellent biocidal activity.

Marine paints have been made comprising a film-forming polymeric binder which is a salt or ester of a polyanion, but utilizing other biocides, namely metal salts of dithiocarbamates, and the tendency of these paints to gel is said to be reduced by the presence in the paint of a molecular sieve zeolite, as disclosed in European Patent Publication 0,108,634 A1. However, further improvements in providing a paint having an excellent combination of gellation resistance and improved biocidal efficacy would be highly desired by paint manufacturers.

In one aspect, the present invention relates to a paint or paint base composition characterized by enhanced biocidal efficacy and gellation resistance wherein the paint or paint base contains a wood rosin, cuprous oxide and zinc pyrithione and wherein the paint or paint base is essentially water-free. This essentially water-free paint or paint base composition is resistant to gellation during storage thereof.

In another aspect, the present invention relates to a process for providing a gellation-inhibited solvent-based paint or paint base containing zinc pyrithione and cuprous oxide which comprises the steps of:

(a) incorporating wood rosin, zinc pyrithione and cuprous oxide into a solvent-based paint or paint base to provide a biocide-containing paint or paint base, said zinc pyrithione being present in an amount of between about 1% and about 25% (preferably 5-25%, more preferably 10-25%), said cuprous oxide being present in an amount of between about 20% and about 70%, the total amount of said pyrithione salt plus said cuprous oxide

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being between about 20% and about 80%, and said wood rosin being present in an amount of between about 1% and about 15% (preferably 2%-10%, more preferably 3%-7%), said weight percents being based upon the total weight
5 of the biocide-containing paint or paint base, and

(b) removing water from (preferably by means of a desiccant) said biocide-containing paint or paint base to provide an essentially water-free paint or paint base exhibiting enhanced gellation resistance.

10 In yet another aspect, the present invention relates to a process for ungelling a gelled paint containing at least some amount of gels which comprises contacting the gelled paint with a desiccant and an organic solvent.

15 These and other aspects of the invention will become apparent upon reading the following detailed description of the invention.

In accordance with the present invention, it has now been surprisingly found that the tendency toward
20 gellation of a paint containing zinc pyrithione, wood rosin, and cuprous oxide is significantly reduced by reducing the amount of water in the paint. The resulting essentially water-free paint is stable against
25 gellation during storage. It has also been surprisingly found that gels in a paint can be removed, and a gelled paint can be rendered ungelled, by removing essentially all of the water from the paint using a desiccant.

As used herein, the term "essentially water free" is intended to designate a paint or paint base that
30 contains less than 500 ppm, preferably less than 100 ppm, more preferably less than 50 ppm, of water.

Preferably, a desiccant is used to remove water from the paint. Preferred desiccants include alkaline earth metal oxides such as barium oxide, magnesium

oxide, and the like, as well as molecular sieves, activated alumina, silica gel, paraffin wax and water-absorbing clays, including natural and synthetic clays. Other organic desiccants, such as
5 dicyclohexyldicarbodiimide, are also suitably employed in accordance with the present invention. Suitable clays include kaolin, montomorillonite bentonite), clay mica (muscovite), and chlorite (hectonite), and the like. Particularly preferred desiccants include
10 molecular sieves, activated alumina and alkaline earth metal oxides. Magnesium sulfate has been found not to be useful as a desiccant in the process of the present invention.

A desiccant plus a solvent for the paint are
15 suitably employed to remove gels in a gel-containing paint, or to ungel a gelled paint. The solvent is added to replenish the paint, and preferably the solvent is added in an amount of between about 1% and about 25%, more preferably between 5%-10%, based upon the weight of
20 the paint or paint base.

The amount of desiccant employed in the compositions and processes of the present invention is preferably between about 1% and about 30%, more preferably between about 5% and about 20%, most
25 preferably between about 5% and about 15%, based upon the weight of the paint or paint base.

As an alternative to the use of a desiccant, the paint may also be rendered water-free by the use of other drying techniques such as, for example, azeotropic
30 distillation, or by using a dry box or a nitrogen pad during fabrication of the desired paint with dry starting materials to provide the desired water-free paint.

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Although the improved biocidal efficacy and
gellation resistance advantages associated with the
present invention are expected to provide advantages
when used in a wide variety of paints, including indoor
5 and outdoor household paints, industrial and commercial
paints, particularly advantageous results are obtained
when the process and composition of the present
invention are utilized in conjunction with marine paints
for use, for example, on ship's hulls. In addition, the
10 composition and process of the present invention
provides highly desirable results in the context of
exterior paints of both the latex and alkyd types.

Typically, a paint composition will contain a
resin, an organic solvent (such as xylene or
15 methylisobutylketone), a pigment, and various optional
additives such as thickening agent(s), wetting agents,
and the like, as is well-known in the art. The resin is
preferably selected from the group consisting of vinyl,
alkyd, epoxy, acrylic, polyurethane and polyester
20 resins, and combinations thereof. The resin is
preferably employed in an amount of between about 20%
and about 80% based upon the weight of the paint or
paint base.

In addition, the paint composition of the present
25 invention optionally additionally contains optional
additives which have a favorable influence on the
viscosity, the wetting power and the dispersibility, as
well as on the stability to freezing and electrolytes
and on the foaming properties. The total amount of
30 optional additives is preferably no greater than 20% by
weight, more preferably between about 1% and about 5% by
weight, based upon the total weight of the paint
composition.

Illustrative thickening agents include cellulose derivatives, for example methyl, hydroxyethyl, hydroxypropyl and carboxymethyl cellulose, poly(vinyl alcohol), poly(vinylpyrrolidone), poly(ethylene-glycol), salts of poly(acrylic acid) and salts of acrylic acid/acrylamide copolymers.

Suitable wetting and dispersing agents include sodium polyphosphate, aryl or alkyl phosphates, salts of low-molecular-weight poly(acrylic acid), salts of poly(ethane-sulfonic acid), salts of poly(vinyl-phosphonic acid), salts of poly(maleic acid) and salts of copolymers of maleic acid with ethylene, 1-olefins with 3 to 18 carbon atoms and/or styrene.

In order to increase the stability to freezing and electrolytes there may be added to the paint composition various monomer 1,2-diols, for example glycol, propylene-glycol-(1,2), and butylene-glycol-(1,2) or polymers thereof, or ethoxylated compounds, for example reaction products of ethylene oxide with long-chain alkanols, amines, carboxylic acids, carboxylic acid amides, alkyd phenols, poly(propylene-glycol) or poly(butylene-glycol).

The minimum temperature of film formation (white point) of the paint composition may be reduced by adding solvents, such as ethylene-glycol, butyl-glycol, ethyl-glycol acetate, ethyl-diglycol acetate, butyl-diglycol acetate, benzene or alkylated aromatic hydrocarbons. As defoaming agents there are suitable for example poly(propylene-glycol) and polysiloxanes.

The paint composition of the present invention may be used as a paint for natural or synthetic materials, for example wood, paper, metals, textiles and plastics. It is particularly suitable as an outdoor paint, and is excellent for use as a marine paint.

The invention is further illustrated by the following Examples. Unless otherwise stated, the "parts" and "%" are "parts by weight" and "percent by weight", respectively based upon the weight of the paint or paint
5 base.

While the invention has been described above with references to specific embodiments thereof, it is apparent that many changes, modifications and variations can be made without departing from the inventive concept
10 disclosed herein. Accordingly, it is intended to embrace all such changes, modifications and variations that fall within the spirit and broad scope of the appended claims.

Comparative Example A

Demonstration of Gellation Results in a Paint
Containing Cuprous Oxide Plus Zinc Pyrithione
and Wood Rosin

5 A paint was prepared using the following formulation:

The solvent mixture used was a 2:1 mixture of MIBK and xylene (called mixed solvent).

The zinc pyrithione used was standard commercial grade and assayed 97.8% pure by iodometric titration.

10	<u>Material</u>	<u>Parts</u>	<u>%</u>
	VAGH resin (1)	9.3	2.95
	DISPERBYK 163 (2)	5.1	1.62
	Tricresyl Phosphate	6.45	2.05
	Cuprous Oxide	170.0	54.0
15	Zinc pyrithione powder	16.0	5.08
	Wood Rosin (4)	16.0	5.08
	Solvent Mixture	92.0	29.22

20 (1) vinyl chloride-vinyl acetate-vinyl alcohol terpolymer, a product of Union Carbide Corporation.

(2) a high molecular weight block copolymer, a product of BYK-Chemie.

(3) titanium dioxide, a product of DuPont Company.

25 (4) a product of Hercules, Incorporated

The procedure employed for preparing the paint was as follows:

30 (1) A one pint paint can was charged with 41.93 g of a 22.2% VAGH resin solution in a 2:1 mixture by volume of MIBK and xylene.

(2) A mixture of 5.1 g Disperbyk 163 and 5.1 g mixed solvent was added.

35 (3) Tributyl phosphate was added to the paint can and mixed with a high speed disperser at 1000 RPM for 10 minutes.

(4) The cuprous oxide, zinc pyrithione, and 5.0 g solvent were added to the paint can and mixing was continued at 7000 RPM for 1 hr.

40 (5) The mixing speed was reduced to 2500 RPM and 15 g of mixed solvent was added.

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(6) Once the temperature dropped from 45°C to below 35°, a solution of 16 g of wood rosin in 30 g of mixed solvent was added to the can and the mixture was mixed for 1.0 hr. at 2500 RPM.

5 The paint formulation made according to this procedure was analyzed for water and found to contain 0.4 weight percent of water based upon the weight of the formulation. The formulation was of suitable viscosity for application by brush immediately after preparation,
10 but thickened to an unpourable paste after approximately 6 hours.

Examples of Paints of the Present Invention

General Procedure for Making Essentially Water-Free Paints Used in all of the Following Examples

15 Mill Base (MB):

(1) A one pint paint can was charged with 35.2 g of a 22.2% VAGH resin solution in a 2:1 mixture by volume of MIBK and xylene.

20 (2) A mixture of 5.4 g Disperbyk 163 and 4.0 g mixed solvent was added to the can, along with 7.2 g of tricresyl phosphate.

(3) The above materials were mixed with a high speed disperser at 1000 RPM for 10 minutes.

Pigment Grind (PG):

25 (4) The specified amounts of desiccant, cuprous oxide, zinc pyrithione (added as zinc OMADINE® biocide, a product of Olin Corporation), and 20.0 g solvent mixture in aliquot portions to provide a good pigment grind were

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added to the paint can and mixing was continued at 7000 RPM for 1 hour. The sample temperature was kept below 45°C using a water bath.

Letdown Stage (LD):

5 (5) Next a solution of 14.5 g of the rosin in 25 g of mixed solvent was added to the can and the mixture was mixed for 1.0 hr at 4000 RPM.

(6) The solvent mixture which was lost during work-up was added back to the paint and mixed for 5 minutes.
10 Solvent mixture used was a 40% mixture of xylene and 60% MIBK.

EXAMPLE I Paint Composition

Using 15 wt.% of 1/8 Inch Diameter Molecular Sieves

	<u>INGREDIENT</u>	<u>MASS</u>	<u>PERCENT</u>
15	MOLEC. SIEVES POWDER (1)	25.00	14.73
	VAGH RESIN (22%)	3.90	2.30
	DISPERBYK 163	2.70	1.59
	CUPROUS OXIDE	75.00	44.20
	Zn pyrithione	7.75	4.57
20	TRICRESYL PHOSPHATE	3.60	2.12
	WOOD ROSIN	7.75	4.57
	SOLVENT MIXTURE*	44.00	25.93
	*60% MIBK/40% XYLENE		
	<u>TOTAL</u>	<u>169.70</u>	<u>100.00</u>

25 (1) Molec. sieves 4A, a product of Aldrich Chemical Co. Inc..

The paint of Example I was found to have less than 500 ppm of water and was of a suitable viscosity for application by brush 10 weeks after its preparation.

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EXAMPLE II Paint Composition
Using 5 wt.% Molecular Sieves Having a
2-3 Microns particle size

	INGREDIENT	MASS	PERCENT
5	MOLEC. SIEVES POWDER (1)	7.25	4.93
	VAGH RESIN (22%)	3.90	2.65
	DISPERBYK 163	2.70	1.84
	CUPROUS OXIDE	75.00	51.04
	Zn pyrithione	7.25	4.93
10	TRICRESYL PHOSPHATE	3.60	2.45
	WOOD ROSIN	7.25	4.93
	SOLVENT MIXTURE*	40.00	27.22
	*60% MIBK/40% XYLENE		
	TOTAL	146.95	100.00

15 (1) Product of Aldrich Chemical Co. Inc.

The paint of Example II contained less than 500 ppm of water, and thickened slightly but was still of suitable viscosity for application by brush 10 weeks after its preparation.

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EXAMPLE III

15 wt. % of BAYLITH L Powder Molecular Sieves 3A

	INGREDIENT	MASS	PERCENT
	MOLEC. SIEVES POWDER (1)	24.70	15.02
	VAGH RESIN (22%)	3.90	2.37
25	DISPERBYK 163	2.70	1.64
	CUPROUS OXIDE	75.00	45.62
	Zn Pyrithione	7.25	4.41
	TRICRESYL PHOSPHATE	3.60	2.19
	WOOD ROSIN	7.25	4.41
30	SOLVENT MIXTURE*	40.00	24.33
	*60% MIBK/40% XYLENE		
	TOTAL	164.40	100.00

(1) Product of Miles Inc.

35 The paint of Example III contained less than 500 ppm of water, and was of suitable viscosity for application by brush 10 weeks after its preparation.

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EXAMPLE IV

Using 15 wt.% Silica Gel Desiccant

	<u>INGREDIENT</u>	<u>MASS</u>	<u>PERCENT</u>
	SILICA GEL (1)	24.70	15.02
5	VAGH RESIN (22%)	3.90	2.37
	DISPERBYK 163	2.70	1.64
	CUPROUS OXIDE	75.00	45.62
	Zn Pyrithione	7.25	4.41
	TRICRESYL PHOSPHATE	3.60	2.19
10	WOOD ROSIN	7.25	4.41
	SOLVENT MIXTURE*	40.00	24.33
	*60% MIBK/40% XYLENE		
	<u>TOTAL</u>	<u>164.40</u>	<u>100.00</u>

(1) Keselgel 60, a product of EM Reagents.

15 This paint product contained less than 500 ppm of water and was stable for two to three days.

EXAMPLE V

Using as a Desiccant 15% Alumina Neutral Al Oxide

	<u>INGREDIENT</u>	<u>MASS</u>	<u>PERCENT</u>
20	ALUMINA (2)	24.70	15.02
	VAGH RESIN (22%)	3.90	2.37
	DISPERBYK 163	2.70	1.64
	CUPROUS OXIDE	75.00	45.62
	Zn Pyrithione	7.25	4.41
25	TRICRESYL PHOSPHATE	3.60	2.19
	WOOD ROSIN	7.25	4.41
	SOLVENT MIXTURE*	40.00	24.33
	*60% MIBK/40% XYLENE		
	<u>TOTAL</u>	<u>164.40</u>	<u>100.00</u>

30 (2) Alumina N, Act I, a product of Fisher Scientific.

This paint product contained less than 500 ppm of water and was stable for one week.

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EXAMPLE VI

Using Barium Oxide as a desiccant

	<u>INGREDIENT</u>	<u>MASS</u>	<u>PERCENT</u>
	BARIUM OXIDE (3)	11.33	7.50
5	VAGH RESIN (22%)	3.90	2.58
	DISPERBYK 163	2.70	1.79
	CUPROUS OXIDE	75.00	49.66
	Zn Pyrithione	7.25	4.80
	TRICRESYL PHOSPHATE	3.60	2.38
10	WOOD ROSIN	7.25	4.80
	SOLVENT MIXTURE*	40.00	26.48
	*60% MIBK/40% XYLENE		
	TOTAL	151.03	100.00

(3) Product of Aldrich Chemical Co. Inc.

15 The above sample was gel free after 2 weeks.

EXAMPLE VII

Demonstration of a gelled paint being Ungelled

A paint was prepared using the following formulation.

	<u>INGREDIENT</u>	<u>MASS</u>	<u>PERCENT</u>
20	VAGH RESIN (22%)	3.90	2.44
	DISPERBYK 163	2.70	1.69
	CUPROUS OXIDE	91.00	56.96 (57.0%)
	Zn Pyrithione	7.75	4.85
	TRICRESYL PHOSPHATE	3.60	2.25
25	WOOD ROSIN	7.75	4.85
	SOLVENT MIXTURE*	43.00	26.93

30 This paint was made according to the general procedure described above. This paint had thickened to an unpourable paste after 6 hours and had gelled after approximately 15 hours.

General procedure for ungelling a gelled paint.

(1) Added 5-10% (wt) of solvent to the gelled paint. Chopped the gel up with a spatula.

(2) Dispersed at 4000 rpm for 30 minutes.

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(3) Added 15% (wt) (24.7 g) of Molecular Sieves 4A powder Aldrich.

Following this procedure, the ungelled paint was stable after 10 weeks.

5 While the invention has been described above with references to specific embodiments thereof, it is apparent that many changes, modifications and variations in the materials, arrangements of parts and steps can be made without departing from the inventive concept
10 disclosed herein. Accordingly, the spirit and broad scope of the appended claims is intended to embrace all such changes, modifications and variations that may occur to one of skill in the art upon a reading of the disclosure.

15 Having thus described the invention, what is claimed is:

WHAT IS CLAIMED IS:

1. A paint or paint base composition characterized by enhanced biocidal efficacy and gellation resistance wherein the paint or paint base
5 comprises a wood rosin, cuprous oxide and zinc pyrithione and wherein the paint or paint base is essentially water-free.
2. The paint or paint base of claim 1 characterized in that the total amount of said
10 pyrithione salt plus said copper salt is between about 20% and about 80% based upon the total weight of the paint or paint base composition and wherein the paint additionally contains desiccant selected from the group
15 consisting of molecular sieves, activated alumina, silica gel, alkaline earth metal oxides, paraffin wax, water absorbing clays, and combinations thereof.
3. The paint or paint base of claim 2 characterized in that the amount of said desiccant is
20 between about 1% and 20% based upon the total weight of the paint or paint base composition.
4. A solvent-based paint or paint base composition characterized by enhanced biocidal efficacy and gellation resistance wherein the paint or paint base
25 comprises a biocide consisting essentially of cuprous oxide and zinc pyrithione, and the paint or paint base further comprises a desiccant.

5 5. The paint or paint base of claim 4
characterized in that the total amount of said zinc
pyrithione plus said cuprous oxide is between about 20%
and about 80% based upon the total weight of the paint
or paint base composition and wherein the desiccant is
selected from molecular sieves, activated alumina,
silica gel, barium oxide, paraffin wax, water absorbing
clays and combinations thereof.

10 6. The paint or paint base of claim 4
characterized by additionally containing a resin
selected from the group consisting of vinyl, alkyd,
epoxy, acrylic, polyurethane and polyester resins, and
combinations thereof.

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7. A process for providing a gellation-inhibited solvent-based paint or paint base containing zinc pyrithione and cuprous oxide characterized by the steps of:

- 5 (a) incorporating wood rosin, zinc pyrithione and cuprous oxide into a solvent-based paint or paint base to provide a biocide-containing paint or paint base, said zinc pyrithione being present in an amount of between about 1% and
10 about 25%, said cuprous oxide being present in an amount of between about 20% and about 70%, the total amount of said zinc pyrithione plus said cuprous oxide being between about 20% and
15 about 80%, and said wood rosin being present in an amount of between about 1% and about 15% , said weight percents being based upon the total weight of the biocide-containing paint or paint base, and
20 (b) removing water from said biocide-containing paint or paint base to provide an essentially water-free paint or paint base exhibiting enhanced gellation resistance.

8. The process of claim 7 characterized in that
25 said paint or paint base contains said zinc pyrithione in an amount of between about 5% and about 25% weight percent, said wood rosin in an amount of between about 2% and about 10%, and a desiccant in an amount of between 1% and about 30%, based upon the weight of the paint or paint base, and water in an amount of less than
30 500 ppm.

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9. The process of claim 7 characterized in that
said paint or paint base contains said zinc pyrithione
in an amount of between about 10% and about 25% weight
percent, said wood rosin in an amount of between about
5 3% and about 7%, and a desiccant in an amount of between
5% and about 25%, and water in an amount of less than
100 ppm.

10. A process for ungelling a gelled paint
containing gels which is characterized by contacting the
10 gelled paint with a desiccant and an organic solvent in
amounts sufficient to remove any gels from said paint.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/07620

A. CLASSIFICATION OF SUBJECT MATTER IPC(5) :C09D 5/14 US CL : 106/15.05, 16, 18.33, 18.34; 424/78.09; 514/345, 499, 500 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 106/15.05, 16, 18.33, 18.34; 424/78.09; 514/345, 499, 500 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched N/A Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) N/A		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A 3,615,744 (Yokoo et al) 26 OCTOBER 1971, See abstract.	1-10
A	US, A, 4,039,312 (Patru) 02 AUGUST 1977, col. 1, lines 20-69.	1-10
A	US, A, 4,581,351 (Berke et al) 08 APRIL 1986, col. 1, lines 10-50.	1-10
A	US, A, 4,918,147 (Yamamori et al) 17 APRIL 1990, col. 6, line 63 - col. 7, line 47.	1-10
A	US, A, 5,057,153 (Ruggiero) 15 OCTOBER 1991, col. 1, lines 44-65 and the claims.	1-10
A	US, A, 5,098,473 (Hani et al) 24 MARCH 1992, col. 1, lines 30-60.	1-10
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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"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	"&" document member of the same patent family
Date of the actual completion of the international search 01 September 1993		Date of mailing of the international search report 02 NOV 1993
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5,112,397 (Farmer, Jr. et al) 12 MAY 1992, col. 1, line 30 - col. 2, line 4.	1-10
A	US, A, 5,137,569 (Waldron et al) 11 AUGUST 1992, col. 1, line 40 - col. 2, line 15.	1-10