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(54) **FLAME-RETARDANT FIBER.**

(57) A flame-retardant fiber excellent in the resistance to thermal coloration and a process for producing the same, which fiber is mainly composed of 80 to 20 parts by weight of a halogenated polymer and 20 to 80 parts by weight of polyvinyl alcohol and contains 5 to 35 parts by weight of an antimony compound such as antimony pentaoxide, 0.13 to 5.0 parts by weight of an octyltin heat stabilizer composed of 50 to 30 % of mercaptide and 50 to 70 % of laurate, and further preferably 0.3 to 10 parts by weight of stannic acid, each based on 100 parts by weight of the main components. This fiber can make various flammable fibers, when composited therewith, flame-retardant effectively and provide textile products excellent in flame retardation and the capability of passing through the post-treatment step in professional laundries.

EP 0 505 578 A1

TECHNICAL FIELD

The present invention relates to a flame-retardant fiber and a process for producing the same, said flame-retardant fiber exhibiting not only good flame retardance even in the form of composite fiber combined with a combustible fiber but also good colorfastness to heat.

BACKGROUND ART

There are known several kinds of flame-retardant fibers which are produced by the post-treatment of combustible natural or synthetic fiber with a flame retardant or by the incorporation of a raw material of synthetic fiber with a flame retardant at the time of spinning. An example of flame retardant synthetic fibers is one which is produced by wet spinning from a spinning solution containing polyvinyl chloride (as a halogen-containing polymer), polyvinyl alcohol, and stannic acid (as a flame retardant), followed by acetalization. It finds use as furnishing fabrics, bedclothes, and industrial materials because of its good flame retardance and its extremely low toxic combustion gas.

Any attempt to improve flame retardance by copolymerization with a flame retardant monomer or incorporation of a flame retardant into a spinning solution usually ends up with impaired fiber performance. In this case it is common practice to mix a flame-retardant fiber with a combustible fiber having good performance, thereby forming a composite fiber.

In this connection, one Japanese Patent Application relating to a flame-retardant fiber was Laid-open under No. 6611/1990. It is composed of 100 parts by weight of a major constituent (which is composed of a halogen-containing polymer and polyvinyl alcohol in a weight ratio of from 80:20 to 20:80), 0.3-10 parts by weight of stannic acid, and 1-5 parts by weight of antimony pentoxide.

With consumers' increasing interest in flame retardance, new flame retardant products are appearing one after another. They include not only those articles regulated by the Fire Service Law but also bedclothes and garments, mostly for business use. Commercial bed sheets and bathrobes for business use should withstand repeated washing (about 100 times in most cases), not to mention flame retardance. What is important in washing is drying and ironing. These steps are usually accomplished simultaneously by passing the wash between a stationary hot metal plate and a rotating metal roll wrapped with felt of heat-resistant fiber for business use (hereinafter referred to "passage property"). They pose no problems if the products are such bed sheets and bathrobes as are made of moisture-absorbing composite fiber composed of a cellulosic fiber and a flame-retardant fiber proposed in JP Laid-open No.6611/1990. However, there is a problem if the composite fiber contains more flame-retardant fiber than cellulosic fiber for improved flame retardance. The problem is that the resulting composite fiber is poor in moisture absorption and unsuitable for the above-mentioned passage property because the flame-retardant fiber is essentially thermoplastic. On the other hand, if the ratio of the flame-retardant fibers is decreased for passage property a flame retardance as the composite fiber becomes unsatisfactory. For this reason, the above-mentioned flame-retardant fiber proposed in JP Laid-open No. 6611/1990 has never found use for textile products when used as a composite fiber which are subject to repeated washing because it can not satisfy simultaneously the flame retardance and the passage property.

DISCLOSURE OF THE INVENTION

The present inventors carried out a series of researches on the formulation of a flame-retardant fiber to be combined with a cellulosic fiber for the production of a composite fiber which meets the above-mentioned flame retardance and passage property. It was experimentally found that a flame-retardant fiber that facilitates passage property should contain a cellulosic fiber in an amount more than 65%, preferably more than 70%. It was also found that in the composite fiber contains a flame-retardant fiber in an amount less than 35%, preferably less than 30%, it improves in flame retardance in proportion to the amount of flame retardant it contains but becomes poor in colorfastness to heat. To address this problem, the present inventors investigated the combination of a flame retardant and a heat stabilizer. The investigation revealed that it is possible to combine a combustible fiber such as cellulosic fiber more than 65%, preferably more than 70%, with a flame-retardant fiber to give a composite flame-retardant fiber which meets the requirements for flame retardance, colorfastness to heat and the passage property, if the flame-retardant fiber contains a specific flame retardant and a specific heat stabilizer in combination. These findings led to the present invention.

The present invention relates to a flame-retardant fiber having good colorfastness to heat and a process for the production thereof, said flame-retardant fiber comprising 100 parts by weight of a principal

constituent composed of a halogen-containing polymeric substance and polyvinyl alcohol in a weight ratio of from 80:20 to 20:80, 5-35 parts by weight of antimony pentoxide, and 0.13-5.0 parts by weight of octyl tin-type heat stabilizer in which the compositional ratio of mercaptans to laurates is from 5/5 to 3/7.

The halogen-containing polymeric substance used in the present invention includes homopolymers of halogen-containing polymerizable monomers such as vinyl chloride, vinylidene chloride, and chloroprene, and copolymers of two or more of these monomers and optional other polymerizable monomers, or mixtures of the homopolymers and copolymers. They may be in the form of fine particles in suspension or emulsion. Further, the polyvinyl alcohol should preferably be one which contains vinyl acetate in an amount less than 2%.

The ratio of the halogen-containing polymeric substance and polyvinyl alcohol is important for adequate spinning. With a ratio greater than 80:20, it is difficult to perform smooth spinning and the resulting fiber is poor in strength and elongation required for practical use. Conversely, with a ratio lower than 20:80, it is difficult to achieve the desired flame retardance despite the incorporation with additional antimony compounds such as antimony trioxide and antimony pentoxide.

According to the present invention, the antimony compound to be added to the flame-retardant fiber should preferably be antimony pentoxide in the form of colloid having a particle diameter smaller than 100 μm. The amount of the antimony compound should be 5-35 parts by weight for 100 parts by weight of the principal constituent (as solids). An amount less than 5 parts by weight is not enough for the antimony compound to impart sufficient flame retardance to the composite fiber containing a combustible fiber such as cellulosic fiber. Conversely, with an amount in excess of 35 parts by weight, the antimony compound improves the flame retardance only at the expense of spinnability and colorfastness to heat. Incorporation as much as 45 parts by weight is of no practical use because the resulting fiber solution is capable of spinning but gives rise to a fiber which is poor in strength.

There are several known heat stabilizers which are based on metal soaps such as barium/zinc and calcium/zinc, organic phosphite esters, epoxy resins, butyl tins, or octyl tins. The first one is not so effective and needs such a large amount to produce the desired effect that it adversely affects the stability of the spinning solution and its spinning. The second one also is not effective for the spinning solution in the present invention. The third one has a problem associated with dispersion stability of heat stability composition. The forth one is undesireble because of its toxicity. Thus the heat stabilizer based on octyl tin is desirable.

The octyl tins heat stabilizer includes those of laurates, malates, mercaptomalates and mercaptans. Those of malates and mercaptomalates are undesirable because they become ineffective due to hydrolysis that takes place during spinning repeated washing. That of mercaptans, if used alone in large quantities, improves the colorfastness to heat but gives off smoke and odor when exposed to high temperatures during spinning, which poses a problem associated with environmental hygiene. That of laurates contributes only to colorfastness to heat mainly on account of its function to capture hydrochloric acid; therefore, it is slightly inferior in colorfastness to heat to that of mercaptans when it is used alone. It is possible to overcome these disadvantages by using those of laurates and mercaptans in combination. The ratio of combination should preferably be from 5/5 to 3/7 (mercaptans/laurates).

The octyl tins heat stabilizer should be added in the form of heat stabilizer composition containing a phthalate plasticizer and a surface active agent. Examples of the phthalate plasticizer include dialkyl phthalate such as dioctyl phthalate and dibutyl phthalate. The surface active agent is not specifically limited so long as it stably disperses the octyl tin heat stabilizer and phthalate plasticizer and keeps the spinning solution stable. Its preferred examples include aromatic nonionic surface active agents such as polyoxyethylene nonylphenyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene dodecylphenyl ether, and polyoxyethylene alkylaryl ether.

The above-mentioned heat stabilizer, phthalate plasticizer, and surface active agent should preferably be handled in the form of composition so that the antimony compound is stably dispersed. Such a composition should be composed of 65-75 parts by weight of octyl tin heat stabilizer, 20-30 parts by weight of phthalate plasticizer, and 5-15 parts by weight of surface active agent, with the total amount being 100 parts by weight. The amount of the surface active agent should be more than 5 parts by weight from the standpoint of dispersion stability. The amount of the oxtyl tins heat stabilizer is preferably less than 75 parts by weight from the standpoint of the stability and spinnability of the spinning solution. The phthalate plasticizers in an amount less than 20 parts by weight is not enough to provide sufficient slip between fibers and metal rolls during spinning, which prevents smooth spinning. The phthalate plasticizer in an amount more than 30 parts by weight lowers the colorfastness to heat on account of the relative decrease of the octyl tins heat stabilizer.

According to the present invention, the above-mentioned heat stabilizer composition should be used in

an amount of 0.2-5 parts by weight (depending on the amount of the antimony compound) for 100 parts by weight of the principal constituent of the flame-retardant fiber of the present invention which is composed of a halogen-containing polymeric substance and polyvinyl alcohol in a weight ratio of from 80:20 to 20:80. The beat stabilizer composition in an amount less than 0.2 part by weight is not enough to protect the flame retardant fiber from discoloration that takes place during spinning and also during drying and ironing that follow washing for business use. The heat stabilizer composition in an amount more than 5 parts by weight unstabilizes the spinning solution, making spinning difficult.

For the flame-retardant fiber of the present invention to have further improved flame retardance, it is desirable to add 0.3-10 parts by weight of stannic acid for 100 parts by weight of the principal constituent (as solids). The stannic acid is composed of SnO_2 and H_2O in a molar ratio of 0.5-0.7. With an amount less than 0.3 part by weight, the stannic acid does not improve the flame retardance sufficiently. With an amount in excess of 10 parts by weight, the stannic acid improves the flame retardance of the flame-retardant fiber in proportion to its amount but does not improve so much the flame retardance of the composite fiber (composed of the flame-retardant fiber and combustible fiber). It rather deteriorates the spinnability of the fiber solution.

The following is a detailed description of the process for producing the flame-retardant fiber having good colorfastness to heat.

First, the above-mentioned emulsion of halogen-containing polymeric substance and aqueous solution of polyvinyl alcohol are mixed in a ratio of from 80:20 to 20:80 in terms of solids to give an aqueous solution containing 15-30% solids. Then, this aqueous solution is incorporated with stannic acid, antimony pentoxide, heat stabilizer, plasticizer, and surface active agent in prescribed amounts. The resulting spinning solution undergoes wet spinning, which is followed by optional post treatments for individual uses. Thus there is obtained the flame-retardant fiber of the present invention which has good colorfastness to heat. The stannic acid, antimony compound, heat stabilizer, plasticizer, and surface active agent may be added one by one sequentially or in a group of two or more members. They are preferably formed into a composition of liquid dispersion before incorporation into the spinning solution. After wet spinning, the fibers undergo wet-heat treatment, water washing, drying, hot drawing, and heat setting. The fibers are acetalized in a bath containing an aldehyde compound and subjected to washing, finishing, crimping, cutting, and drying. These post treatments may be partly omitted or supplemented by other treatments.

The above-mentioned aldehyde compound includes formalin, acetaldehyde, furfural, glyoxal, and benzaldehyde.

The flame-retardant fiber of the present invention is superior in both flame retardance and colorfastness to heat. It may be combined with any combustible fiber such as cellulosic fiber, polyester fiber, acrylic fiber, vinylon fiber, nylon fiber, and polypropylene fiber to give a composite flame-retardant fiber. It is effective particularly for cellulosic fiber, especially cotton fiber. The fact that the flame retardant fiber of the present invention is superior in both flame retardance and colorfastness to heat is contradictory to the common knowledge that flame retardance is improved only at the expense of colorfastness to heat.

Needless to say, the flame-retardant fiber of the present invention may be incorporated with other additives and adjuvants than mentioned above according to need, such as pigment, antistatic agent, light resistance improver, dyeability improver, and delusterizing agent which are commonly used in the production and processing of fibers.

BEST MOVE FOR CARRYING OUT THE INVENTION

The invention will be described in more detail with reference to the following examples, which are not intended to restrict the scope of the invention.

Examples 1 to 3

(Preparation of heat stabilizer composition)

A 4:6 mixture (by weight) was prepared from two kinds of octyl tin heat stabilizers. The first one is "Gleck T-130FM" (a mercaptan-based heat stabilizer made by Dainippon Ink and Chemicals, Inc.) and the second one is "Breck T-7048" (a laurate-based heat stabilizer made by Dainippon Ink and Chemicals, Inc.). To 70 parts by weight of this mixture were added 25 parts by weight of "Monocizer W-520" (DOP made by Dainippon Ink and Chemicals, Inc.) and 5 parts by weight of "Noigen EA-112" (made by Dai-ichi Kogyo Seiyaku Co., Ltd.), followed by mixing for 30 minutes using a homomixer. The resulting mixture was added to water to make a 15 wt% aqueous solution. The aqueous solution was mixed using a homomixer at room

temperature for 10 minutes to ensure dispersion.

(Production of fiber)

A liquid mixture containing 22 wt% solids was prepared by mixing polyvinyl chloride emulsion (composed mainly of vinyl chloride) and polyvinyl alcohol aqueous solution in a ratio of 50:50 by weight as solids. To 100 parts by weight (as solids) of the liquid mixture were added 1.5 parts by weight of stannic acid (SnO_2 : H_2O = 1 : 0.6 in mol), a varied amount of colloidal antimony pentoxide (aqueous sol "A-2550M" made by Nissan Chemical Industries, Ltd.), and a varied amount (as solids) of the heat stabilizer mentioned above, to prepare spinning solutions.

	Amount of colloidal antimony pentoxide	Amount of heat stabilizer composition
Example 1	8.5 parts	2 parts
Example 2	15 parts	3.5 parts
Example 3	30 parts	7 parts

Each of the spinning solutions, kept at 80 °C, was spun out through a spinneret into a saturated aqueous solution at 40 °C of sodium sulfate for wet spinning. The emergent fibers underwent wet heat treatment in a saturated aqueous solution of sodium sulfate at 95 °C, washing with cold water, drying, drawing, and heat-setting. It turned out that the spinning solution was stable and capable of spinning in the satisfactory manner.

The thus obtained filaments were acetalized by immersion in a bath at 70 °C for 60 minutes, containing 15 parts by weight of sulfuric acid, 15 parts by weight of sodium sulfate, 5.5 parts by weight of formaldehyde, and 64.5 parts by weight of water. The acetalized filaments were squeezed, thoroughly washed with warm water (at 40 °C), washed with an aqueous solution containing 30 g/L of sodium carbonate at 50 °C for neutralization, and washed again with water at room temperature. The fibers were finally treated with a finishing agent, dried, crimped,and cut into 2-denier staples of flame-retardant fiber.

Comparative Examples 1 and 2

For comparison, the same procedure as in Examples 1 to 3 was repeated except that the heat stabilizer composition was not used and the amount of the flame retardant was changed as follows:

	Stannic acid	Colloidal antimony pentoxide
Comparative Example 1	1.0 part	4.0 parts
Comparative Example 2	1.5 parts	8.5 parts

A sample of blended yarn having a cotton count of 20 was prepared by blending 30 parts by weight of the flame-retardant fiber in staple form obtained in Examples 1 to 3 and Comparative Examples 1 and 2 mentioned above and 70 parts by weight of cotton fiber. The blended yarn was made into a fabric of plain weave having a basis weight of 140 g/m^2. This fabric underwent washing repeatedly under the conditions employed by laundries. The washed fabric was dried and ironed by passing over a hot metal plate at 175 °C at a speed of 40 m/min. This passage property posed no problems at all. Each sample of the fabric was tested for flame retardance and whiteness before and after repeated washing (100 times). The results are shown in Table 1. It is noted that the fabric composed of the flame-retardant fiber of the present invention and cotton fiber is superior in whiteness and colorfastness to heat to the comparative sample which is not incorporated with the heat stabilizer.

Example 4 and Comparative Example 3

A sample of blended yarn having a cotton count of 20 was prepared by blending 60 parts by weight of the flame-retardant fiber obtained in Examples 1 to 3 or the fiber obtained in Comparative Example 1 and 40 parts by weight of cotton fiber. The blended yarn was made into a circular knitted fabric having a basis weight of 165-170 g/m^2. This fabric underwent scoring at 45 °C for 30 minutes in a bath containing 2 g/L of "Scorerol 700" (an ether-type nonionic scoring-washing agent made by Kao Atlas Co., Ltd.) After drying at

75 °C, the sample fabric was tested for LOI (limited oxygen index). The results are shown in Table 2. It is noted that the flame-retardant fiber of the present invention retains its good flame retardance even when combined with combustible fiber such as cotton.

Example 5 and Comparative Example 4

Samples of blended yarn having a cotton count of 20 were prepared by blending the flame retardant fiber obtained in Example 1 or the fiber obtained in Comparative Example 1 and combustible fiber selected from cotton fiber, polyester fiber, acrylic fiber, vinylon fiber, nylon fiber, and polypropylene fiber, according to the blending ratio shown in Tables 3 and 4. The blended yarn was made into a circular knitted fabric having a basis weight of 165-170 g/m^2. This fabric underwent scoring at 45 °C for 30 minutes in a bath containing 2 g/L of "Scorerol 700" (an ether-type nonionic scoring-washing agent made by Kao Atlas Co., Ltd.). After drying at 75 °C, the sample fabric was tested for LOI (limited oxygen index). The results are shown in Tables 3 and 4. It is noted that the flame-retardant fiber of the present invention effectively prevents the LOI value from lowering even when it is blended with any one of the combustible fibers used.

CAPABILITY OF INDUSTRIAL USE

The present invention provides a flame-retardant fiber, which is suitable for use of business washing, containing an antimony compound as a flame retardant and a heat stabilizer of specific formulation, thereby the products having superior properties in such as flame-retardance, colorfastness to heat, passage property of post treatment of business washing are obtained. When it is combined with a variety of combustible fiber to use as a composite fiber, it exhibits good flame retardance and colorfastness to heat. By adding small amount of the flame-retardant fiber, the compsosite thus obtained shows a superior flame retardance and passage property without coloration.

Table 1

Flame retardance and colorfastness to heat			
	Flame retardance length of carbonization, mm) after washing 100 times	Degree of whiteness (%)	
		Before washing	After washing (100 times)
Fiber obtained in Example 1 (blended with 70% cotton)	20	92.5	90.4
Fiber obtained in Example 2 (blended with 70% cotton)	19	91.2	90.1
Fiber obtained in Example 3 (blended with 70% cotton)	19	90.8	89.8
Fiber obtained in Comparative Example 1 (blended with 70% cotton)	>200	92.0	85.5
Fiber obtained in Comparative Example 2 (blended with 70% cotton)	23	86.3	62.5
Flame retardance was tested according to JIS L-1091, 45 ° Mesenamine method. Degree of whiteness was measured using a color computer, SM-4-2, (of integrating sphere and two optical paths type) made by Suga Shikenki Co., Ltd., for four specimens piled on top of the other and pressed under a white standard plate.			

Table 2

Flame retardance (LOI) of composite fiber		
Flame retardant fiber	Flame retardance (in terms of LOI)	
	100% flame retardant fiber	Blended with 40% cotton fiber
Flame retardant fiber obtained in Example 1	32.5	29.5
Flame retardant fiber obtained in Example 2	32.8	31.8
Flame retardant fiber obtained in Example 3	33.0	32.5
Flame retardant fiber obtained in Comparative Example 1	32.0	26.5

Table 3

Flame retardance (LOI) of composite fiber							
Blending ratio: Fiber in Example 1/Combustible fiber	100/0	70/30	60/40	50/50	40/60	30/70	0/100
Cotton fiber	32.5	31.0	29.5	26.8	24.8	22.8	18.0
Polyester fiber	-	29.0	28.3	27.5	25.0	23.3	22.8
Acrylic fiber	-	27.5	26.0	24.3	22.8	21.5	17.8
Vinylon fiber	-	29.3	28.3	26.0	23.8	21.3	18.5
Nylon fiber	-	28.0	27.0	25.5	24.5	22.8	21.0
Polypropylene fiber	-	30.0	29.0	28.8	27.5	27.0	22.8

Table 4

Flame retardance (LOI) of composite fiber							
Blending ratio: Fiber in Comparative Example 1/Combustible fiber	100/0	70/30	60/40	50/50	40/60	30/70	0/100
Cotton fiber	32.0	-	26.5	24.5	22.5	20.8	18.0
Polyester fiber	-	28.3	27.5	26.5	23.8	-	22.8
Acrylic fiber	-	27.3	25.3	24.0	22.0	20.5	17.8
Vinylon fiber	-	28.5	27.0	24.8	22.5	21.0	18.5
Nylon fiber	-	26.5	25.5	24.8	24.0	22.0	21.0
Polypropylene fiber	-	30.0	29.0	28.3	27.3	27.0	22.8

Claims

1. A flame-retardant fiber having good colorfastness to heat which comprises 100 parts by weight of a principal constituent composed of a halogen-containing polymeric substance and polyvinyl alcohol in a weight ratio of from 80:20 to 20:80, 5-35 parts by weight of antimony pentoxide, and 0.13-5.0 parts by weight of heat stabilizer in which the compositional ratio of octyl tin mercaptans heat stabilizer to octyl tin laurates heat stabilizer is from 5/5 to 3/7.

2. A flame-retardant fiber having good colorfastness to heat as defined in Claim 1, which further comprises 0.3-10 parts by weight of stannic acid as a flame retardant.

3. A flame-retardant composite fiber having good flame retardance and colorfastness to heat which is composed mainly of a flame-retardant fiber as defined in Claim 1 or 2 and a combustible fiber.

4. A flame-retardant composite fiber having good flame retardance and colorfastness to heat as defined in Claim 3, which is characterized in that the content of flame-retardant fiber is less than 70 wt% and the content of combustible fiber is more than 30 wt%.

5. A flame-retardant composite fiber as defined in Claim 3 or 4, wherein the combustible fiber is one or more species selected from the group consisting of cellulosic fiber, polyester fiber, acrylic fiber, vinylon fiber, polyamide fiber, and polypropylene fiber.

6. A flame-retardant composite fiber as defined in Claim 3 or 4, wherein the combustible fiber is cotton fiber.

7. A flame-retardant composite fiber having an LOI value higher than 22.0 and a degree of whiteness higher than 70% which comprises less than 35 wt% of flame-retardant fiber, whose principal constituent is composed of a halogen-containing polymeric substance and polyvinyl alcohol in a ratio from 80:20 to 20:80 (by weight), and more than 65 wt% of cotton fiber.

8. A process for producing a flame-retardant fiber having good colorfastness to heat, said process comprising mixing 100 parts by weight (as solids) of a principal constituent in the form of aqueous dispersion in which the ratio of an emulsion of halogen-containing polymeric substance to polyvinyl alcohol is from 80:20 to 20:80 (by weight as solids), with 5-35 parts by weight of antimony compound and 0.2-5 parts by weight of a heat stabilizer composition (which is composed of 65-75 parts by weight of octyl tin-type heat stabilizer as a principal component, 20-30 parts by weight of phthalate plasticizer, and 5-15 parts by weight of surface active agent, with the total amount being 100 parts by weight), thereby forming a spinning solution, and subjecting the spinning solution to wet spinning and optional post treatments.

INTERNATIONAL SEARCH REPORT

International Application No PCT/JP91/01390

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl[5] D01F6/50, 6/48

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	D01F1/00-6/96

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

Jitsuyo Shinan Koho 1926 - 1991
Kokai Jitsuyo Shinan Koho 1926 - 1991

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	JP, A, 2-6611 (Kohjin Co., Ltd.), January 10, 1990 (10. 01. 90), Claim, pages 2 to 3 (Family: none)	1, 3-8
Y	JP, B2, 55-20006 (Kohjin Co., Ltd.), May 30, 1980 (30. 05. 80), Claim, columns 5 to 7, Examples 1 to 6 & US, A, 4127698	1-8
Y	JP, A, 59-211613 (Kanegafuchi Chemical Industry Co., Ltd.), November 30, 1984 (30. 11. 84), Claim, Example 1	1, 2, 8
Y	JP, B1, 44-16218 (Asahi Dow Co., Ltd.), July 18, 1969 (18. 07. 69), Claim, page 1, Examples 3, 6 (Family: none)	1, 8
Y	JP, A, 58-208343 (Robil), December 5, 1983 (05. 12. 83), Claim, Examples 1, 12 & EP, B1, 91384	1, 8

* 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

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
December 13, 1991 (13. 12. 91)	January 14, 1992 (14. 01. 92)
International Searching Authority	**Signature of Authorized Officer**
Japanese Patent Office	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

& BR, A, 8301757 & ES, A5, 521171
& AR, A1, 230458 & FR, B1, 2524475
& US, A, 4529768 & CA, A1, 1199441

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers , because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim numbers , because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.