A graft natural rubber pressure-sensitive adhesive containing in a latex state a copolymer formed by graft polymerizing a vinyl polymer onto a natural rubber having a protein content of 0.1 % by weight or less in terms of nitrogen, and a pressure-sensitive adhesive tape comprising a support having coated on at least one surface thereof the pressure-sensitive adhesive. The pressure-sensitive adhesive is excellent in various properties such as film-forming property, pressure-sensitive characteristics, water resistance, and electrical insulation property.
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DESCRIPTION

GRAFT NATURAL RUBBER PRESSURE-SENSITIVE ADHESIVE
AND PRESSURE-SENSITIVE ADHESIVE TAPE USING IT

Technical Field

The present invention relates to a graft natural rubber
pressure-sensitive adhesive in a latex state excellent in
pressure-sensitive adhesive characteristics, and to a pressure-
sensitive adhesive tape using it.

Background Art

Hitherto, natural rubber pressure-sensitive adhesives
of a latex type using a natural rubber latex the concentration
of which is adjusted have been known. However, in these
conventional pressure-sensitive adhesives, in addition to the
disadvantages that the pressure-sensitive adhesives are poor in
the film-forming property, a high-temperature breaking
treatment of the latex is required for obtaining the practical
pressure-sensitive adhesive characteristics, and also a large
amount of energy by high-temperature drying is required for
forming the pressure-sensitive adhesive layer on a support,
there are further problems that these pressure-sensitive
adhesives are inferior in various properties such as the
pressure-sensitive adhesive characteristics, the water
resistance, the electrical insulation property, etc., to the
pressure-sensitive adhesives of a solution type formed by
dissolving a natural rubber in an organic solvent.

Accordingly, the latex type natural rubber pressure-
sensitive adhesives have not yet practically be used at present although they have a merit of a non-solvent type.

On the other hand, regarding the solution type natural rubber pressure-sensitive adhesives described above, pressure-sensitive adhesives using a natural rubber graft-polymerized with a vinyl monomer are also known.

The graft copolymer of a natural rubber aims at the improvement of the pressure-sensitive adhesive characteristics such as the adhesive force, the selectivity of an adherend, etc.

For example, by graft-polymerizing methyl methacrylate, the cohesive force and the adhesive force to a polar material such as a metal, etc., are improved, the adhesive is prevented from remaining at repeeling, a strong adhesion between a relief rubber plate (sheet) and a metal is attained, and the performance as a surface protective sheet for metal plates, a printing plate-fixing tape having a good peelability to the metal plate, etc., is improved.

However, these pressure-sensitive adhesives are of a solution type as described above, and the disadvantage that safety such as environmental sanitation, prevention of a fire, etc., is poor has not yet been overcome.

Disclosure of Invention

An object of the present invention is to provide a latex-type graft natural rubber pressure-sensitive adhesive, which is excellent in the film-forming property, does not need
high-temperature treatment, and shows excellent various characteristics such as good pressure-sensitive adhesive characteristics, high water resistance, high electrical insulation property, etc., without losing the modification effect by grafting using a vinyl monomer.

According to one embodiment of the present invention, there is provided a graft natural rubber pressure-sensitive adhesive comprising in a latex state a copolymer formed by graft-polymerizing a natural rubber having a protein content of 0.1% by weight or less in terms of nitrogen, with a vinyl polymer.

According to another embodiment of the present invention, there is provided a pressure-sensitive adhesive tape comprising a support having coated on one surface or both surfaces thereof the graft natural rubber pressure-sensitive adhesive.

According to the present invention, a latex-type natural rubber pressure-sensitive adhesive excellent in the safety such as an environmental sanitation, the prevention of a fire, etc., is obtained while attaining the improvement of the pressure-sensitive adhesive characteristics by grafting the natural rubber, and the pressure-sensitive adhesive can form a film or layer by coating without high-temperature treatment. The coating layer of the pressure-sensitive adhesive can show various excellent characteristics such as excellent pressure-sensitive adhesive characteristics, high water resistance, high
electrical insulation property, etc.

The present invention is described in detail below.

The graft natural rubber pressure-sensitive adhesive of the present invention contains in a latex state a copolymer formed by graft-polymerizing a natural rubber having a protein content of 0.1% by weight or less in terms of nitrogen, based on the weight of the entire rubber solid contents, with a vinyl polymer. Such a natural rubber can be prepared by, for example, a method of applying a deproteinizing treatment and a graft polymerization treatment to a natural rubber latex.

There is no particular restriction on the deproteinizing treatment method. For example, the deproteinizing treatment can be carried out by an appropriate method such as a method of adding a proteolytic enzyme or bacteria to a natural rubber latex to decompose the protein in the natural rubber latex, a method of adding a surface active agent to a natural rubber latex followed by repeatedly washing the mixture, a combined method of the above methods, etc. Also, an industrial latex such as a field latex, a latex obtained by applying an ammonia treatment to the field latex or by controlling the concentration of the field latex, etc., can be used as the natural rubber latex to be treated in the present invention.

A protein which highly stabilizes the natural rubber latex by the emulsifying action is removed by the deproteinizing treatment, and a natural rubber latex which can
be broken without high-temperature treatment, shows a good coating film-forming property, and has a good compatibility with a tackifier, etc., can be obtained, whereby a latex type pressure-sensitive adhesive excellent in the safety such as an environmental sanitation, prevention of a fire, etc., can be prepared.

The protein content of in the natural rubber by the deproteining treatment is 0.1% by weight or less in terms of nitrogen, based on the weight of the entire rubber solid contents. That is, because the nitrogen content in the protein in 16% by weight based on the total weight of the protein, the total weight percent of the protein \( \times 0.16 \) equals to the weight percent of the nitrogen portion (the total weight percent of the protein = the weight percent of the nitrogen portion \( \div \) 0.16). Therefore, the natural rubber latex is subjected to the deproteining treatment such that this converted value becomes 0.1% by weight or less calculated as nitrogen, based on the weight of the entire rubber solid contents.

If the protein content is over 0.1% by weight, the pressure-sensitive adhesive becomes poor in the improvement effects of the film-forming property, theunnecessity of a high-temperature treatment, the electrical insulation property, etc. Further, it is difficult for the adhesive to exhibit the pressure-sensitive adhesive characteristics, the water resistance, etc., comparable to the solution type pressure-sensitive adhesives.
The protein content in terms of nitrogen is preferably 0.05% by weight or less, more preferably 0.03% by weight or less, and most preferably 0.01% by weight or less. Particularly, when the content is 0.01% by weight or less, retention force (creep resistance) of the adhesive is improved in addition to the improvement effects of the adhesive force and the electrical insulation property. The reason that the latex type pressure-sensitive adhesive of the present invention is excellent in the electrical insulation property in spite of the adhesive being a latex type of a natural rubber is considered due to that a protein which is liable to be electrically charged is removed.

The deproteinizing treatment method by a proteolytic enzyme described above has the advantage that a protein can be removed at high efficiency, but there is no particular restriction on the proteolytic enzyme used. That is, a proteolytic enzyme originated from a bacterium, a proteolytic enzyme originated from a mold, a proteolytic enzyme originated from a yeast, etc., can be used. The proteolytic enzyme preferably used is protease originated from a bacterium.

The treatment conditions, that is, the amount of the proteolytic enzyme added, the addition system thereof, the treatment temperature, the treatment time, etc., may be appropriately determined. For example, there is a deproteinizing treatment system that a proteolytic enzyme is added to a field latex in an amount of from 0.001 to 10% by
weight, the resulting mixture is allowed to stand or mixed for from several minutes to one week, in necessary, under a temperature control of from 5 to 90°C, and preferably from 20 to 60°C, the mixture is diluted with water or an aqueous solution of a surface active agent, and a protein is then separated and removed by an appropriate separation system using a centrifugal separator, a separation membrane, etc., to purify the latex.

An appropriate surface active agent such as a cationic surface active agent, anionic surface active agent, a nonionic active agent, an amphoteric surface active agent, etc., can be used as the surface active agent for the purification described above. A preferable surface active agent is excellent in the emulsification action and is difficult to absorb water. Such an emulsification action relates to the stability of the latex at the graft polymerization treatment and is handling the pressure-sensitive adhesive, such as storage or coating, and also the non-absorption property of water relates to the water resistance of the pressure-sensitive adhesive.

On the other hand, the deproteinizing treatment method using a surface active agent performs the deproteinization by cleaning and purifying the natural rubber latex with the surface active agent according to the cleaning and purification system described above, and the surface active agent used is appropriately selected. A preferred surface active agent is excellent in the emulsification action and is difficult to
absorb water in the same reason described above.

Examples of the surface active agent for the
deproteinizing treatment described above include an anionic
surface active agent such as a carboxylic acid surface active
agent, a sulfonic acid surface active agent, sulfuric acid
ester surface active agent, a phosphoric acid ester surface
active agent, etc.; a nonionic surface active agent such as a
POA (polyoxyalkylene) ether surface active agent, a POA ester
surface active agent, a polyhydric alcohol ester surface active
agent, a POA polyhydric alcohol ester surface active agent, a
glucoside surface active agent, and a POA glucoside surface
active agent; and an amphoteric surface active agent such as an
amino acid surface agent, a betaine surface active agent, an
imidazoline surface active agent, and an amine oxide surface
active agent.

Specific examples of the anionic surface active agent
include the metal salts and ammonium salts of fatty acids,
alkylbenzenesulfonic acids, alkylsulfuric acid esters,
alkylphenolphosphoric acid esters, etc., and alkanolamine
salts. Specific examples of the nonionic surface active agent
include POA alkyl ethers, POA fatty acid esters, sorbitol fatty
acid esters, fatty acid esters of polysaccharides, POA poly-
saccharide fatty acid esters, alkyl(poly)glucoxides, and POA
alkylamines. Specific examples of the amphoteric surface
active agent include acylaminoacid salts, alkyldimethyl-
betaines, alkylcarboxymethylhydroxyethyl imidazolium betaines,
and alkylidimethylamine oxides.

The surface active agent used may contain at least one kind of the surface active agents for the deproteinizing treatment described above as the effective component, and the addition amount thereof is preferably from 0.001 to 10% by weight based on the weight of the natural rubber latex from the points of the stability and the pressure-sensitive adhesive characteristics of the latex formed. In addition, the surface active agents for the deproteinizing treatment described above can also be used for purification treatment of a liquid after being subjected to the deproteinizing treatment by the proteolytic enzyme.

The copolymer formed by graft polymerizing a vinyl polymer onto a natural rubber, that is, the latex of a graft natural rubber, can be prepared by, for example, a method of adding a vinyl monomer and a polymerization initiator to the natural rubber latex before or after the deproteinizing treatment and subjecting the mixture to an emulsion polymerization treatment. Accordingly, the order of the deproteinizing treatment and the graft polymerization treatment of the natural rubber latex is not limited.

The vinyl monomer which can be used is appropriately selected according to the modification purpose by grafting, and any vinyl monomer can be graft polymerized. Examples of the vinyl monomer include carboxyl group-containing monomers such as (meth)acrylic acid or itaconic acid; esters of an alkyl
group, preferably an alkyl group having up to 20 carbon atoms (e.g., methyl, isopropyl, butyl or isoctyl), and (meth)acrylic acid; esters of a hydroxyalkyl group (e.g., hydroxyethyl or hydroxypropyl), and (meth)acrylic acid; and hydroxyl group-containing monomers such as glycidyl methacrylate.

Examples of the vinyl monomer further include vinyl monomers such as vinyl acetate, styrene, (meth)acrylonitrile, (meth)acrylamide, isopropylmaleimide, cyclohexylmaleimide, N-vinylpyrrolidone, (meth)acryloylmorpholine, N,N-dimethylacrylamide, glycidyl methacrylate, etc.

The vinyl monomers which can be preferably used from the point of the pressure-sensitive adhesive characteristics, etc., are vinyl monomers containing a polar group, which form a homopolymer having a high glass-transition temperature, such as methyl methacrylate and styrene.

The vinyl monomers can be used alone or as a mixture of them. There is no particular restriction on the amount of the vinyl monomers added, and the amount thereof can be appropriately determined. In general, the amount of the vinyl monomer added is from 5 to 100 parts by weight, and preferably from 10 to 50 parts by weight, per 100 parts by weight of the natural rubber from the points of the reactivity and the modification effect of the graft polymerization.

The graft polymerization by an emulsion polymerization of the vinyl monomer can employ an appropriate method such as a method of adding an emulsifying agent to the natural rubber
latex and adding thereto a vinyl monomer, or a method of emulsifying a vinyl monomer with an emulsifying agent and adding the emulsion formed to the natural rubber latex. The emulsifying agent which can be used is a material containing at least one of the surface active agents for the deproteinizing treatment described above, amine surface active agents, and reactive surface active agents, as the effective component.

Specific examples of the amine surface active agent include (mono, di, tri)alkylamines, and the acid salts or the quaternary ammonium salts of the alkylene oxide addition product of the alkylamine. Specific examples of the reactive surface active agent include anionic, cationic, and nonionic surface active agents such as POA alkylprobenyl phenyl ether sulfuric acid ester salts, POA (meth)acrylic acid esters, and dimethylalkylallyloxyhydroxypropylammonium chloride.

There is no particular restriction on the graft polymerization initiator used, and initiators for various vinyl polymerizations can be used. Also, there is no particular restriction on a method of adding the initiator.

Examples of the polymerization initiator generally used include azo compounds such as 2,2'-azobisisobutyronitrile and 2,2'-azobis[2-diaminopropane] dihydrochloride; persulfates such as potassium persulfate and ammonium persulfate; peroxides such as benzoyl peroxide, t-butyl hydroperoxide, cumene hydroperoxide; and redox initiators such as a combination of a persulfate and sodium hydrosulfite and a combination of a
peroxide and an amine.

Examples of the addition method of the polymerization initiator include a method of adding the entire amount of the initiator before the polymerization treatment, a method of adding the initiator by portions or at once in heating for the polymerization reaction, and a method of adding two or more kinds of the initiators as a mixture thereof, or separately, or with a time difference. The preferred addition method is a method of previously adding the entire amount of a redox initiator using a peroxide to initiate the polymerization.

The amount of the polymerization initiator added is preferably from about 0.001 to 1 mol% per mole of the vinyl monomer from the points of a stable progress of the graft polymerization, the suppression property of the occurrence of rubber crosslinking, etc.

It is preferred to carry out the polymerization treatment under a nitrogen gas atmosphere at 10°C to 80°C for 2 to 100 hours from the points of the stabilized progressing property of the graft polymerization, the completion property of the polymerization, and suppression of the formation of the condensate due to instabilization of the latex.

The graft natural rubber pressure-sensitive adhesive of the present invention can be prepared as various pressure-sensitive adhesives containing the deproteinized graft natural rubber in a latex state. Examples of the graft natural rubber pressure-sensitive adhesive include an emulsion type or water-

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dispersion type pressure-sensitive adhesive using a graft natural rubber having a desired decreased content of protein in place of a conventional natural rubber latex, and a pressure-sensitive adhesive obtained by adding a graft natural rubber having a desired decreased content of protein to other emulsion type or water-dispersion type pressure-sensitive adhesive.

The typical graft natural rubber pressure-sensitive adhesive of the present invention is of a dispersion type obtained by compounding a graft natural rubber and a tackifier by, for example, mixing a latex of a graft natural rubber having the desired protein content and having a solid component concentration of from 30 to 80% by weight, and preferably from 45 to 70% by weight, and the emulsion of a tackifier. In this embodiment, appropriate additives such as a softening agent, a plasticizer, an antioxidant, a pigment, a coloring agent, etc., can be compounded with the mixture.

An appropriate tackifier can be used, and examples thereof include rosin resins such as a rosin ester, a hydrogenated rosin ester, a disproportionated rosin ester, or a polymerized rosin ester; coumarone-indene resins such as a coumarone-indene resin, a hydrogenated coumarone-indene resin, a phenol-modified coumarone-indene resin, or an epoxy-modified coumarone-indene resin; terpene resins such as a polyterpene resin, a styrene-modified terpene resin, or a phenol-modified terpene resin; and petroleum resins such as aliphatic petroleum resins, aromatic petroleum resins, aromatic-modified aliphatic
petroleum resins, or aromatic pure resins.

The amount of the tackifier compounded is generally from 10 to 200 parts by weight per 100 parts by weight of the graft natural rubber although the amount is not limited to these amounts.

The pressure-sensitive adhesive tape of the present invention comprises a support having coated on one surface or both surfaces thereof a layer of the graft natural rubber pressure-sensitive adhesive described above. The pressure-sensitive adhesive layer may be fixed to the support or may be the layer which is peelable from the support. The peelable pressure-sensitive adhesive tape can be prepared by, for example, a method of using a support treated with a releasing agent.

An appropriate support can be used, and examples thereof include a plastic film, a paper, a nonwoven fabric, a foam, a metal foil, a laminated material thereof, etc. The thickness of the pressure-sensitive adhesive layer formed on the support is generally from 1 to 500 μm, but the thickness is not limited thereto and an appropriate thickness may be employed.

Best Mode for Carrying Out the Invention

The present invention is described in more detail with reference to the following examples, but the invention is not limited thereto.
Example 1

To a Malaysia-produced HA-type natural rubber latex (commercially available product, rubber solid content: 60% by weight) was added pure water to reduce concentration of the rubber solid content to 30% by weight. To the natural rubber latex were added 2% by weight of a nonionic-anionic composite surface active agent and a proteolytic enzyme originated from bacteria in a concentration of 0.02% by weight followed by allowing the resulting mixture to stand at 40°C for 24 hours to apply a proteolytic treatment. Pure water was then added to the natural rubber latex to reduce the rubber solid content concentration to 10% by weight. A procedure of washing and concentrating the natural rubber latex was repeated three times with a De-Laval type continuous centrifugal separator such that the concentration thereof became 60% by weight. A deproteinized natural rubber latex having a protein content measured by a Kjeldahl method of 0.01% by weight calculated as nitrogen was obtained.

To the deproteinized natural rubber latex obtained above was added pure water to reduce the rubber solid content concentration to 50% by weight. After adding thereto a nonionic surface active agent in a concentration of 2% by weight, the atmosphere of the system was displaced with nitrogen, and 30% by weight of methyl methacrylate and 0.3% by weight of aromatic peroxide based on the weight the rubber solid content were added to the natural rubber latex under
stirring at a temperature of 40°C. A diluted aqueous solution of 0.1% by weight, based on the weight the rubber solid content, of an amine compound was gradually added dropwise to the natural rubber latex, and the graft polymerization treatment was further continued for about 2 hours followed by lowering the temperature to obtain a latex of the graft natural rubber.

50 Parts (by weight, and hereinafter the same) of a terpene tackifier resin, 50 parts of a polybutene softening agent, 100 parts of toluene, and 1 part of an antioxidant were added to 140 parts of water containing 2 parts of a nonionic surface active agent followed by stirring to obtain an emulsion. The emulsion thus obtained was mixed with 200 parts of the graft natural rubber latex having the rubber solid content concentration of 50% by weight obtained in the above to obtain a graft natural rubber pressure-sensitive adhesive. The pressure-sensitive adhesive thus obtained was coated on a polyester film having a thickness of 30 µm and dried at 100°C for 5 minutes to obtain a pressure-sensitive adhesive tape having a pressure-sensitive adhesive layer having a thickness of about 40 µm.

Example 2

The same procedure as in Example 1 was followed except that the time of the proteolytic treatment was changed to 2 hours.

A deproteinized natural rubber latex having a protein
content of 0.03% by weight calculated as nitrogen was obtained.

**Comparative Example 1**

The same procedure as in Example 1 was followed except that the HA type natural rubber latex (protein content calculated as nitrogen: about 0.25% by weight) was subjected to the graft polymerization treatment without applying the proteolytic treatment, to obtain a graft natural rubber pressure-sensitive adhesive and a pressure-sensitive adhesive tape.

**Comparative Example 2**

The same procedure as in Example 1 was followed except that the natural rubber latex subjected to the proteolytic treatment was used without being subjected to the graft polymerization treatment, to obtain a graft natural rubber pressure-sensitive adhesive and a pressure-sensitive adhesive tape.

[Evaluation Test]

The pressure-sensitive adhesive tapes obtained in the example and the comparative examples were evaluated as follows.

**Film-Forming Property:**

The pressure-sensitive adhesive layer in each pressure-sensitive adhesive tape immediately after drying was observed. When the film-forming property was good, the property was evaluated as o and when the film-forming property was bad, the property was evaluated as x. The evaluation of the film-forming property of each pressure-sensitive adhesive layer was
based on each electron microphotograph. That is, when the film-forming property is good, the emulsion is fractured well by heat, and the components are compatible well with each other. In this case, the pressure-sensitive adhesive layer is visually excellent in transparency. On the other hand, when the film-forming property is bad, the fracture of the emulsion by heat is insufficient, and the components are inferior in the compatibility with each other. In this case, the pressure-sensitive adhesive layer is visually white turbid.

Adhesive Force:

Each pressure-sensitive adhesive tape having a width of 20 mm was press-adhered to a stainless steel plate having a thickness of 2 mm surface-polished with a waterproof abrasive paper of #280 by reciprocating a rubber roller of 2 kg, and after 30 minutes, the adhesive force was determined (180° peel, tensile speed 300 mm/minute, 23°C, 65% R.H.).

Retention Force:

Each pressure-sensitive adhesive tape was press-adhered to a Bakelite plate at an area of 5 mm in width and 20 mm in length at 23°C according to the above manner to hang the tape, a uniform load of 500 g was applied to the lower end of the pressure-sensitive adhesive tape, the system was retained at 40°C, and the time until the pressure-sensitive adhesive tape was peeled and fallen was measured by a creep test machine.

Water Resistance:

After press-adhering each pressure-sensitive adhesive
tape to a stainless steel plate according to the adhesive force measurement test described above, the assembly was immersed in water at 23°C for 72 hours and taken out. Water on the surface was wiped off and after 30 minutes, the adhesive force was determined.

Electrical Insulation Property:

The surface resistivity of the pressure-sensitive adhesive layer of each pressure-sensitive adhesive tape was determined according to the method of JIS K 6911.

The results obtained are shown in the Table below.

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<th>Film-Forming Property</th>
<th>Adhesive Force (g/20 mm)</th>
<th>Retention Force (min.)</th>
<th>Water Resistance (g/20 mm)</th>
<th>Electrical Insulation Property (Ω)</th>
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<td>○</td>
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<td>Comp. Ex 2</td>
<td>x</td>
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<td>349</td>
<td>Less than 29</td>
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<tr>
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<td>463</td>
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Ex: Example; Comp. Ex: Comparative Example

It can be seen from the results shown in the above table that the graft natural rubber pressure-sensitive adhesive and the pressure-sensitive adhesive tape obtained in the Example of the present invention are excellent in the film-forming property, the adhesive force, the cohesion (retention force), the water resistance, and the electrical insulation
property and thus are excellent in practical use.
CLAIMS

1. A graft natural rubber pressure-sensitive adhesive comprising in a latex state a copolymer formed by graft polymerizing a vinyl polymer onto a natural rubber having a protein content of 0.1% by weight or less in terms of nitrogen, based on the weight of the entire rubber solid contents.

2. The graft natural rubber pressure-sensitive adhesive as claimed in claim 1, wherein the vinyl polymer comprises at least one of methyl methacrylate and styrene.

3. A pressure-sensitive adhesive tape comprising a support having coated on one surface or both surfaces thereof a layer of a graft natural rubber pressure-sensitive adhesive comprising in a latex state a copolymer formed by graft polymerizing a vinyl polymer onto a natural rubber having a protein content of 0.1% by weight or less in terms of nitrogen.

4. The pressure-sensitive adhesive tape as claimed in claim 3, wherein the vinyl polymer comprises at least one of methylmethacrylate and styrene.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC G C08F253/00 C09J151/04 C09J7/02

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)

IPC G C08F C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Relevant to claim No.</th>
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<td>DATABASE WPI Week 9507 Derwent Publications Ltd., London, GB; AN 95-048854 XP002016439 &amp; JP,A,06 329 702 (KA0 CORP), 29 November 1994 see abstract ---</td>
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Further documents are listed in the continuation of box C. Patent family members are listed in annex.

Special categories of cited documents:

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'&' document member of the same patent family

Date of the actual completion of the international search

24 October 1996

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HJ Rijswijk Tel. (+31-70) 340-2040, Tx. 31 655 epo nl, Fax (+31-70) 340-3010

Authorized officer

Andriollo, G

Date of mailing of the international search report

11.11.96

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