

200102346-4

This Sheet Has Been Replaced



1

**LIQUID CRYSTAL ALIGNING AGENT
AND LIQUID CRYSTAL DISPLAY ELEMENT**

Detailed Description of the Invention

5 Field of the Invention

The present invention relates to a liquid crystal aligning agent used to form a liquid crystal alignment film for a liquid crystal display element and to a liquid crystal display element. More specifically, it relates to a liquid crystal aligning agent which gives a liquid crystal alignment film having excellent liquid crystal aligning properties and a short after image erase time for a liquid crystal display element and which also gives a liquid crystal alignment film for providing long-term reliability to a liquid crystal display element.

Prior Art

There has been known a liquid crystal display element (TN liquid crystal display element) having a TN (twisted nematic) liquid crystal cell formed by sandwiching a nematic liquid crystal having positive dielectric anisotropy between substrates with a transparent electrode having a liquid crystal alignment film made from polyimide or the like and twisting the major axis of each liquid crystal molecule at 90° between the substrates continuously. The liquid crystals of this TN liquid crystal display element is aligned by rubbed alignment.

In recent years, liquid crystal display elements having excellent contrast and view angle dependence, such as STN (Super Twisted Nematic) liquid crystal display element and homeotropic alignment liquid crystal display element, have been developed. The STN liquid crystal display element makes use of a birefringence effect caused by using a blend of a nematic liquid crystal and a chiral agent which is an optically active agent and continuously twisting the major

This Sheet Has Been Replaced



2

axis of each liquid crystal molecule at 180° C or more between substrates. The simple matrix drive of the homeotropically aligned liquid crystal display element is carried out in such a manner that the dielectric anisotropy of liquid crystal molecules aligns negative liquid crystals homeotropically and molecules are brought down by the application of voltage.

However, when a liquid crystal display element is formed using a liquid crystal aligning agent such as a conventionally known polyamic acid or imide polymer having a structure obtained by dehydrating and ring closing the polyamic acid, an after image is formed due to the large residual voltage of the liquid crystal display element and the time for erasing this after image is long, thereby making it impossible to obtain sufficient contrast. Further, when this liquid crystal display element is used for a long time, a stain-like display defect may be formed, thereby impairing the reliability of the liquid crystal display element.

Summary of the Invention

It is an object of the present invention to provide a liquid crystal aligning agent which can exhibit excellent aligning properties and is capable of forming a liquid crystal alignment film having a short time from the time when the application of voltage to the liquid crystal display element is released to the time when an after image is erased (to be referred to as "after image erase time" hereinafter) and free from a smear when voltage is applied for a long time.

It is another object of the present invention to provide a liquid crystal display element having a liquid crystal alignment film made from the liquid crystal aligning agent of the present invention.

Other objects and advantages of the present invention will become apparent from the following description.

According to the present invention, firstly, the above objects and advantages of the present invention are attained

This Sheet Has Been Replaced



by a liquid crystal aligning agent which contains at least one end-capped polymer selected from the group consisting of (A) an end-capped polyamic acid having an alicyclic structure and obtained by reacting (a) a tetracarboxylic dianhydride, (b) a diamine compound and (c) at least one compound selected from the group consisting of a dicarboxylic anhydride, a monoamine compound and a monoisocyanate compound, and (B) end-capped imidized polymers obtained by dehydrating and ring closing the polyamic acid.

10 Preferably, the liquid crystal aligning agent of the present invention contains at least one end-uncapped polymer selected from the group consisting of an end-uncapped polyamic acid obtained by reacting (A) a tetracarboxylic dianhydride and (B) a diamine compound, and an end-uncapped
15 imidized polymers obtained by dehydrating and ring closing the polyamic acid, in addition to the above end-capped polyamic acid and/or end-capped imidized polymer.

More preferably, the liquid crystal aligning agent of the present invention contains an end-capped imidized
20 polymer and an end-uncapped polyamic acid.

According to the present invention, secondly, the above objects and advantages of the present invention are attained by a liquid crystal display element having a liquid crystal alignment film obtained from the liquid crystal aligning
25 agent of the present invention.

The present invention will be described in detail hereinbelow.

tetracarboxylic dianhydride

An alicyclic structure can be introduced into the
30 end-capped polyamic acid and an end-capped imidized polymer used in the present invention by using an alicyclic tetracarboxylic dianhydride and/or alicyclic diamine, and an alicyclic structure is preferably introduced into them by using an alicyclic tetracarboxylic dianhydride. Examples

This Sheet Has Been Replaced

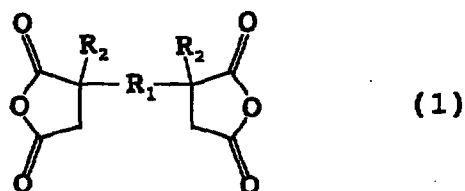


4

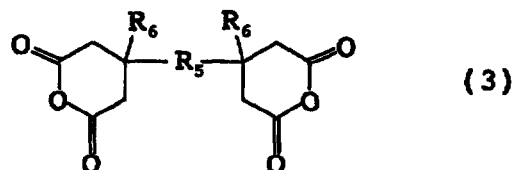
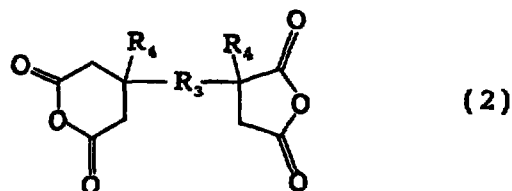
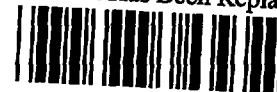
- of the alicyclic tetracarboxylic dianhydride include
2,3,5-tricarboxycyclopentylacetic dianhydride, 3,5,6-
tricarboxynorbornane-2-acetic dianhydride, 2,4,5-
tricarboxycyclohexylacetic dianhydride, 1,2,3,4-
5 cyclobutanetetracarboxylic dianhydride, 1,2-dimethyl-
1,2,3,4-cyclobutanetetracarboxylic dianhydride, 1,3-
dimethyl-1,2,3,4-cyclobutanetetracarboxylic dianhydride,
1,3-dichloro-1,2,3,4-cyclobutanetetracarboxylic
dianhydride, 1,2,3,4-tetramethyl-1,2,3,4-
10 cyclobutanetetracarboxylic dianhydride, 1,2,3,4-
cyclopentanetetracarboxylic dianhydride, 1,2,4,5-
cyclohexanetetracarboxylic dianhydride, 3,3',4,4'-
dicyclohexyltetracarboxylic dianhydride, 2,3,4,5-
tetrahydrofuran-tetracarboxylic dianhydride,
15 1,3,3a,4,5,9b-hexahydro-5(tetrahydro-2,5-dioxo-3-
furanyl)-naphtho[1,2-c]-furan-1,3-dione, 1,3,3a,4,5,9b-
hexahydro-5-methyl-5(tetrahydro-2,5-dioxo-3-furanyl)-
naphtho[1,2-c]-furan-1,3-dione, 1,3,3a,4,5,9b-hexahydro-
5-ethyl-5(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-
20 c]-furan-1,3-dione, 1,3,3a,4,5,9b-hexahydro-7-methyl-
5(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]-furan-
1,3-dione, 1,3,3a,4,5,9b-hexahydro-7-ethyl-5(tetrahydro-
2,5-dioxo-3-furanyl)-naphtho[1,2-c]-furan-1,3-dione,
1,3,3a,4,5,9b-hexahydro-8-methyl-5(tetrahydro-2,5-dioxo-
25 3-furanyl)-naphtho[1,2-c]-furan-1,3-dione,
1,3,3a,4,5,9b-hexahydro-8-ethyl-5(tetrahydro-2,5-dioxo-
3-furanyl)-naphtho[1,2-c]-furan-1,3-dione,
1,3,3a,4,5,9b-hexahydro-5,8-dimethyl-5(tetrahydro-2,5-
dioxo-3-furanyl)-naphtho[1,2-c]-furan-1,3-dione, 5-(2,5-
30 dioxotetrahydrofural)-3-methyl-3-cyclohexane-1,2-
dicarboxylic dianhydride, bicyclo[2,2,2]-oct-7-ene-
2,3,5,6-tetracarboxylic dianhydride, 3-
oxabicyclo[3.2.1]octane-2,4-dione-6-spiro-3'-
(tetrahydrofuran-2',5'-dione), and tetracarboxylic

5

dianhydrides represented by the following formulas (1), (2), and (3).



This Sheet Has Been Replaced



(wherein R^1 , R^3 and R^5 are each an alicyclic divalent organic group, and R^2 , R^4 and R^6 are each a hydrogen atom or alkyl group, with the proviso that R^2 's, R^4 's and R^6 's may be the same or different.)

These tetracarboxylic dianhydrides may be used alone or in combination of two or more.

Out of these, 2,3,5-tricarboxycyclopentylacetic dianhydride, 3,5,6-tricarboxynorbornane-2-acetic dianhydride, 2,4,5-tricarboxycyclohexylacetic dianhydride, 1,2,3,4-cyclobutanetetracarboxylic dianhydride, 1,3-dimethyl-1,2,3,4-cyclobutanetetracarboxylic dianhydride, 1,2,3,4-cyclopentanetetracarboxylic dianhydride, 5-(2,5-dioxotetrahydrofural)-3-methyl-3-cyclohexene-1,2-dicarboxylic dianhydride, 1,3,3a,4,5,9b-hexahydro-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]furan-1,3-dione, 1,3,3a,4,5,9b-hexahydro-8-methyl-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]furan-1,3-dione, 1,3,3a,4,5,9b-hexahydro-5,8-dimethyl-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]furan-1,3-dione, bicyclo[2,2,2]-oct-7-ene-2,3,5,6-

This Sheet Has Been Replaced



6

- tetracarboxylic dianhydride and 3-oxabicyclo[3.2.1]octane-2,4-dione-6-spiro-3'-(tetrahydrofuran-2',5'-dione) are preferable because they can exhibit excellent liquid crystal aligning properties.
- 5 Particularly preferred are 2,3,5-tricarboxycyclopentylacetic dianhydride, 2,4,5-tricarboxycyclohexylacetic dianhydride, 1,2,3,4-cyclobutanetetracarboxylic dianhydride, 1,3-dimethyl-1,2,3,4-cyclobutanetetracarboxylic dianhydride,
- 10 1,3,3a,4,5,9b-hexahydro-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]furan-1,3-dione, 1,3,3a,4,5,9b-hexahydro-8-methyl-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]furan-1,3-dione and 3-oxabicyclo[3.2.1]octane-2,4-dione-6-spiro-3'-(tetrahydrofuran-2',5'-dione).
- 15

The end-capped polyamic acid and end-capped imidized polymer used in the present invention may be obtained by using another tetracarboxylic dianhydride in limits that do not impair the effect of the present invention. The end-uncapped

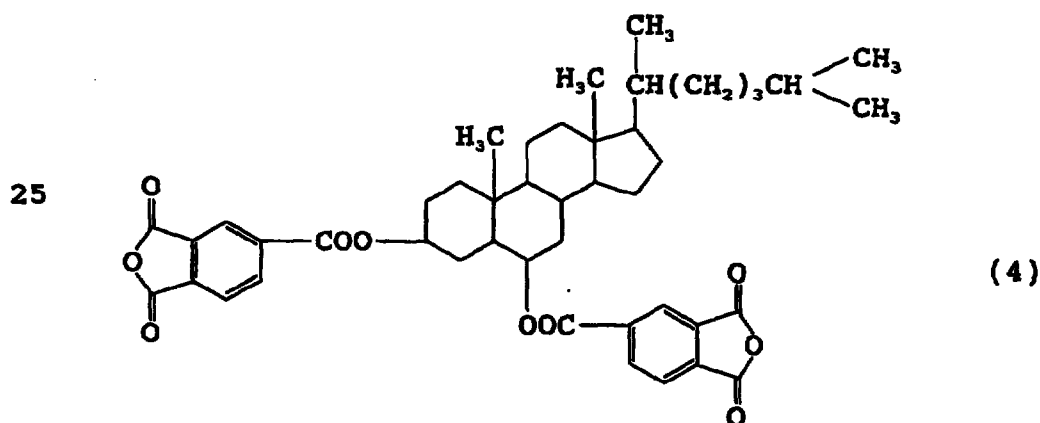
20 polyamic acid and end-uncapped imidized polymer may be obtained from an aromatic tetracarboxylic dianhydride or an aliphatic tetracarboxylic dianhydride other than the above alicyclic tetracarboxylic dianhydrides.

Examples of the tetracarboxylic dianhydride other than

25 the alicyclic tetracarboxylic dianhydrides include aromatic tetracarboxylic dianhydrides such as pyromellitic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 3,3',4,4'-biphenylsulfonetetracarboxylic dianhydride, 1,4,5,8-naphthalenetetracarboxylic

30 dianhydride, 2,3,6,7-naphthalenetetracarboxylic dianhydride, 3,3',4,4'-biphenylethertetracarboxylic dianhydride, 3,3',4,4'-dimethyldiphenylsilanetetracarboxylic dianhydride, 3,3',4,4'-tetraphenylsilanetetracarboxylic dianhydride,

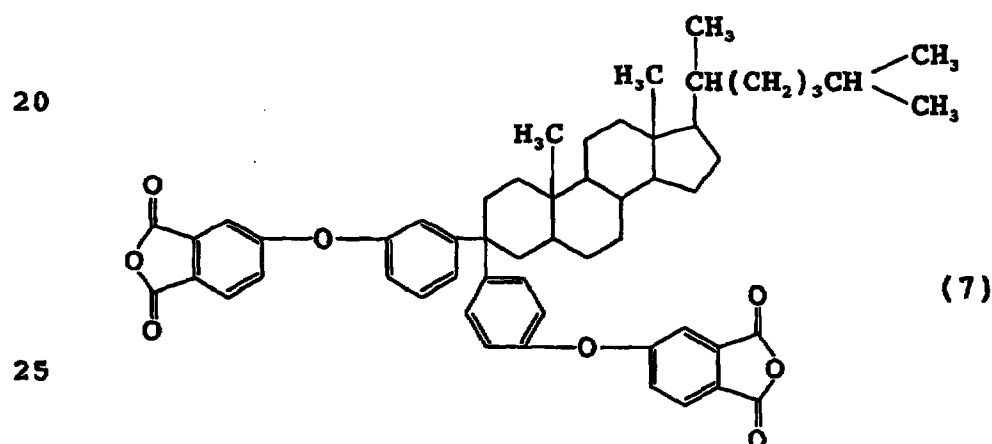
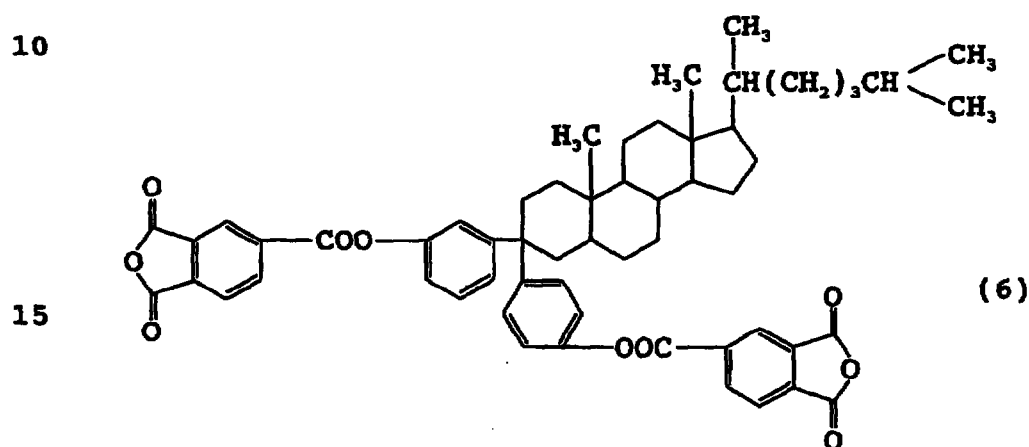
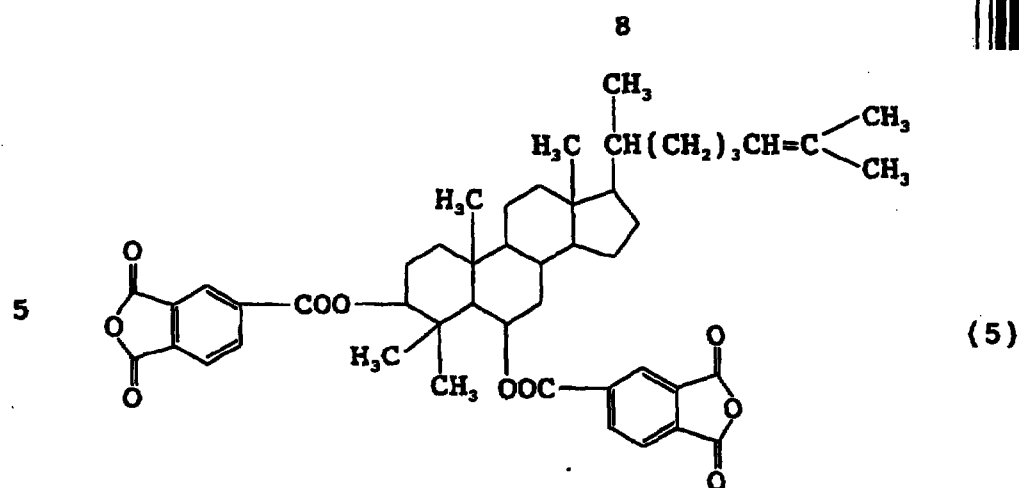
- 1,2,3,4-furantetracarboxylic dianhydride, 4,4'-bis(3,4-dicarboxyphenoxy)diphenylsulfide dianhydride, 4,4'-bis(3,4,-dicarboxyphenoxy)diphenylsulfonic dianhydride, 4,4'-bis(3,4-dicarboxyphenoxy)diphenylpropane dianhydride,
- 5 3,3',4,4'-biphenyltetracarboxylic dianhydride, bis(phthalic acid)phenylphosphine oxide dianhydride, p-phenylene-bis(triphenylphthalic)dianhydride, m-phenylene-bis(triphenylphthalic)dianhydride, bis(triphenylphthalic acid)-4,4'-diphenylether dianhydride,
- 10 bis(triphenylphthalic acid)-4,4'-diphenylmethane dianhydride, ethylene glycol-bis(anhydrotrimellitate), propylene glycol-bis(anhydrotrimellitate), 3,3',4,4'-perfluoroisopropylidenediphthalic dianhydride, 1,4-butanediol-bis(anhydrotrimellitate), 1,6-hexanediol-
- 15 bis(anhydrotrimellitate), 1,8-octanediol-bis(anhydrotrimellitate), 2,2-bis(4-hydroxyphenyl)propane-bis(anhydrotrimellitate), and compounds represented by the following formulas (4) to (7); and aliphatic tetracarboxylic dianhydrides such as
- 20 butanetetracarboxylic dianhydride. They may be used alone or in combination of two or more.



This Sheet Has Been Replaced



This Sheet Has Been Replaced



diamine compound

Examples of the diamine compound include aromatic

30 diamines such as paraphenylenediamine, metaphenylenediamine,

4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylethane,

4,4'-diaminodiphenylsulfide, 4,4'-diaminodiphenylsulfone,

3,3'-dimethyl-4,4'-diaminobiphenyl, 4,4'-

diaminobenzanilide, 4,4'-diaminodiphenylether, 1,5-

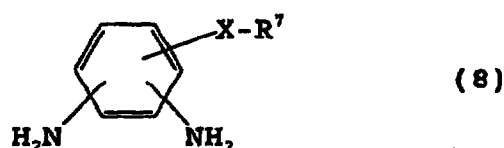
- diaminonaphthalene, 3,3-dimethyl-4,4'-diaminobiphenyl,
5-amino-1-(4'-aminophenyl)-1,3,3-trimethylindane, 6-
amino-1-(4'-aminophenyl)-1,3,3-trimethylindane, 3,4'-
diaminodiphenylether, 3,3'-diaminobenzophenone, 3,4'-
5 diaminobenzophenone, 4,4'-diaminobenzophenone, 2,2-
bis[4-(4-aminophenoxy)phenyl]propane, 2,2-bis[4-(4-
aminophenoxy)phenyl]hexafluoropropane, 2,2-bis(4-
aminophenyl)hexafluoropropane, 2,2-bis[4-(4-
aminophenoxy)phenyl]sulfone, 1,4-bis(4-
10 aminophenoxy)benzene, 1,3-bis(4-aminophenoxy)benzene,
1,3-bis(3-aminophenoxy)benzene, 9,9-bis(4-aminophenyl)-
10-hydroanthracene, 2,7-diaminofluorene, 9,9-bis(4-
aminophenyl)fluorene, 4,4'-methylene-bis(2-chloroaniline),
2,2',5,5'-tetrachloro-4,4'-diaminobiphenyl, 2,2'-
15 dichloro-4,4'-diamino-5,5'-dimethoxybiphenyl, 3,3'-
dimethoxy-4,4'-diaminobiphenyl, 1,4,4'-
(paraphenyleneisopropylidene)bisaniline, 4,4'-
(metaphenyleneisopropylidene)bisaniline, 2,2'-bis[4-(4-
amino-2-trifluoromethylphenoxy)phenyl]hexafluoropropane,
20 4,4'-diamino-2,2'-bis(trifluoromethyl)biphenyl and 4,4'-
bis[(4-amino-2-trifluoromethyl)phenoxy]-
octafluorobiphenyl; aliphatic diamines such as 1,1-
metaxylylenediamine, 1,3-propanediamine,
tetramethylenediamine, pentamethylenediamine,
25 hexamethylenediamine, heptamethylenediamine,
octamethylenediamine, nonamethylenediamine and 4,4-
diaminoheptamethylenediamine; alicyclic diamines such as
1,4-diaminocyclohexane, isophoronediamine,
tetrahydrodicyclopentadienylenediamine, hexahydro-4,7-
30 methanoindanylenedimethylenediamine, tricyclo[6.2.1.0^{2,7}]-
undecylenedimethyldiamine, 4,4'-
methylenebis(cyclohexylamine), 1,3-
bis(aminomethyl)cyclohexane, 1,4-
bis(aminomethyl)cyclohexane, 2,5-

This Sheet Has Been Replaced

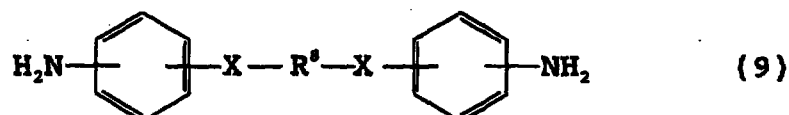




bis(aminomethyl)bicyclo[2.2.1]heptane and 2,6-bis(aminomethyl)bicyclo[2.2.1]heptane; diamines having two primary amino groups and a nitrogen atom other than the primary amino group in the molecule such as 2,3-diaminopyridine, 2,6-diaminopyridine, 3,4-diaminopyridine, 2,4-diaminopyrimidine, 5,6-diamino-2,3-dicyanopyrazine, 5,6-diamino-2,4-dihydroxypyrimidine, 2,4-diamino-6-dimethylamino-1,3,5-triazine, 1,4-bis(3-aminopropyl)piperazine, 2,4-diamino-6-isopropoxy-1,3,5-triazine, 2,4-diamino-6-methoxy-1,3,5-triazine, 2,4-diamino-6-phenyl-1,3,5-triazine, 2,4-diamino-6-methyl-s-triazine, 2,4-diamino-1,3,5-triazine, 4,6-diamino-2-vinyl-s-triazine, 2,4-diamino-5-phenylthiazole, 2,6-diaminopurine, 5,6-diamino-1,3-dimethyluracil, 3,5-diamino-1,2,4-triazole, 6,9-diamino-2-ethoxyacridinelactate, 3,8-diamino-6-phenylphenanthridine, 1,4-diaminopiperazine, 3,6-diaminoacridine, bis(4-aminophenyl)phenylamine and compounds represented by the following formulas (8) and (9):



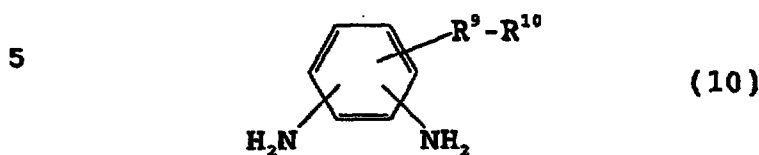
(wherein R⁷ is a monovalent organic group having a ring structure including a nitrogen atom selected from pyridine, pyrimidine, triazine, piperidine and piperazine, and X is a divalent organic group);



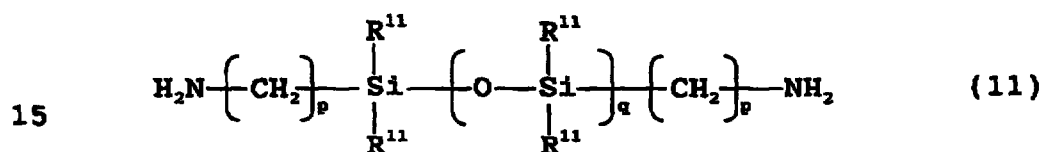
(wherein R⁸ is a divalent organic group having a ring structure including a nitrogen atom selected from pyridine, pyrimidine, triazine, piperidine and piperazine, and X is a divalent organic group, with the proviso that X's may be the same or

11

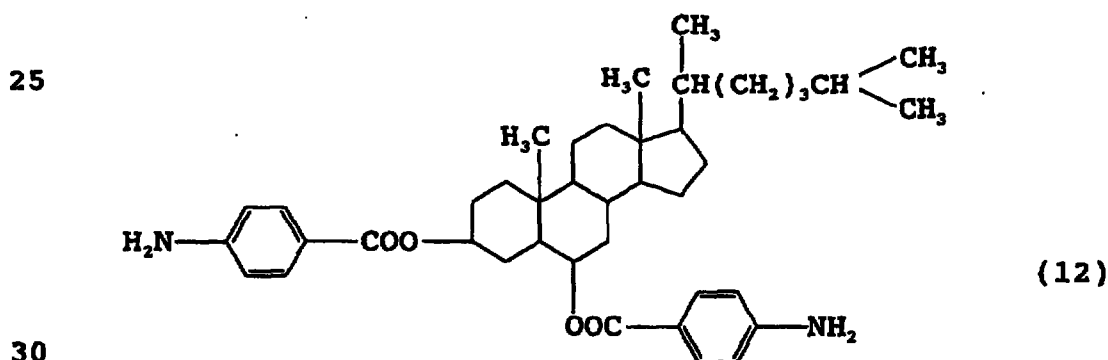
different); mono-substituted phenylene diamines represented by the following formula (10); diaminoorganosiloxanes represented by the following formula (11);



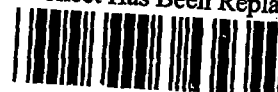
(wherein R^9 is a divalent organic group selected from -O-, -COO-, -OCO-, -NHCO-, -CONH- and -CO-, R^{10} is a monovalent organic group having a group selected from a steroid structure, trifluoromethyl group and fluoro group, or alkyl group having 6 to 30 carbon atoms)



(wherein R^{11} is a hydrocarbon group having 1 to 12 carbon atoms and R^{11} 's may be the same or different, p is an integer of 1 to 3, and q is an integer of 1 to 20),
20 and compounds represented by the following formulas (12) to (16). These diamine compounds may be used alone or in combination of two or more.



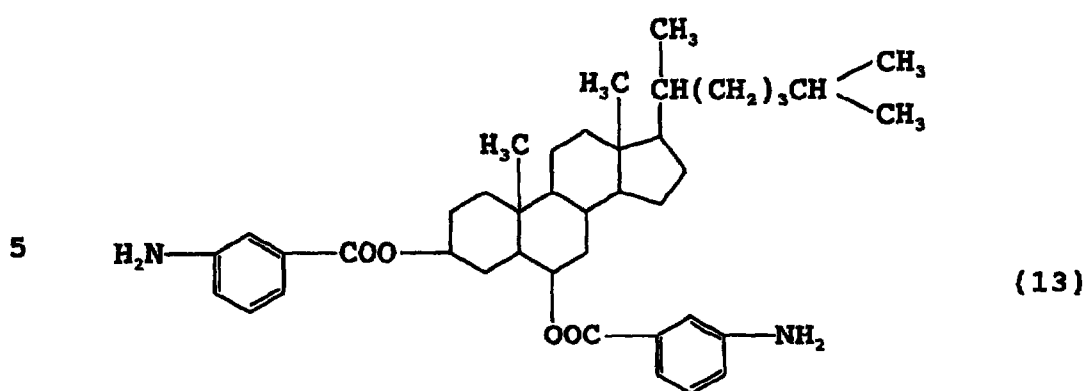
This Sheet Has Been Replaced



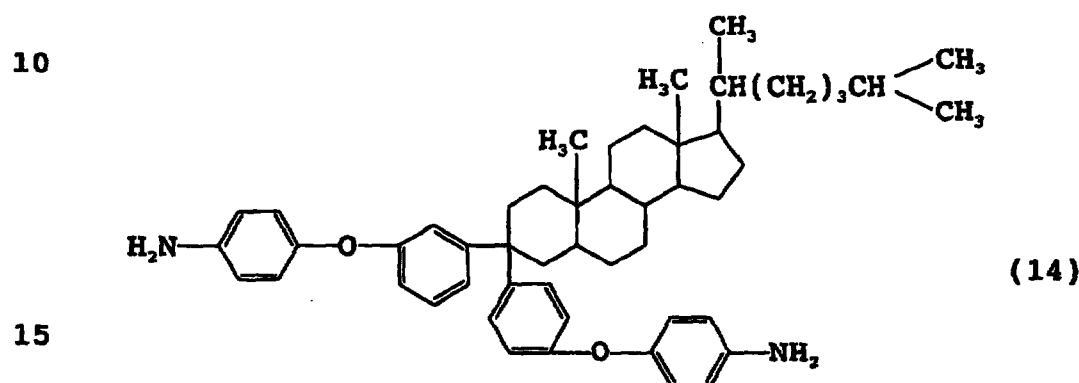
This Sheet Has Been Replaced



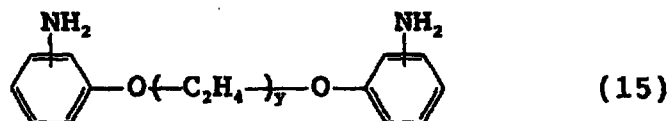
12



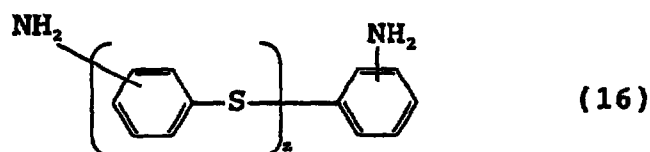
10



15



20



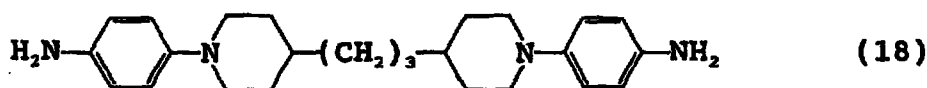
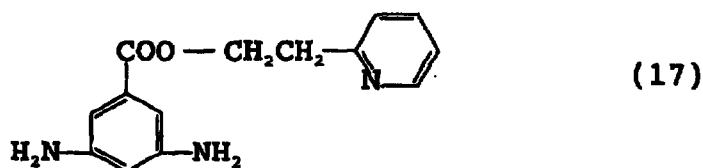
25

(wherein y is an integer of 2 to 12, and z is an integer of 1 to 5).

30

Out of these, paraphenylenediamine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylsulfide, 1,5-diaminonaphthalene, 2,7-diaminofluorene, 4,4'-diaminodiphenylether, 2,2-bis[4-(4-aminophenoxy)phenyl]propane, 9,9-bis(4-aminophenyl)fluorene, 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane, 2,2-bis(4-aminophenyl)hexafluoropropane, 4,4'-diamino-2,2'-bis(trifluoromethyl)biphenyl, 4,4'-

(paraphenylenediisopropylidene)bis(aniline, 4,4'-
 (metaphenylenediisopropylidene)bis(aniline, 1,4-
 cyclohexanediamine, 4,4'-methylenebis(cyclohexylamine),
 1,4-bis(4-aminophenoxy)benzene, 4,4'-bis(4-
 5 aminophenoxy)biphenyl, 1,3-bis(aminomethyl)cyclohexane,
 1,4-bis(aminomethyl)cyclohexane, 2,5-
 bis(aminomethyl)bicyclo[2.2.1]heptane, 2,6-
 bis(aminomethyl)bicyclo[2.2.1]heptane, compounds
 represented by the above formulas (12) to (16), 2,6-
 10 diaminopyridine, 3,4-diaminopyridine, 2,4-
 diaminopyrimidine, 3,6-diaminoacridine, compound
 represented by the following formula (17) as examples of the
 compound represented by the above formula (8), compound
 represented by the following formula (18) as examples of the
 15 compound represented by the above formula (9), and
 decanoxy-2,4-diaminobenzene, undecanoxy-2,4-
 diaminobenzene, dodecanoxy-2,4-diaminobenzene,
 pentadecanoxy-2,4-diaminobenzene, hexadecanoxy-2,4-
 diaminobenzene, octadecanoxy-2,4-diaminobenzene and
 20 compounds represented by the following formulas (19) to (24)
 as examples of the compound represented by the above formula
 (10). An alicyclic structure may be introduced into the
 end-capped polyamic acid and end-capped imidized polymer
 used in the present invention by using any one of the above
 25 alicyclic diamines.

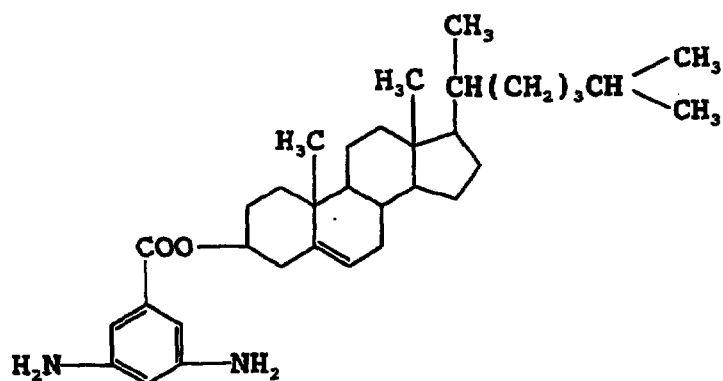


This Sheet Has Been Replaced



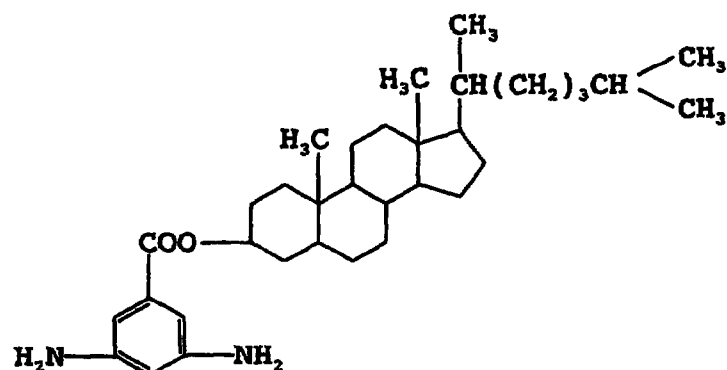
14

5



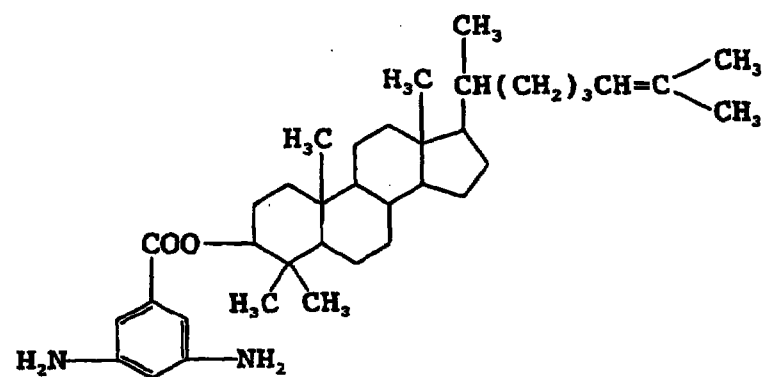
(19)

10



(20)

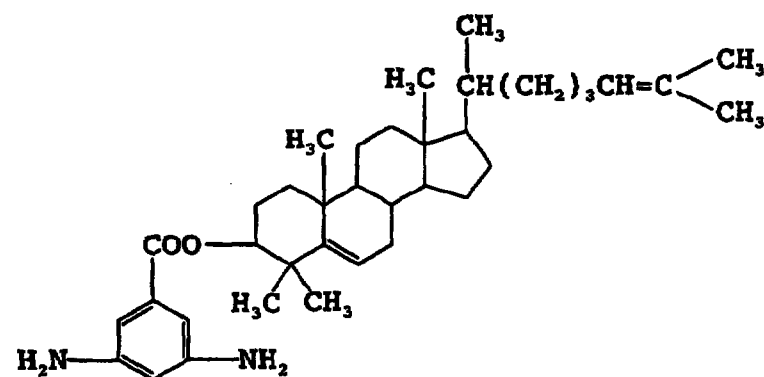
15



(21)

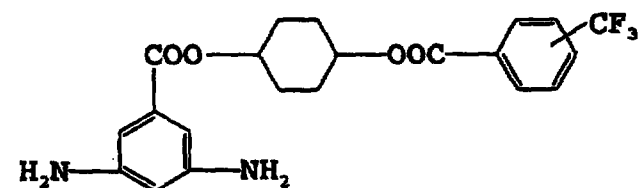
20

25



(22)

30

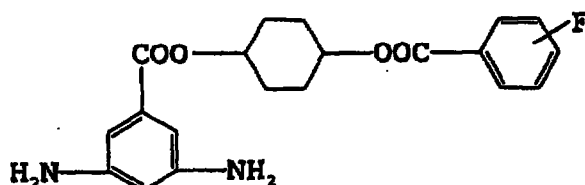


(23)

This Sheet Has Been Replaced



15



(24)

5

dicarboxylic anhydride

Examples of the dicarboxylic anhydride include maleic anhydride, phthalic anhydride, itaconic anhydride, n-decylsuccinic anhydride, n-dodecylsuccinic anhydride, n-tetradecylsuccinic anhydride and n-hexadecylsuccinic anhydride. They may be used alone or in combination of two or more.

monoamine compound

Examples of the monoamine compound include aniline and aniline derivatives such as p-trifluoromethylaniline, m-trifluoromethylaniline and bistrifluoromethylaniline; (cyclo)alkylamines such as cyclohexylamine, n-butylamine, n-pentylamine, n-hexylamine, n-heptylamine, n-octylamine, n-nonylamine, n-decylamine, n-undecylamine, n-dodecylamine, n-tridecylamine, n-tetradecylamine, n-pentadecylamine, n-hexadecylamine, n-heptadecylamine, n-octadecylamine and n-eicosylamine; and aminosilanes such as aminomethyl trimethylsilane, aminomethyl triethylsilane, aminomethyl tripropylsilane, aminoethyl trimethylsilane, aminoethyl triethylsilane, aminoethyl tripropylsilane, aminopropyl trimethylsilane, aminopropyl triethylsilane, aminopropyl tripropylsilane, aminomethyl trimethoxysilane, aminomethyl triethoxysilane, aminomethyl tripropoxysilane, aminomethyl dimethoxymethylsilane, aminomethyl methoxydimethylsilane, aminomethyl diethoxymethylsilane, aminomethyl ethoxydimethylsilane, aminomethyl dimethoxyethylsilane, aminomethyl methoxydiethylsilane, aminomethyl diethoxyethylsilane, aminoethyl dimethoxymethylsilane, aminoethyl

This Sheet Has Been Replaced



16

methoxydimethylsilane, aminoethyl diethoxymethylsilane, aminoethyl ethoxydimethylsilane, aminoethyl dimethoxyethylsilane, aminoethyl methoxydiethylsilane, aminoethyl diethoxyethylsilane, aminoethyl ethoxydiethylsilane, aminopropyl dimethoxymethylsilane, aminopropyl methoxydimethylsilane, aminopropyl diethoxymethylsilane, aminopropyl ethoxydimethylsilane, aminopropyl dimethoxyethylsilane, aminopropyl methoxydiethylsilane, aminopropyl diethoxyethylsilane, aminopropyl ethoxydiethylsilane and aminomethyl phenyldimethylsilane. Out of these, aniline and aniline derivatives such as p-trifluoromethylaniline, m-trifluoromethylaniline and bistrifluoromethylaniline; alkylamines having 10 or more carbon atoms such as n-decylamine, n-undecylamine, n-dodecylamine, n-tridecylamine, n-tetradecylamine, n-pentadecylamine, n-hexadecylamine, n-heptadecylamine, n-octadecylamine and n-eicosylamine; and aminoalkyl trialkylsilanes such as aminomethyl trimethylsilane, aminomethyl triethylsilane, aminomethyl tripropylsilane, aminoethyl trimethylsilane, aminoethyl triethylsilane, aminoethyl tripropylsilane, aminopropyl trimethylsilane, aminopropyl triethylsilane and aminopropyl tripropylsilane. They may be used alone or in combination of two or more.

25 monoisocyanate compound

Examples of the monoisocyanate compound include cyclohexyl isocyanate, n-decylisocyanate, n-undecylisocyanate, n-dodecylisocyanate, n-tridecylisocyanate, n-tetradecylisocyanate, n-pentadecylisocyanate, n-hexadecylisocyanate, n-heptadecylisocyanate, n-octadecylisocyanate, n-eicosylisocyanate, phenylisocyanate and naphthylisocyanate. They may be used alone or in combination of two or more.

polyamic acid

This Sheet Has Been Replaced



As for the ratio of the tetracarboxylic dianhydride to the diamine compound used for the synthesis reaction of the polyamic acid, the amount of the acid anhydride group of the tetracarboxylic dianhydride is preferably 0.2 to 2

5 equivalents, more preferably 0.3 to 1.2 equivalents based on 1 equivalent of an amino group contained in the diamine compound. To produce the end-capped polyamic acid, an end-capping agent such as dicarboxylic anhydride, monoamine compound or monoisocyanate compound is further used. As for

10 the amount of the dicarboxylic anhydride, monoamine compound or monoisocyanate compound, the amount of the acid anhydride group of the dicarboxylic anhydride, the amino group of the monoamine compound or the isocyanate group of the monoisocyanate compound is preferably 0.001 to 0.8

15 equivalent, more preferably 0.01 to 0.2 equivalent based on 1 equivalent of an amino group contained in the diamine compound.

The synthesis reaction of the polyamic acid is carried out in an organic solvent at a temperature of preferably 0

20 to 150°C, more preferably 0 to 100°C for 1 to 48 hours. The organic solvent is not particularly limited if it can dissolve the reaction product formed by the reaction. Examples of the organic solvent include nonprotic solvents such as N-methyl-2-pyrrolidone, N,N-dimethylacetamide, N,N-

25 dimethylformamide, dimethyl sulfoxide, γ -butyrolactone, tetramethylurea and hexamethylphosphoric triamide; and phenolic solvents such as m-cresol, xylene, phenol and phenol halide. The amount of the organic solvent is preferably such that the total amount of the tetracarboxylic

30 dianhydride and the diamine compound should be 0.1 to 40 wt% based on the total amount of the reaction solution.

The above organic solvent may be used in conjunction with a poor solvent for the polyamic acid such as an alcohol, ketone, ester, ether, hydrocarbon halide or hydrocarbon in

This Sheet Has Been Replaced



limits that the formed polyamic acid does not separate out. Examples of the poor solvent include methyl alcohol, ethyl alcohol, isopropyl alcohol, cyclohexanol, ethylene glycol, propylene glycol, 1,4-butanediol, triethylene glycol, acetone, methyl ethyl ketone, cyclohexanone, methylacetate, ethyl acetate, butyl acetate, diethyl oxalate, diethyl malonate, diethyl ether, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol monophenyl ether, ethylene glycol methylphenyl ether, ethylene glycol ethylphenyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethyl glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monomethyl ether acetate, diethylene glycol monoethyl ether acetate, ethylene glycol methyl ether acetate, ethylene glycol ethyl ether acetate, 4-hydroxy-4-methyl-2-pentanone, 2,4-pentanedione, 2,5-hexanedione, ethyl 2-hydroxypropionate, ethyl 2-hydroxy-2-methylpropionate, ethyl 2-hydroxy-2-methylpropionate, ethyl ethoxyacetate, ethyl hydroxyacetate, methyl 2-hydroxy-3-methylbutanoate, methyl 3-methoxypropionate, ethyl 3-methoxypropionate, ethyl 3-ethoxypropionate, methyl 3-ethoxypropionate, methyl pyruvate, ethyl pyruvate, hydroxymethyl pyruvate, methyl acetacetate, ethyl acetacetate, methyl methoxybutanol, ethyl methoxybutanol, methyl ethoxybutanol, ethyl ethoxybutanol, tetrahydrofuran, tetrahydrofurfuryl alcohol, tetrahydro-3-furanmethanol, 1,3-dioxolan, 1,3-dioxepane, 4-methyl-1,3-dioxolan, dichloromethane, 1,2-dichloroethane, 1,4-dichlorobutane, trichloroethane, chlorobenzene, o-dichlorobenzene, hexane, heptane, octane, benzene, toluene and xylene. They may be used alone or in combination of two or more.

The reaction solution containing the polyamic acid is obtained by the above synthesis reaction. This reaction solution is added to a large amount of a poor solvent to obtain

This Sheet Has Been Replaced



a precipitate which is then dried under reduced pressure to obtain a polyamic acid. The step of dissolving this polyamic acid in an organic solvent again and precipitating the polyamic acid by a poor solvent is repeated once or several
5 times to purify the polyamic acid.

imidized polymer

The end-capped or end-uncapped imidized polymer constituting the liquid crystal aligning agent of the present invention can be prepared by dehydrating and ring closing
10 the above polyamic acid. The dehydration and ring closure of the polyamic acid are carried out by (i) a method in which the polyamic acid is heated or (ii) a method in which the polyamic acid is dissolved in an organic solvent and a dehydrating agent and a dehydration and ring closing catalyst
15 are added to the obtained solution and heated as required. The imidized polymer used in the present invention may include a partly dehydrated and ring closed imidized polymer having an imidization ratio (ratio (%)) of the number of recurring units of an imide to the total number of the recurring units
20 of amic acid and the recurring units of an imide contained in the polymer) of less than 100 %. The imidized polymer has an imidization ratio of preferably 40 % or more, particularly preferably 80 % or more.

The reaction temperature in the method (i) in which the
25 polyamic acid is heated is preferably 50 to 200°C, more preferably 60 to 170°C. When the reaction temperature is lower than 50°C, a dehydration and ring closure reaction hardly proceeds fully and when the reaction temperature is higher than 200°C, the molecular weight of the obtained
30 imidized polymer may lower.

In the method (ii) in which a dehydrating agent and a dehydration and ring closing catalyst are added to the solution of the polyamic acid, an acid anhydride such as acetic anhydride, propionic anhydride and trifluoroacetic

This Sheet Has Been Replaced



20

anhydride is used as the dehydrating agent. The amount of the dehydrating agent is preferably 0.01 to 20 mols based on 1 mol of the recurring unit of the polyamic acid. A tertiary amine such as pyridine, collidine, lutidine or triethylamine may be used as the dehydration and ring closing catalyst. However, the dehydration and ring closing catalyst is not limited to these. The amount of the dehydration and ring closing catalyst is preferably 0.01 to 10 mols based on 1 mol of the dehydrating agent. Examples of the organic solvent used for the dehydration and ring closure reaction are the same as those enumerated for the synthesis of the polyamic acid. The temperature of the dehydration and ring closure reaction is preferably 0 to 180°C, more preferably 10 to 150°C. The same operation as for the purification of the polyamic acid is made on the obtained reaction solution to purify the imidized polymer.

logarithmic viscosity of polymer

The polymers constituting the liquid crystal aligning agent used in the present invention, namely, the end-capped or end-uncapped polyamic acid and imidized polymer have a logarithmic viscosity (η_{ln}) of preferably 0.05 to 10 dl/g, more preferably 0.05 to 4 dl/g. The value of logarithmic viscosity (η_{ln}) is obtained from the following equation (1) by measuring the viscosity of solution having a polymer content of 0.5 g/100 ml at 30°C with an N-methyl-2-pyrrolidone used as a solvent.

$$\eta_{ln} = \ln (\text{solution falling time/solvent falling time}) / (\text{concentration of polymer})$$

<liquid crystal aligning agent>

The liquid crystal aligning agent of the present invention is a solution of an end-capped polyamic acid and/or an end-capped imidized polymer dissolved in an organic solvent. The polyamic acid and/or imidized polymer used in this liquid crystal aligning agent may be each one or a

This Sheet Has Been Replaced



combination of two or more of the above examples.

The liquid crystal aligning agent of the present invention may further contain an end-uncapped polyamic acid and/or an end-uncapped imidized polymer. The proportion of the end-capped polyamic acid and/or end-capped imidized polymer to the total of the polyamic acid(s) and/or imidized polymer(s) contained in the liquid crystal aligning agent is preferably 5 to 80 wt%, more preferably 10 to 60 wt%. It is particularly preferred to use a combination of the end-capped imidized polymer and the end-uncapped polyamic acid. In this case, the end-capped imidized polymer is preferably obtained by using a monoamine compound as an end-capping agent. Examples of the organic solvent constituting the liquid crystal aligning agent are the same as those enumerated for a synthesis reaction or an dehydration and ring closure reaction of the polyamic acid. A poor solvent suitably selected from examples usable for the synthesis reaction of the polyamic acid enumerated above may also be used.

The total amount of the end-capped polymer(s) and/or the end-uncapped polymer(s) in the liquid crystal aligning agent of the present invention is selected in consideration of viscosity and volatility but it preferably 1 to 10 wt%. The liquid crystal aligning agent of the present invention is applied to the surface of a substrate to form a coating film which will become a liquid crystal alignment film. When the amount is smaller than 1 wt%, the thickness of this coating film becomes excessively small, thereby making it difficult to obtain a satisfactory liquid crystal alignment film. When the amount is larger than 10 wt%, the thickness of the coating film becomes too large, thereby making it difficult to obtain a satisfactory liquid crystal alignment film as well and the viscosity of the liquid crystal aligning agent increases with the result of deteriorated coatability.

This Sheet Has Been Replaced



The liquid crystal aligning agent of the present invention may contain a functional silane-containing compound to improve the adhesion of the polyamic acid and/or imidized polymer to the surface of the substrate. Examples of the functional silane-containing compound include 3-aminopropyl trimethoxysilane, 3-aminopropyl triethoxysilane, 2-aminopropyl trimethoxysilane, 2-aminopropyl triethoxysilane, N-(2-aminoethyl)-3-aminopropyl trimethoxysilane, N-(2-aminoethyl)-3-aminopropylmethyl dimethoxysilane, 3-ureidopropyl trimethoxysilane, 3-ureidopropyl triethoxysilane, N-ethoxycarbonyl-3-aminopropyl trimethoxysilane, N-ethoxycarbonyl-3-aminopropyl triethoxysilane, N-triethoxysilylpropyl triethylenetriamine, N-trimethoxysilylpropyl triethylenetriamine, 10-trimethoxysilyl-1,4,7-triazadecane, 10-triethoxysilyl-1,4,7-triazadecane, 9-trimethoxysilyl-3,6-diazanonylacetate, 9-triethoxysilyl-3,6-diazanonylacetate, N-benzyl-3-aminopropyl trimethoxysilane, N-benzyl-3-aminopropyl triethoxysilane, N-phenyl-3-aminopropyl trimethoxysilane, N-phenyl-3-aminopropyl triethoxysilane, N-bis(oxyethylene)-3-aminopropyl trimethoxysilane and N-bis(oxyethylene)-3-aminopropyl triethoxysilane.

The liquid crystal aligning agent of the present invention may contain an epoxy group-containing compound to further improve its adhesion to the substrate. Examples of the epoxy group-containing compound include ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, tripropylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, neopentyl glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, glycerin diglycidyl ether, 2,2-dibromoneopentyl glycol diglycidyl ether, 1,3,5,6-tetraglycidyl-2,4-hexanediol, N,N,N',N'-tetraglycidyl-m-

This Sheet Has Been Replaced



23

xylenediamine, 1,3-bis(N,N-diglycidylaminomethyl)cyclohexane, N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenylmethane, 3-(N-allyl-N-glycidyl)aminopropyl trimethoxysilane and 3-(N,N-diglycidyl)aminopropyl trimethoxysilane. Out of these, compounds having a tertiary nitrogen atom in the molecule preferable and the amount of the epoxy group-containing compound is preferably 40 parts or less by weight, more preferably 0.1 to 30 parts by weight based on 100 parts by weight of the polymer.

<liquid crystal display element>

A liquid crystal display element obtained by using the liquid crystal aligning agent of the present invention can be produced by the following method, for example.

(1) The liquid crystal aligning agent of the present invention is applied to one side of a substrate having a transparent conductive film patterned by such means as a roll coater, spinner or printing and the coated side is heated to form a coating film. As the substrate may be used a transparent substrate made from glass such as float glass or soda glass; or plastic such as polyethylene terephthalate, polybutylene terephthalate, polyether sulfone or polycarbonate. The transparent conductive film formed on one side of the substrate may be an NESA film made from tin oxide (SnO_2) (registered trademark of PPG Co., Ltd. of the US) or ITO film made from indium oxide-tin oxide (In_2O_3 - SnO_2). The patterning of the transparent conductive film is carried out by photoetching or by using a mask. To further improve the adhesion of the coating film of the liquid crystal aligning agent to the surface of the substrate and the transparent conductive film, a functional silane-containing compound or functional titanium-containing compound may be applied to the surface of the substrate in advance before the liquid crystal aligning agent applied. The heating

This Sheet Has Been Replaced



temperature is preferably 80 to 250°C, more preferably 120 to 200°C. The thickness of the formed film is preferably 0.001 to 1 μm, more preferably 0.005 to 0.5 μm. The coating film which will become a liquid crystal alignment film is
5 formed by removing the organic solvent after the application of the liquid crystal aligning agent of the present invention which comprises an end-capped and/or an end-uncapped polyamic acid(s). Further, a partly imidized or completely imidized coating film may be formed by promoting dehydration
10 and ring closure by heating.

(2) The surface of the coating film formed from the liquid crystal aligning agent is rubbed with a roll wound with fiber cloth of nylon, rayon or cotton in a predetermined direction. Thereby, aligning force for liquid crystal molecules is
15 provided to the coating film to convert it into a liquid crystal alignment film. Besides rubbing, aligning force may be provided by exposing the surface of the resin film to polarized ultraviolet radiation, ion beams or electron beams, or a liquid crystal alignment film may be formed by means
20 for obtaining a coating film, such as uniaxial stretching or Langmuir-Blodgett technique. To remove fine powders (foreign matter) formed at the time of rubbing so as to keep clean the surface, the formed liquid crystal alignment film is preferably washed with isopropyl alcohol. The view angle
25 characteristics of the formed liquid crystal display element can be improved by carrying out a treatment for changing the pretilt angle by partly exposing the surface of the formed liquid crystal alignment film to ultraviolet radiation, ion beams or electron beams (JP-A 6-222366, JP-A 6-281937, JP-A
30 7-168187 and JP-A 8-234207) or treatment that a resist film is partly formed on the surface of the formed liquid crystal alignment film, the liquid crystal alignment film is rubbed in a direction different from that of the previous rubbing, the resist film is removed and the aligning force of the liquid

This Sheet Has Been Replaced



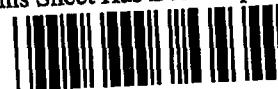
crystal alignment film is changed (JP-A 5-107544).

(3) Two substrates each having the liquid crystal alignment film formed as described above are prepared and opposed to each other with a cell gap therebetween so that the aligning
5 directions, that is, rubbing directions of their liquid crystal alignment films become perpendicular or parallel to each other in opposite directions, the peripheral portions of the two substrates are bonded together by a sealing agent, liquid crystals are injected and filled into the cell gap
10 defined by the surfaces of the substrates and the sealing agent, and an injection hole is sealed up to form a liquid crystal cell. A polarizing plate is bonded to the exterior surfaces of the liquid crystal cell, that is, the other sides of the substrates forming the liquid crystal cell such that
15 its polarizing direction becomes the same or perpendicular to the rubbing direction of the liquid crystal alignment films formed on one sides of the substrates to obtain a liquid crystal display element.

As the sealing agent may be used an epoxy resin
20 containing aluminum oxide balls as a curing agent and spacer.

The liquid crystal may be nematic liquid crystal or smectic liquid crystal. Out of these, nematic liquid crystal is preferred, as exemplified by Schiff base liquid crystal, azoxy-based liquid crystal, biphenyl-based liquid crystal,
25 phenylcyclohexane-based liquid crystal, ester-based liquid crystal, terphenyl-based liquid crystal, biphenylcyclohexane-based liquid crystal, pyrimidine-based liquid crystal, dioxane-based liquid crystal, bicyclooctane-based liquid crystal and cumene-based liquid
30 crystal. A cholesteric liquid crystal such as cholesteryl chloride, cholesteryl nonanoate or cholesteryl carbonate, or a chiral agent marketed under the trade name of C-15 or CB-15 (of Merck Co., Ltd.) may be added to the above liquid crystal. Further, ferroelectric liquid crystal such as

This Sheet Has Been Replaced



p-decyloxybenzylidene-p-amino-2-methylbutyl cinnamate may also be used.

The polarizer used on the exterior side of the liquid crystal cell is a polarizer produced by interposing between
5 cellulose acetate protective films a polarizing film having iodine adsorbed, which is called H film, while stretching and orienting a polyvinyl alcohol, or a polarizer composed of the H film itself.

10 Examples

The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting.

The measurement of the pretilt angle in the examples
15 was carried out in accordance with the method described in "T.J. Schffer, et al., J. Appl. Phys., 19, 2013, (1980)" by a crystal rotation method using He-Ne laser light.

In the following examples and comparative examples, the after image erase time and liquid crystal alignment
20 properties of the liquid crystal display element were evaluated as follows.

(after image erase time)

After a DC voltage of 10 V was applied to a liquid crystal cell for 1 hour, the application of the voltage was released,
25 the displayed image was observed visually and the time elapsed from the release of the application of voltage to the erasure of an after image on the screen was measured.

(liquid crystal alignment properties)

The existence of an abnormal domain when voltage was
30 turned on and off (application and release) was checked through a polarization microscope. When the abnormal domain was not observed, liquid crystal alignment properties were judged as satisfactory.

(reliability test of liquid crystal display element)

This Sheet Has Been Replaced



The liquid crystal display element was driven by 5V and 60 Hz rectangular waves in a high-temperature and high-humidity environment (temperature of 70°C, relative humidity of 80 %) and the existence of a white stain-like display defect was checked through a polarization microscope after the passage of 1,500 hours.

Synthesis Example 1

32.84 g (146.48 mmol) of 2,3,5-tricarboxycyclopentylacetic dianhydride, 15.37 g (142.09 mmol) of paraphenylenediamine, 1.53 g (2.93 mmol) of cholesteryl-3,5-diaminobenzoate (compound represented by the above formula (19)) and 0.27 g (2.93 mmol) of aniline were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 45.42 g of a polyamic acid (to be designated as "polyamic acid (1)") having a logarithmic viscosity of 1.18 dl/g.

40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 46.35 g of pyridine and 35.89 g of acetic anhydride were added and heated at 110°C for 4 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 36.4 g of polyimide (to be designated as "polyimide (1)") having a logarithmic viscosity of 1.05 dl/g.

Synthesis Example 2

32.92 g (146.85 mmol) of 2,3,5-tricarboxycyclopentylacetic dianhydride, 15.40 g (142.41 mmol) of paraphenylenediamine, 1.24 g (2.94 mmol) of 4-(4'-trifluoromethylbenzoyloxy)cyclohexyl-3,5-

This Sheet Has Been Replaced



28

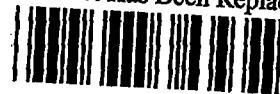
diaminobenzoate (compound represented by the above formula (23)) and 0.44 g (2.94 mmol) of phthalic anhydride were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 45.22 g of a polyamic acid (to be designated as "polyamic acid (2)") having a logarithmic viscosity of 1.10 dl/g.

40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 46.46 g of pyridine and 35.98 g of acetic anhydride were added and heated at 110°C for 4 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 36.1 g of polyimide (to be designated as "polyimide (2)") having a logarithmic viscosity of 1.01 dl/g.

Synthesis Example 3

31.14 g (138.3 mmol) of 2,3,5-tricarboxycyclopentylacetic dianhydride, 11.57 g (106.98 mmol) of paraphenylenediamine, 5.51 g (27.79 mmol) of diaminodiphenylmethane, 1.45 g (2.78 mmol) of cholesteryl-3,5-diaminobenzoate (compound represented by the above formula (19)) and 0.33 g (2.78 mmol) of phenylisocyanate were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 44.28 g of a polyamic acid (to be designated as "polyamic acid (3)") having a

This Sheet Has Been Replaced



logarithmic viscosity of 0.90 dl/g.

40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 43.96 g of pyridine and 34.04 g of acetic anhydride were added and heated at 110° C for 4 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 36.06 g of polyimide (to be designated as "polyimide (3)") having a logarithmic viscosity of 0.88 dl/g.

10 Synthesis Example 4

36.05 g (114.70 mmol) of 1,3,3a,4,5,9b-hexahydro-8-methyl-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]furan-1,3-dione, 11.78 g (108.96 mmol) of paraphenylenediamine, 1.94 g (4.59 mmol) of 4-(4'-trifluoromethylbenzoyloxy)cyclohexyl-3,5-diaminobenzoate (compound represented by the above formula (23)) and 0.23 g (2.29 mmol) of cyclohexylamine were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40° C under reduced pressure for 15 hours to obtain 45.78 g of a polyamic acid (to be designated as "polyamic acid (4)") having a logarithmic viscosity of 0.92 dl/g.

40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 29.03 g of pyridine and 65.58 g of acetic anhydride were added and heated at 80° C for 4 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 35.66 g of polyimide (to be designated as "polyimide (4)") having a logarithmic viscosity of 0.85 dl/g.

Synthesis Example 5

This Sheet Has Been Replaced



30

33.96 g (108.05 mmol) of 1,3,3a,4,5,9b-hexahydro-8-methyl-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]furan-1,3-dione, 8.76 g (81.04 mmol) of paraphenylenediamine, 4.28 g (21.61 mmol) of diaminodiphenylmethane, 2.78 g (4.32 mmol) of 3,6-bis(4-aminobenzoyloxy)cholestane (compound represented by the above formula (12)) and 0.21 g (2.16 mmol) of maleic anhydride were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 43.71 g of a polyamic acid (to be designated as "polyamic acid (5)") having a logarithmic viscosity of 0.90 dl/g.

40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 27.35 g of pyridine and 61.77 g of acetic anhydride were added and heated at 80°C for 4 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 34.39 g of polyimide (to be designated as "polyimide (5)") having a logarithmic viscosity of 0.83 dl/g.

25 Synthesis Example 6

31.38 g (99.83 mmol) of 1,3,3a,4,5,9b-hexahydro-8-methyl-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]furan-1,3-dione, 8.10 g (74.87 mmol) of paraphenylenediamine, 8.20 g (19.97 mmol) of 2,2-bis(4-aminophenoxyphenyl)propane, 2.08 g (3.99 mmol) of cholesteryl-3,5-diaminobenzoate (compound represented by the above formula (19)) and 0.25 g (2.00 mmol) of cyclohexylisocyanate were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry

This Sheet Has Been Replaced



31

out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried
5 at 40°C under reduced pressure for 15 hours to obtain 43.96 g of a polyamic acid (to be designated as "polyamic acid (6)") having a logarithmic viscosity of 0.91 dl/g.

40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 25.27 g of pyridine and 57.07 g
10 of acetic anhydride were added and heated at 80°C for 4 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 34.67 g of polyimide (to be designated as "polyimide
15 (6)") having a logarithmic viscosity of 0.84 dl/g.

Synthesis Example 7

18.07 g (57.50 mmol) of 1,3,3a,4,5,9b-hexahydro-8-methyl-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]furan-1,3-dione, 12.89 g (57.50 mmol) of 2,3,5-
20 tricarboxylcyclopentylacetic dianhydride, 9.58 g (88.55 mmol) of paraphenylenediamine, 7.37 g (23.00 mmol) of 4,4'-diamino-2,2'-bis(trifluoromethyl)biphenyl, 1.48 g (2.30 mmol) of 3,6-bis(4-aminobenzoyloxy)cholestane and 0.62 g (2.3 mmol) of stearylamine were dissolved in 450 g
25 of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried
30 at 40°C under reduced pressure for 15 hours to obtain 44.42 g of a polyamic acid (to be designated as "polyamic acid (7)") having a logarithmic viscosity of 0.98 dl/g.

40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 29.11 g of pyridine and 37.57 g

This Sheet Has Been Replaced



32

of acetic anhydride were added and heated at 110° C for 4 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 36.82 g of polyimide (to be designated as "polyimide (7)") having a logarithmic viscosity of 0.96 dl/g.

Synthesis Example 8

31.63 g (100.64 mmol) of 1,3,3a,4,5,9b-hexahydro-8-methyl-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]furan-1,3-dione, 1.19 g (5.30 mmol) of 2,3,5-tricarboxylcyclopentylacetic dianhydride, 8.82 g (81.56 mmol) of paraphenylenediamine, 6.78 g (21.19 mmol) of 4,4'-diamino-2,2'-bis(trifluoromethyl)biphenyl, 1.36 g (2.12 mmol) of 3,6-bis(4-aminobenzoyloxy)cholestane (compound represented by the above formula (12)) and 0.22 g (2.12 mmol) of aminomethyltrimethylsilane were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40° C under reduced pressure for 15 hours to obtain 43.63 g of a polyamic acid (to be designated as "polyamic acid (8)") having a logarithmic viscosity of 0.92 dl/g.

40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 26.81 g of pyridine and 34.60 g of acetic anhydride were added and heated at 80° C for 4 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 34.81 g of polyimide (to be designated as "polyimide (8)") having a logarithmic viscosity of 0.91 dl/g.

Synthesis Example 9

This Sheet Has Been Replaced



28.56 g (90.86 mmol) of 1,3,3a,4,5,9b-hexahydro-8-methyl-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]furan-1,3-dione, 3.64 g (16.22 mmol) of 2,3,5-tricarboxylcyclopentylacetic dianhydride, 9.12 g (84.37 mmol) of paraphenylenediamine, 7.23 g (21.63 mmol) of 2,2-bis(4-aminophenyl)-1,1,1,3,3,3-hexafluoropropane, 1.13 g (2.16 mmol) of cholesteryl-3,5-diaminobenzoate (compound represented by the above formula (20)) and 0.32 g (2.16 mmol) of phthalic anhydride were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40° C under reduced pressure for 15 hours to obtain 44.23 g of a polyamic acid (to be designated as "polyamic acid (9)") having a logarithmic viscosity of 0.92 dl/g.

40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 27.65 g of pyridine and 35.69 g of acetic anhydride were added and heated at 80° C for 4 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 35.19 g of polyimide (to be designated as "polyimide (9)") having a logarithmic viscosity of 0.89 dl/g.

Synthesis Example 10

24.71 g (78.61 mmol) of 1,3,3a,4,5,9b-hexahydro-8-methyl-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]furan-1,3-dione, 7.55 g (33.69 mmol) of 2,3,5-tricarboxylcyclopentylacetic dianhydride, 10.32 g (95.43 mmol) of paraphenylenediamine, 4.86 g (11.23 mmol) of bis[4-(4-aminophenoxy)phenyl]sulfone, 1.90 g (4.49 mmol) of 4-(4'-trifluoromethylbenzoyloxy)cyclohexyl-3,5-

This Sheet Has Been Replaced



diaminobenzoate (compound represented by the above formula (23)) and 0.66 g (2.25 mmol) of octadecylisocyanate were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 44.68 g of a polyamic acid (to be designated as "polyamic acid (10)") having a logarithmic viscosity of 0.94 dl/g.

40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 28.43 g of pyridine and 36.69 g of acetic anhydride were added and heated at 80°C for 4 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 36.02 g of polyimide (to be designated as "polyimide (10)") having a logarithmic viscosity of 0.92 dl/g.

Synthesis Example 11

28.62 g (95.31 mmol) of 1,3,3a,4,5,9b-hexahydro-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]furan-1,3-dione, 6.25 g (23.83 mmol) of 3,5,6-tricarboxynorbornane-2-acetic dianhydride, 11.98 g (110.79 mmol) of paraphenylenediamine, 2.24 g (5.96 mmol) of octadecanoxy-2,4-diaminobenzene and 0.91 g (4.77 mmol) of 3-aminopropylmethyl diethoxysilane were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 44.25 g of a polyamic acid (to be designated as "polyamic acid (11)")

This Sheet Has Been Replaced



having a logarithmic viscosity of 0.91 dl/g.

40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 15.08 g of pyridine and 19.46 g of acetic anhydride were added and heated at 60°C for 3 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 35.81 g of polyimide (to be designated as "polyimide (11)") having a logarithmic viscosity of 0.88 dl/g.

10 Synthesis Example 12

34.06 g (113.45 mmol) of 1,3,3a,4,5,9b-hexahydro-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]furan-1,3-dione, 10.80 g (99.80 mmol) of paraphenylenediamine, 4.27 g (11.34 mmol) of octadecanoxo-2,4-diaminobenzene and 15 0.87 g (4.54 mmol) of 3-aminopropylmethyl diethoxysilane were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 44.25 g of a polyamic acid (to be designated as "polyamic acid (12)") having a logarithmic viscosity of 0.91 dl/g.

25 40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 14.36 g of pyridine and 18.53 g of acetic anhydride were added and heated at 60°C for 3 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 35.81 g of polyimide (to be designated as "polyimide (12)") having a logarithmic viscosity of 0.88 dl/g.

30 Synthesis Example 13

34.06 g (126.79 mmol) of 3,5,6-

This Sheet Has Been Replaced



36

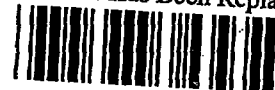
tricarboxynorbornane-2-acetic dianhydride, 12.34 g (114.11 mmol) of paraphenylenediamine, 3.82 g (10.14 mmol) of octadecanoxo-2,4-diaminobenzene and 0.59 g (5.07 mmol) of 3-aminomethylethyl dimethylsilane were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 43.94 g of a polyamic acid (to be designated as "polyamic acid (13)") having a logarithmic viscosity of 0.90 dl/g.

40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 32.11 g of pyridine and 41.41 g of acetic anhydride were added and heated at 110°C for 4 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 35.41 g of polyimide (to be designated as "polyimide (13)") having a logarithmic viscosity of 0.86 dl/g.

Synthesis Example 14

34.29 g (130.77 mmol) of 3,5,6-tricarboxynorbornane-2-acetic dianhydride, 13.71 g (126.84 mmol) of paraphenylenediamine, 1.36 g (2.62 mmol) of cholesteryl-3,5-diaminobenzoate (compound represented by the above formula (19)) and 0.63 g (2.62 mmol) of hexadecylamine were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 44.84 g of a polyamic acid (to be designated as "polyamic acid (14)") having a

This Sheet Has Been Replaced



37

logarithmic viscosity of 0.95 dl/g.

40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 33.10 g of pyridine and 42.72 g of acetic anhydride were added and heated at 110°C for 4 hours to carry out a dehydration and ring closure reaction.

Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 35.88 g of polyimide (to be designated as "polyimide (14)") having a logarithmic viscosity of 0.92 dl/g.

10 Synthesis Example 15

31.62 g (120.59 mmol) of 3,5,6-tricarboxynorbornane-2-acetic dianhydride, 9.05 g (83.67 mmol) of paraphenylenediamine, 1.28 g (2.46 mmol) of cholesteryl-3,5-diaminobenzoate (compound represented by the above formula (19)) and 0.73 g (4.92 mmol) of phthalic anhydride were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 43.73 g of a polyamic acid (to be designated as "polyamic acid (15)") having a logarithmic viscosity of 0.78 dl/g.

25 40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 15.88 g of pyridine and 20.50 g of acetic anhydride were added and heated at 110°C for 4 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 34.24 g of polyimide (to be designated as "polyimide (15)") having a logarithmic viscosity of 0.74 dl/g.

Synthesis Example 16

33.51 g (149.47 mmol) of 2,3,5-

This Sheet Has Been Replaced.



tricarboxycyclopentylacetic dianhydride and 16.49 g (149.47 mmol) of paraphenylenediamine were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 46.83 g of a polyamic acid (to be designated as "polyamic acid (16)") having a logarithmic viscosity of 1.31 dl/g.

Synthesis Example 17

16.84 g (75.12 mmol) of 2,3,5-tricarboxycyclopentylacetic dianhydride and 33.16 g (75.12 mmol) of bis[4-(4-aminophenoxy)phenyl]sulfone were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 46.23 g of a polyamic acid (to be designated as "polyamic acid (17)") having a logarithmic viscosity of 1.24 dl/g.

Synthesis Example 18

17.43 g (77.75 mmol) of 2,3,5-tricarboxycyclopentylacetic dianhydride and 32.57 g (79.34 mmol) of 2,2-bis[4-(4-aminophenoxy)phenyl]propane were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 46.33 g of a polyamic acid (to be

This Sheet Has Been Replaced



designated as "polyamic acid (18)") having a logarithmic viscosity of 1.34 dl/g.

40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 24.60 g of pyridine and 25.40 g of acetic anhydride were added and heated at 110° C for 4 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 37.24 g of polyimide (to be designated as "polyimide (18)") having a logarithmic viscosity of 0.94 dl/g.

Synthesis Example 19

33.20 g (152.21 mmol) of pyromellitic dianhydride and 16.80 g (152.21 mmol) of paraphenylenediamine were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40° C under reduced pressure for 15 hours to obtain 47.26 g of a polyamic acid (to be designated as "polyamic acid (19)") having a logarithmic viscosity of 1.46 dl/g.

Synthesis Example 20

13.25 g (60.76 mmol) of pyromellitic dianhydride, 11.92 g (60.76 mmol) of 1,2,3,4-cyclobutanetetracarboxylic dianhydride and 24.83 g (124.00 mmol) of diaminodiphenyl ether were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40° C under reduced pressure for 15 hours to obtain 46.37 g of a polyamic acid (to be designated as "polyamic acid (20)") having a

This Sheet Has Been Replaced



40

logarithmic viscosity of 1.36 dl/g.

Synthesis Example 21

13.32 g (61.06 mmol) of pyromellitic dianhydride, 11.98 g (61.06 mmol) of 1,2,3,4-cyclobutanetetracarboxylic dianhydride and 24.71 g (124.61 mmol) of diaminodiphenylmethane were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 46.37 g of a polyamic acid (to be designated as "polyamic acid (21)") having a logarithmic viscosity of 1.35 dl/g.

15 Synthesis Example 22

37.01 g (117.74 mmol) of 1,3,3a,4,5,9b-hexahydro-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]furan-1,3-dione and 12.99 g (120.15 mmol) of paraphenylenediamine were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 45.77 g of a polyamic acid (to be designated as "polyamic acid (22)") having a logarithmic viscosity of 1.31 dl/g.

Synthesis Example 23

30.42 g (96.78 mmol) of 1,3,3a,4,5,9b-hexahydro-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]furan-1,3-dione and 19.58 g (98.76 mmol) of diaminodiphenylmethane were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured

This Sheet Has Been Replaced



41

into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 45.96 g of a polyamic acid (to be designated as "polyamic acid (23)") having a logarithmic viscosity of 1.30 dl/g.

40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 24.40 g of pyridine and 55.12 g of acetic anhydride were added and heated at 80°C for 4 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 36.62 g of polyimide (to be designated as "polyimide (23)") having a logarithmic viscosity of 0.98 dl/g.

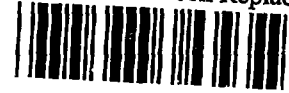
15 Synthesis Example 24

36.36 g (123.59 mmol) of 3,3',4,4'-biphenyltetracarboxylic dianhydride and 13.64 g (126.11 mmol) of paraphenylenediamine were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 45.16 g of a polyamic acid (to be designated as "polyamic acid (24)") having a logarithmic viscosity of 1.22 dl/g.

Synthesis Example 25

28.81 g (64.85 mmol) of 4,4'-(hexafluoroisopropylidene)diphthalic dianhydride and 21.19 g (66.17 mmol) of 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol

This Sheet Has Been Replaced



to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 44.27 g of a polyamic acid (to be designated as "polyamic acid (25)") having a logarithmic viscosity of 1.20 dl/g.

Synthesis Example 26

26.16 g (116.69 mmol) of 1,2,4,5-cyclohexanetetracarboxylic dianhydride and 23.84 g (119.07 mmol) of diaminodiphenyl ether were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 44.18 g of a polyamic acid (to be designated as "polyamic acid (26)") having a logarithmic viscosity of 1.25 dl/g.

Synthesis Example 27

13.52 g (60.32 mmol) of 1,2,4,5-cyclohexanetetracarboxylic dianhydride, 11.83 g (60.32 mmol) of 1,2,3,4-cyclobutanetetracarboxylic dianhydride and 24.65 g (123.10 mmol) of diaminodiphenyl ether were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 44.49 g of a polyamic acid (to be designated as "polyamic acid (27)") having a logarithmic viscosity of 1.26 dl/g.

Synthesis Example 28

35.19 g (134.20 mmol) of 3,5,6-tricarboxynorbornane-2-acetic dianhydride and 14.81 g

This Sheet Has Been Replaced



43

(136.94 mmol) of paraphenylenediamine were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours.

Thereafter, the reaction solution was poured into an

5 excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40° C under reduced pressure for 15 hours to obtain 45.72 g of a polyamic acid (to be designated as "polyamic acid (28)") having a logarithmic viscosity of 1.26
10 dl/g.

Synthesis Example 29

18.07 g (57.50 mmol) of 1,3,3a,4,5,9b-hexahydro-8-methyl-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]furan-1,3-dione, 12.89 g (57.50 mmol) of 2,3,5-
15 tricarboxycyclopentylacetic dianhydride, 9.58 g (88.55 mmol) of paraphenylenediamine, 7.37 g (23.00 mmol) of 4,4'-diamino-2,2'-bis(trifluoromethyl)biphenyl, 1.48 g (2.30 mmol) of 3,6-bis(4-aminobenzoyloxy)cholestane and 0.37 g (2.3 mmol) of p-trifluoromethylaniline were dissolved
20 in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl
25 alcohol and dried at 40° C under reduced pressure for 15 hours to obtain 44 g of a polyamic acid (to be designated as "polyamic acid (29)") having a logarithmic viscosity of 0.90 dl/g.

40 g of the obtained polyamic acid was dissolved in 360
30 g of N-methylpyrrolidone, 29.11 g of pyridine and 37.57 g of acetic anhydride were added and heated at 110° C for 4 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to

This Sheet Has Been Replaced



44

obtain 37.0 g of a polyimide (to be designated as "polyimide (29)" having a logarithmic viscosity of 0.91 dl/g.

Synthesis Example 30

20.81 g (92.83 mmol) of 3,5,6-tricarboxynorbornane-
5 2-acetic dianhydride, 5.0 g (46.4 mmol) of
paraphenylenediamine, 24.17 g (46.4 mmol) of
cholesteryl-3,5-diaminobenzoate (compound represented by
the above formula (19)), and 0.91 g (9.28 mmol) of maleic
anhydride were dissolved in 205 g of N-methyl-2-pyrrolidone
10 in a 500 ml separable flask to carry out a reaction at room
temperature for 6 hours. Thereafter, the reaction solution
was poured into an excessive amount of methyl alcohol to
precipitate a reaction product. The reaction product was
then washed with methyl alcohol and dried at 40°C under
15 reduced pressure for 15 hours to obtain 43.73 g of a polyamic
acid (to be designated as "polyamic acid (30)") having a
logarithmic viscosity of 0.48 dl/g.

Comparative Synthesis Example 1

32.91 g (146.82 mmol) of 2,3,5-
20 tricarboxycyclopentylacetic dianhydride, 15.56 g (143.88
mmol) of paraphenylenediamine and 1.53 g (2.94 mmol) of
cholesteryl-3,5-diaminobenzoate (compound represented by
the above formula (19)) were dissolved in 450 g of N-
methyl-2-pyrrolidone in a 500 ml separable flask to carry
25 out a reaction at room temperature for 6 hours. Thereafter,
the reaction solution was poured into an excessive amount
of methyl alcohol to precipitate a reaction product. The
reaction product was then washed with methyl alcohol and dried
at 40°C under reduced pressure for 15 hours to obtain 45.52
30 g of a polyamic acid (to be designated as "polyamic acid (A)")
having a logarithmic viscosity of 1.21 dl/g.

40 g of the obtained polyamic acid was dissolved in 360
g of N-methylpyrrolidone, 46.45 g of pyridine and 35.97 g
of acetic anhydride were added and heated at 110°C for 4 hours

This Sheet Has Been Replaced



to carry out a dehydration and ring closure reaction.

Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 36.5 g of polyimide (to be designated as "polyimide (A)") having a logarithmic viscosity of 1.08 dl/g.

Comparative Synthesis Example 2

35.87 g (114.12 mmol) of 1,3,3a,4,5,9b-hexahydro-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]furan-1,3-dione, 11.72 g (108.41 mmol) of paraphenylenediamine and 2.41 g (5.71 mmol) of 4-(4'-trifluoromethylbenzoyloxy)cyclohexyl-3,5-diaminobenzoate (compound represented by the above formula (23)) were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 44.58 g of a polyamic acid (to be designated as "polyamic acid (B)") having a logarithmic viscosity of 1.01 dl/g.

40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 28.88 g of pyridine and 65.24 g of acetic anhydride were added and heated at 80°C for 4 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 36.19 g of polyimide (to be designated as "polyimide (B)") having a logarithmic viscosity of 0.98 dl/g.

Comparative Synthesis Example 3

33.19 g (105.59 mmol) of 1,3,3a,4,5,9b-hexahydro-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]furan-1,3-dione, 1.25 g (5.56 mmol) of 2,3,5-tricarboxycyclopentylacetic dianhydride, 10.58 g (97.81

This Sheet Has Been Replaced



46

mmol) of paraphenylenediamine, 3.56 g (11.12 mmol) of 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl and 1.43 g (2.22 mmol) of 3,6-bis(4-aminobenzoyloxy)cholestane (compound represented by the above formula (12)) were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 44.29 g of a polyamic acid (to be designated as "polyamic acid (C)") having a logarithmic viscosity of 0.91 dl/g.

40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 28.13 g of pyridine and 36.31 g of acetic anhydride were added and heated at 80°C for 4 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 35.79 g of polyimide (to be designated as "polyimide (C)") having a logarithmic viscosity of 0.89 dl/g.

Comparative Synthesis Example 4

34.63 g (132.06 mmol) of 3,5,6-tricarboxynorbornane-2-acetic dianhydride, 14.00 g (129.42 mmol) of paraphenylenediamine and 1.38 g (2.64 mmol) of cholesteryl-3,5-diaminobenzoate (compound represented by the above formula (19)) were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 45.23 g of a polyamic acid (to be designated as "polyamic acid (D)")

This Sheet Has Been Replaced



having a logarithmic viscosity of 0.95 dl/g.

40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 41.78 g of pyridine and 43.14 g of acetic anhydride were added and heated at 110°C for 4 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 35.86 g of polyimide (to be designated as "polyimide (D)" having a logarithmic viscosity of 0.92 dl/g.

10 Comparative Synthesis Example 5

29.00 g (96.57 mmol) of 1,3,3a,4,5,9b-hexahydro-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-c]furan-1,3-dione, 6.33 g (24.14 mmol) of 3,5,6-tricarboxynorbornane-2-acetic dianhydride, 12.40 g (114.67 mmol) of paraphenylenediamine and 2.27 g (6.04 mmol) of octadecanoxy-2,4-diaminobenzene were dissolved in 450 g of N-methyl-2-pyrrolidone in a 500 ml separable flask to carry out a reaction at room temperature for 6 hours. Thereafter, the reaction solution was poured into an excessive amount of methyl alcohol to precipitate a reaction product. The reaction product was then washed with methyl alcohol and dried at 40°C under reduced pressure for 15 hours to obtain 44.25 g of a polyamic acid (to be designated as "polyamic acid (E)") having a logarithmic viscosity of 0.91 dl/g.

40 g of the obtained polyamic acid was dissolved in 360 g of N-methylpyrrolidone, 15.28 g of pyridine and 19.72 g of acetic anhydride were added and heated at 60°C for 3 hours to carry out a dehydration and ring closure reaction. Thereafter, the reaction product was precipitated and dried in the same manner as the synthesis of the polyamic acid to obtain 35.81 g of polyimide (to be designated as "polyimide (E)" having a logarithmic viscosity of 0.88 dl/g.

Example 1

(1) preparation of liquid crystal aligning agent:



The polyimide (1) (end-capped) obtained in Synthesis Example 1 and the polyamic acid (16) (end-uncapped) obtained in Synthesis Example 16 were dissolved in γ -butyrolactone in a weight ratio of 1:3 to prepare a solution having a solid content of 4 wt% which was then filtered with a filter having a pore diameter of 1 μ m to prepare the light crystal aligning agent of the present invention.

(2) preparation of liquid crystal display element:

(1) The liquid crystal aligning agent of the present invention prepared as described above was applied to a transparent conductive film which comprises an ITO film formed on one side of a 1 mm thick glass substrate with a spinner and dried at 180°C for 1 hour to form a coating film having a dry thickness of 600 Å.

(2) The formed coating film was rubbed with a rubbing machine having a roll wound with nylon cloth to form a liquid crystal alignment film. The rubbing conditions include a roll revolution speed of 500 rpm and a stage moving speed of 1 cm/sec.

(3) Two substrates each having the above liquid crystal alignment film formed thereon were prepared, an epoxy resin adhesive containing aluminum oxide balls having a diameter of 17 μ m was applied to the peripheral edge portion of each of the substrates by screen printing, the two substrates were opposed to each other with a space therebetween so that the rubbing directions of the liquid crystal alignment films thereof became parallel to each other in opposite directions, the peripheral edge portions of the two substrates were contacted and bonded together by pressure, and the adhesive was cured.

(4) A nematic liquid crystal "MLC-5081" (of Merck Co., Ltd.) was injected and filled into a cell gap defined by the surfaces of the substrates and the adhesive of the peripheral edge portions and then an injection hole was sealed up by

an epoxy-based adhesive to prepare a liquid crystal cell. Thereafter, a polarizing plate was joined to the exterior surfaces of the liquid crystal cell such that the polarization direction matches the rubbing direction of the liquid crystal alignment film formed on one side of the substrate to prepare a liquid crystal display element.

(5) When voltage was applied to or released from the liquid crystal cell, an abnormal domain was not observed and the thus formed liquid crystal display element was satisfactory in terms of liquid crystal alignment properties. When the pretilt angle was measured, it was 4.8° . The after image erase time of the liquid crystal display element was very short at 0.72 second. When the pretilt angle was measured by changing the rubbing conditions to a roll revolution speed of 200 to 800 rpm and a stage moving speed of 0.5 to 5 cm/sec., process condition stability was excellent with a variation of $4.8 \pm 0.3^\circ$. When the alignment properties and reliability test result of the obtained liquid crystal display element were evaluated, the liquid crystal alignment properties were satisfactory, and a white smear was not observed on the liquid crystal display element after the reliability test. The results are shown in Table 1.

Examples 2 to 91

Liquid crystal aligning agents were prepared in the same manner as in Example 1 except that the polyimides and polyamic acids obtained in Synthesis Examples 2 to 29 were used in ratios shown in Tables 1 to 3 to fabricate liquid crystal display elements. The liquid crystal alignment properties, pretilt angles and the after image erase times of the obtained liquid crystal display elements were measured and a reliability test was made on these liquid crystal display elements. The results are shown in Tables 1 to 3.



Table 1

Ex.	end-capped polymer	end-uncapped polymer	ratio of end-capped polymers (%)	alignment properties	pretilt angle (°)	after image erase time (s)	reliability
Ex.1	polyimide 1	polyamic acid 16	25	satisfactory	4.8	0.72	satisfactory
Ex.2	polyimide 1	polyamic acid 19	20	satisfactory	4.7	0.75	satisfactory
Ex.3	polyimide 1	polyamic acid 22	30	satisfactory	5.0	0.82	satisfactory
Ex.4	polyimide 1	polyamic acid 26	15	satisfactory	4.6	0.70	satisfactory
Ex.5	polyimide 2	polyamic acid 17	20	satisfactory	4.9	0.80	satisfactory
Ex.6	polyimide 2	polyamic acid 19	25	satisfactory	5.1	0.84	satisfactory
Ex.7	polyimide 2	polyamic acid 23	20	satisfactory	4.8	0.79	satisfactory
Ex.8	polyimide 2	polyamic acid 26	20	satisfactory	4.7	0.81	satisfactory
Ex.9	polyimide 3	polyamic acid 18	20	satisfactory	4.4	0.83	satisfactory
Ex.10	polyimide 3	polyamic acid 24	25	satisfactory	4.6	0.79	satisfactory
Ex.11	polyimide 3	polyamic acid 22	30	satisfactory	5.0	0.88	satisfactory
Ex.12	polyimide 3	polyamic acid 27	20	satisfactory	4.8	0.83	satisfactory
Ex.13	polyimide 4	polyamic acid 16	25	satisfactory	4.6	0.72	satisfactory
Ex.14	polyimide 4	polyamic acid 21	20	satisfactory	4.5	0.65	satisfactory
Ex.15	polyimide 4	polyamic acid 22	15	satisfactory	4.4	0.77	satisfactory

Ex.: Example

g

This Sheet Has Been Replaced



Table 1 (continued)

Ex.	end-capped polymer	end-uncapped polymer	ratio of end- capped polymers (%)	alignment properties	pretilt angle (°)	after image erase time (s)	reliability
Ex.16	polyimide 4	polyamic acid 26	25	satisfactory	4.6	0.78	satisfactory
Ex.17	polyimide 5	polyamic acid 17	20	satisfactory	4.2	0.84	satisfactory
Ex.18	polyimide 5	polyamic acid 19	35	satisfactory	4.8	0.78	satisfactory
Ex.19	polyimide 5	polyamic acid 23	18	satisfactory	4.2	0.83	satisfactory
Ex.20	polyimide 5	polyamic acid 26	30	satisfactory	4.6	0.80	satisfactory
Ex.21	polyimide 6	polyamic acid 18	20	satisfactory	4.5	0.85	satisfactory
Ex.22	polyimide 6	polyamic acid 22	12	satisfactory	4.3	0.86	satisfactory
Ex.23	polyimide 6	polyamic acid 24	25	satisfactory	4.5	0.81	satisfactory
Ex.24	polyimide 6	polyamic acid 27	25	satisfactory	4.5	0.82	satisfactory
Ex.25	polyimide 7	polyamic acid 18	30	satisfactory	5.9	0.70	satisfactory
Ex.26	polyimide 7	polyamic acid 20	25	satisfactory	5.8	0.61	satisfactory
Ex.27	polyimide 7	polyamic acid 21	20	satisfactory	5.7	0.63	satisfactory
Ex.28	polyimide 7	polyamic acid 25	30	satisfactory	6.1	0.65	satisfactory
Ex.29	polyimide 7	polyamic acid 27	20	satisfactory	5.9	0.63	satisfactory
Ex.30	polyimide 8	polyamic acid 17	25	satisfactory	4.5	0.74	satisfactory

51

Ex.: Example

This Sheet Has Been Replaced



Table 2

Ex.	end-capped polymer	end-uncapped polymer	ratio of end-capped polymers (%)	alignment properties	pretilt angle (°)	after image erase time (s)	reliability
Ex.31	polyimide 8	polyamic acid 20	20	satisfactory	4.4	0.59	satisfactory
Ex.32	polyimide 8	polyamic acid 21	20	satisfactory	4.4	0.60	satisfactory
Ex.33	polyimide 8	polyamic acid 24	25	satisfactory	4.6	0.69	satisfactory
Ex.34	polyimide 8	polyamic acid 25	30	satisfactory	4.7	0.68	satisfactory
Ex.35	polyimide 8	polyamic acid 27	20	satisfactory	4.5	0.62	satisfactory
Ex.36	polyimide 9	polyamic acid 18	17	satisfactory	4.8	0.72	satisfactory
Ex.37	polyimide 9	polyamic acid 19	24	satisfactory	4.9	0.66	satisfactory
Ex.38	polyimide 9	polyamic acid 23	16	satisfactory	4.7	0.71	satisfactory
Ex.39	polyimide 9	polyamic acid 25	30	satisfactory	5.1	0.68	satisfactory
Ex.40	polyimide 10	polyamic acid 17	30	satisfactory	5.6	0.80	satisfactory
Ex.41	polyimide 10	polyamic acid 19	25	satisfactory	5.5	0.72	satisfactory
Ex.42	polyimide 10	polyamic acid 24	18	satisfactory	5.4	0.74	satisfactory
Ex.43	polyimide 10	polyamic acid 26	20	satisfactory	5.6	0.71	satisfactory
Ex.44	polyimide 11	polyamic acid 21	20	satisfactory	4.8	0.64	satisfactory
Ex.45	polyimide 11	polyamic acid 23	25	satisfactory	4.9	0.70	satisfactory

Ex.: Example



This Sheet Has Been Replaced

Table 2 (continued)

Ex.	end-capped polymer	end-uncapped polymer	ratio of end- capped polymers (%)	alignment properties	pretilt angle (°)	after image erase time (s)	reliability
Ex.46	polyimide 11	polyamic acid 27	22	satisfactory	4.6	0.66	satisfactory
Ex.47	polyimide 11	polyamic acid 28	30	satisfactory	4.9	0.72	satisfactory
Ex.48	polyimide 12	polyamic acid 20	20	satisfactory	5.2	0.68	satisfactory
Ex.49	polyimide 12	polyamic acid 21	20	satisfactory	5.2	0.69	satisfactory
Ex.50	polyimide 12	polyamic acid 27	22	satisfactory	5.1	0.72	satisfactory
Ex.51	polyimide 12	polyamic acid 28	23	satisfactory	5.3	0.75	satisfactory
Ex.52	polyimide 13	polyamic acid 20	25	satisfactory	4.4	0.78	satisfactory
Ex.53	polyimide 13	polyamic acid 21	25	satisfactory	4.4	0.80	satisfactory
Ex.54	polyimide 13	polyamic acid 27	28	satisfactory	4.5	0.81	satisfactory
Ex.55	polyimide 14	polyamic acid 16	14	satisfactory	5.9	0.89	satisfactory
Ex.56	polyimide 14	polyamic acid 21	26	satisfactory	6.2	0.81	satisfactory
Ex.57	polyimide 14	polyamic acid 27	31	satisfactory	6.3	0.82	satisfactory
Ex.58	polyimide 14	polyamic acid 28	21	satisfactory	6.1	0.92	satisfactory
Ex.59	polyimide 15	polyamic acid 18	40	satisfactory	4.6	0.89	satisfactory
Ex.60	polyimide 15	polyamic acid 21	25	satisfactory	4.8	0.84	satisfactory

Ex.: Example

This Sheet Has Been Replaced



Table 3

Ex.	end-capped polymer	end-uncapped polymer	ratio of end- capped polymers (%)	alignment properties	pretilt angle (°)	after image erase time (s)	reliability
Ex.61	polyimide 15	polyamic acid 27	20	satisfactory	4.7	0.85	satisfactory
Ex.62	polyimide 15	polyamic acid 28	18	satisfactory	4.4	0.91	satisfactory
Ex.63	polyamic acid 1	polyamic acid 16	25	satisfactory	4.4	0.88	satisfactory
Ex.64	polyamic acid 2	polyamic acid 22	30	satisfactory	4.3	0.87	satisfactory
Ex.65	polyamic acid 3	polyamic acid 19	20	satisfactory	4.2	0.90	satisfactory
Ex.66	polyamic acid 4	polyamic acid 22	16	satisfactory	4.1	0.87	satisfactory
Ex.67	polyamic acid 5	polyamic acid 19	24	satisfactory	4.5	0.86	satisfactory
Ex.68	polyamic acid 7	polyamic acid 20	30	satisfactory	5.5	0.79	satisfactory
Ex.69	polyamic acid 8	polyamic acid 21	21	satisfactory	4.1	0.80	satisfactory
Ex.70	polyamic acid 11	polyamic acid 20	20	satisfactory	4.2	0.81	satisfactory
Ex.71	polyamic acid 12	polyamic acid 21	20	satisfactory	4.4	0.84	satisfactory
Ex.72	polyimide 1	polyimide 18	30	satisfactory	4.9	0.88	satisfactory
Ex.73	polyimide 2	polyimide 18	25	satisfactory	4.7	0.85	satisfactory
Ex.74	polyimide 4	polyimide 23	20	satisfactory	4.6	0.86	satisfactory
Ex.75	polyimide 5	polyimide 23	24	satisfactory	4.6	0.90	satisfactory

Ex.: Example



This Sheet Has Been Replaced

Table 3 (continued)

Ex.	end-capped polymer	end-uncapped polymer	ratio of end- capped polymers (%)	alignment properties	pretilt angle (°)	after image erase time (s)	reliability
Ex.76	polyimide 7	polyimide 23	35	satisfactory	5.9	0.79	satisfactory
Ex.77	polyimide 8	polyimide 18	18	satisfactory	4.9	0.81	satisfactory
Ex.78	polyimide 12	polyimide 23	20	satisfactory	5.1	0.83	satisfactory
Ex.79	polyimide 13	polyimide 23	20	satisfactory	5.2	0.81	satisfactory
Ex.80	polyamic acid 1	polyimide 18	18	satisfactory	4.8	0.95	satisfactory
Ex.81	polyamic acid 4	polyimide 23	30	satisfactory	4.8	0.94	satisfactory
Ex.82	polyamic acid 7	polyimide 23	20	satisfactory	5.8	0.91	satisfactory
Ex.83	polyamic acid 13	polyimide 23	25	satisfactory	4.8	0.62	satisfactory
Ex.84	polyimide 2	none	100	satisfactory	4.3	0.96	satisfactory
Ex.85	polyimide 5	none	100	satisfactory	4.1	0.94	satisfactory
Ex.86	polyimide 8	none	100	satisfactory	4.2	0.90	satisfactory
Ex.87	polyimide 14	none	100	satisfactory	4.4	0.92	satisfactory
Ex.88	polyamic acid 3	none	100	satisfactory	4.0	0.99	satisfactory
Ex.89	polyamic acid 6	none	100	satisfactory	4.1	0.96	satisfactory
Ex.90	polyamic acid 9	none	100	satisfactory	4.0	0.93	satisfactory
Ex.91	polyimide 29	polyamic acid 21	25	satisfactory	5.2	0.58	satisfactory

Ex.: Example

This Sheet Has Been Replaced



This Sheet Has Been Replaced

**Example 92****(1) preparation of liquid crystal aligning agent:**

The polyamic acid (end-capped) (30) obtained in Synthesis Example 30 was dissolved in N-methylpyrrolidone to prepare a solution having a solid content of 4 wt% which was then filtered with a filter having a pore diameter of 1 μ m to prepare the liquid crystal aligning agent of the present invention.

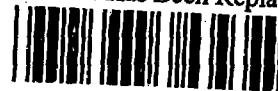
(2) preparation of liquid crystal display element:

- 10 (1) A liquid crystal display element was fabricated in the same manner as in Example 1 except that the nematic liquid crystal was changed to "MLC-2012" (of Merck Co., Ltd.). When voltage was applied to and released from the liquid crystal cell, an abnormal domain was not observed and the liquid
- 15 crystal alignment properties of the fabricated liquid crystal display element was therefore satisfactory. When the pretilt angle was measured, it was 89.5°. It was thus confirmed that the liquid crystals were aligned homeotropically. The after image erase time of the liquid
- 20 crystal display element was short at 0.95 sec. When the alignment properties and reliability test result of the obtained liquid crystal display element were evaluated, the liquid crystal alignment properties were satisfactory and a white smear was not observed on the liquid crystal display
- 25 element after the reliability test.

Comparative Example 1

- A liquid crystal aligning agent was prepared in the same manner as in Example 1 except that the polyimide (A) obtained in Comparative Synthesis Example 1 was used in place of the
- 30 polyimide (1) to fabricate a liquid crystal display element. The liquid crystal alignment properties, pretilt angle and after image erase time of the fabricated liquid crystal display element were measured and a reliability test was made on the liquid crystal display element. The results are shown

This Sheet Has Been Replaced



57

in Table 4.

Comparative Examples 2 to 33

Liquid crystal aligning agents were prepared in the same manner as in Example 1 except that the polyimides obtained in Comparative Synthesis Examples 2 to 5, the polyamic acids and polyimides obtained in Synthesis Examples 16 to 28 were used in ratios shown in Table 4 to fabricate liquid crystal display elements. The liquid crystal alignment properties, pretilt angles and after image erase times of the fabricated liquid crystal display elements were measured and a reliability test was made on these liquid crystal display elements. The results are shown in Table 4.

Table 4

Ex.	end-capped polymer	end-uncapped polymer	ratio of end-capped polymers (%)	alignment properties	pretilt angle (°)	after image erase time (s)	reliability
C.Ex.1	polyimide A	polyamic acid 16	25	satisfactory	4.8	3.35	satisfactory
C.Ex.2	polyimide A	polyamic acid 20	20	satisfactory	4.3	2.55	satisfactory
C.Ex.3	polyimide A	polyamic acid 22	30	satisfactory	4.9	3.25	satisfactory
C.Ex.4	polyimide A	polyamic acid 26	19	satisfactory	4.6	3.08	satisfactory
C.Ex.5	polyimide B	polyamic acid 18	22	satisfactory	4.5	3.20	unsatisfactory
C.Ex.6	polyimide B	polyamic acid 19	25	satisfactory	4.5	0.80	unsatisfactory
C.Ex.7	polyimide B	polyamic acid 24	16	satisfactory	4.8	0.79	unsatisfactory
C.Ex.8	polyimide B	polyamic acid 27	20	satisfactory	4.7	1.11	unsatisfactory
C.Ex.9	polyimide C	polyamic acid 20	20	satisfactory	4.1	1.52	satisfactory
C.Ex.10	polyimide C	polyamic acid 24	25	satisfactory	4.2	1.49	satisfactory
C.Ex.11	polyimide C	polyamic acid 27	30	satisfactory	4.0	1.48	satisfactory
C.Ex.12	polyimide D	polyamic acid 21	20	satisfactory	4.4	3.13	satisfactory
C.Ex.13	polyimide D	polyamic acid 24	18	satisfactory	4.3	3.43	satisfactory
C.Ex.14	polyimide D	polyamic acid 28	20	satisfactory	4.2	3.65	satisfactory
C.Ex.15	polyimide E	polyamic acid 21	25	satisfactory	4.2	1.73	satisfactory

C.Ex.: Comparative Example

This Sheet Has Been Replaced



Table 4 (continued)

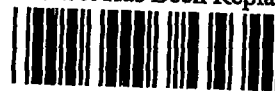
Ex.	end-capped polymer	end-uncapped polymer	ratio of end-capped polymers (%)	alignment properties	pretilt angle (°)	after image erase time (s)	reliability
C.Ex.16	polyimide E	polyamic acid 28	30	satisfactory	4.4	1.78	satisfactory
C.Ex.17	polyamic acid A	polyamic acid 16	25	satisfactory	4.2	4.44	unsatisfactory
C.Ex.18	polyamic acid B	polyamic acid 21	20	satisfactory	4.1	3.78	unsatisfactory
C.Ex.19	polyamic acid C	polyamic acid 20	21	satisfactory	4.2	3.83	unsatisfactory
C.Ex.20	polyamic acid D	polyamic acid 21	20	satisfactory	4.0	3.80	unsatisfactory
C.Ex.21	polyamic acid E	polyamic acid 21	20	satisfactory	4.1	3.68	unsatisfactory
C.Ex.22	polyimide A	polyimide 18	25	satisfactory	4.1	5.80	satisfactory
C.Ex.23	polyimide B	polyimide 23	18	satisfactory	4.6	4.31	unsatisfactory
C.Ex.24	polyimide C	polyimide 23	20	satisfactory	4.1	5.11	unsatisfactory
C.Ex.25	polyimide D	polyimide 23	30	satisfactory	4.2	4.29	unsatisfactory
C.Ex.26	polyimide E	polyimide 18	25	satisfactory	4.3	3.98	satisfactory
C.Ex.27	polyamic acid A	polyimide 18	20	satisfactory	4.1	4.18	unsatisfactory
C.Ex.28	polyamic acid B	polyimide 23	30	satisfactory	4.3	4.83	unsatisfactory
C.Ex.29	polyamic acid C	polyimide 23	10	satisfactory	4.6	4.46	unsatisfactory
C.Ex.30	polyamic acid D	polyimide 18	30	satisfactory	4.6	4.75	satisfactory
C.Ex.31	polyamic acid E	polyimide 23	20	satisfactory	4.6	4.14	satisfactory
C.Ex.32	polyimide A	none	100	satisfactory	4.1	4.64	satisfactory
C.Ex.33	polyimide D	none	100	satisfactory	4.5	4.89	satisfactory

C.Ex.: Comparative Example

As described above in detail, according to the present invention, there can be provided a liquid crystal aligning agent which has excellent alignment characteristics that liquid crystal alignment properties are satisfactory and a high pretilt angle not dependent upon process conditions such as film thickness and rubbing conditions can be obtained when a liquid crystal alignment film is formed therefrom and which is capable of forming a liquid crystal alignment film with a short after image erase time and high reliability for a liquid crystal display element.

The liquid crystal alignment film formed from the liquid crystal aligning agent of the present invention can be advantageously used to form various liquid crystal display elements such as a TN liquid crystal display element, STN liquid crystal display element and SH (Super Homeotropic) liquid crystal display element. The liquid crystal display element comprising the liquid crystal alignment film can be used effectively as a display unit for various devices such as desk-top calculators, wristwatches, clocks, counter display boards, word processors, personal computers and liquid crystal TV sets thanks to its excellent liquid crystal alignment properties and reliability.

This Sheet Has Been Replaced



This Sheet Has Been Replaced



61



What is claimed is:

1. A liquid crystal aligning agent comprising at least one end-capped polymer selected from the group consisting of:
 - (A) an end-capped polyamic acid which has an alicyclic structure and is obtained by reacting (a) a tetracarboxylic dianhydride, (b) a diamine compound and (c) at least one compound selected from the group consisting of a dicarboxylic anhydride, monoamine compound and monoisocyanate compound; and
 - (B) an end-capped imidized polymers obtained by dehydrating and ring closing the polyamic acid.
2. The liquid crystal aligning agent of claim 1, in which the end-capped polyamic acid is obtained by using a dicarboxylic anhydride as the component (c).
3. A liquid crystal aligning agent comprising:
 - (1) at least one end-capped polymer selected from the group consisting of; (A) an end-capped polyamic acid which has an alicyclic structure and is obtained by reacting (a) a tetracarboxylic dianhydride, (b) a diamine compound and (c) at least one compound selected from the group consisting of a dicarboxylic anhydride, monoamine compound and monoisocyanate compound, and (B) end-capped imidized polymers obtained by dehydrating and ring closing the polyamic acid; and
 - (2) at least one end-uncapped polymer selected from the group consisting of an end-uncapped polyamic acid obtained by reacting (a) a tetracarboxylic dianhydride and (b) a diamine compound, and an end-uncapped imidized polymers obtained by dehydrating and ring closing the end-uncapped polyamic acid.
4. The liquid crystal aligning agent of claim 3, wherein



the end-capped polymer is an end-capped imidized polymer and
the end-uncapped polymer is an end-uncapped polyamic acid.

5. The liquid crystal aligning agent of claim 4, wherein
5 the end-capped imidized polymer is obtained by using a
monoamine compound as the component (C).
6. A liquid crystal display element having a liquid
crystal alignment film obtained from the liquid crystal
10 aligning agent of any one of claims 1 to 5.

This Sheet Has Been Replaced

