

967.483



PATENT SPECIFICATION

NO DRAWINGS

967.483

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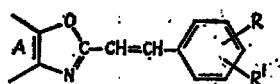
COMPLETE SPECIFICATION

Novel Oxazole Compounds and their use as Optical Brightening Agents

We, MITSUI KAGAKU KOGYO KABUSHIKI KAISHA, a corporation organised under the laws of Japan, of 1 of No. 1,2-chome, Nihonbashi Muromachi, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel 2-styryloxazole compounds useful as optical brightening agents for organic textile materials.

The novel 2-styryloxazole compounds of this invention can be represented by the general structural formula:



I

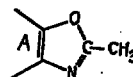
wherein A is an alkyl-, aromatic hydrocarbon- or alkylene-substituted benzene nucleus or an unsubstituted naphthalene nucleus, which is condensed with the oxazole ring, and R and R¹, which may be the same or different, are each a hydrogen atom, a halogen atom, a cyano group, a carboxyl group or ester derivative thereof, an alkyl group or an aromatic hydrocarbon group.

2-styryloxazole compounds are little known although 2-styrylbenzoxazole and 2-(4¹-dimethylaminostyryl)-benzoxazole have been described (D.M. Brown, A. R. Kon, J. Chem. Soc. 1948, 2147).

It has now been found that 2-styryloxazole compounds falling within the definition of formula I exhibit a strong fluorescence and produce an excellent optical brightening effect [Price 4s. 6d.]

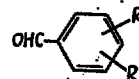
when organic textile materials are treated therewith i.e. the novel 2-styryloxazole compounds are useful substances for the optical brightening of organic textile materials, particularly various man-made fibres, and they also have good light-fastness.

The 2-styryloxazole compounds of the invention can be prepared by heating a 2-methyloxazole compound which can be represented by the general structural formula:



II

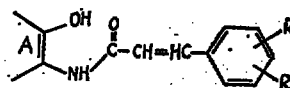
wherein A is defined as above, with a benzaldehyde derivative which can be represented by the general structural formula:



III

wherein R and R¹ are defined as above.

Alternatively, the compounds of the invention can be prepared by intra-molecular ring closure of a novel cinnamic acid amide derivative represented by general structural formula:



IV

wherein A, R and R¹ are defined as above.

The following compounds are examples of 2 - methyloxazole compounds, having the general structural formula II, which can be employed in the preparation of the 2 - styryloxazole compounds of the invention: 2-methylbenzoxazole, 2,5-dimethylbenzoxazole, 2,5,7-trimethylbenzoxazole, 2-methyl-4,5-cyclotetramethylenebenzoxazole, 2-methyl-5-ethylbenzoxazole, 2-methyl-5-isopropylbenzoxazole, 2-methyl-5-tert-butylbenzoxazole, 2-methyl-5-phenylbenzoxazole, 2-methyl- α -naphthoxazole and 2-methyl- β -naphthoxazole.

The following compounds are examples of benzaldehyde derivatives, having the general structural formula III, which can be used in the preparation of the 2 - styryloxazole compounds of the invention: benzaldehyde, 2-chlorobenzaldehyde, 3-chlorobenzaldehyde, 4-chlorobenzaldehyde, 4-bromobenzaldehyde, 4-fluorobenzaldehyde, 2-cyanobenzaldehyde, 3-cyanobenzaldehyde, 4-cyanobenzaldehyde, 4-methylbenzaldehyde, 4-phenylbenzaldehyde, 4-cyano-2-chlorobenzaldehyde, 4-cyano-3-chlorobenzaldehyde, 4-carboxylbenzaldehyde, 4-carboethoxybenzaldehyde, 2-chloro-4-carboxybenzaldehyde and 3-chloro-4-carboxybenzaldehyde.

The condensation reaction between a 2-

methyloxazole compound, having the general structural formula II, and a benzaldehyde derivative, having the general structural formula III, can advantageously be carried out by taking both starting materials in about equal molar quantities and heating them together at 150°-200°C. The reaction may be carried out in the absence or presence of a dehydrating agent.

The cinnamic acid amide derivative can be obtained by N-acylating *o*-aminophenols or *o*-aminonaphthols, for example 4-methyl-2-aminophenol, 4,6-dimethyl-2-aminophenol, 4-ethyl-2-aminophenol, 4-phenyl-2-aminophenol, 1-amino-2-naphthol or 2-amino-1-naphthol, or their inorganic acid salts, with a cinnamic acid halide, for example cinnamic acid chloride, 3-chlorocinnamic acid chloride, 4-chlorocinnamic acid chloride or 4-cyano-3-chlorocinnamic acid chloride, in accordance with conventional methods. The intramolecular ring closure reaction of the cinnamic acid amide thus obtained can advantageously be carried out in an inert organic solvent such as xylene, chlorobenzene and dichlorobenzene, by adding a dehydrating agent and heating.

Examples of novel 2 - styryloxazole compounds of this invention are given in Table 1.

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inorganic

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TABLE 1

No.	Structural Formula	Appearance and melting point	Colour of fluorescence in benzene solution
1		colourless needle-like crystals 154—155°C.	violet
2		light yellow pillar-like crystals 196—197°C.	violet
3		slightly yellow plate crystals 146—147°C.	violet
4		light yellow pillar-like crystals >310°C.	violet
5		colourless needle-like crystals 141—142°C.	violet

TABLE 1 (Continued)

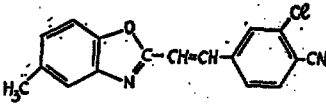
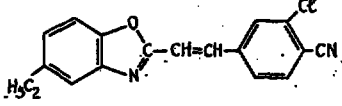
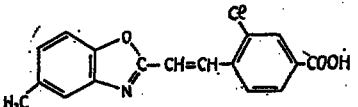
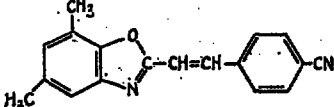
No.	Structural Formula	Appearance and melting point	Fluorescence in benzene solution
6		light yellow needle-like crystals 221°C.	violet
7		light yellow needle-like crystals 155—156°C.	violet
8		light yellow needle-like crystals 260—263°C.	blue
9		slightly yellow needle-like crystals 207—209°C.	blue-violet

TABLE 1 (Continued)

No.	Structural Formula	Property and melting point	Fluorescence in benzene solution
10		silver-white flake-like crystals 134—136°C.	violet
11		light yellow needle-like crystals 184—185°C.	blue-violet
12		light yellow pillar-like crystals 295—297°C.	violet
13		colourless flake-like crystals 175—176°C.	violet-blue
14		colourless needle-like crystals 124—125°C.	blue-violet

TABLE 1 (Continued)

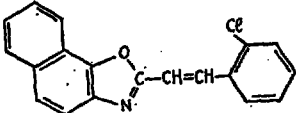
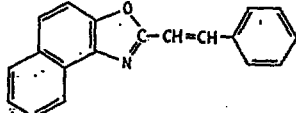
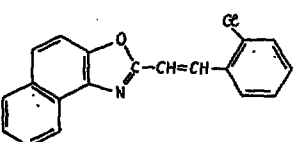
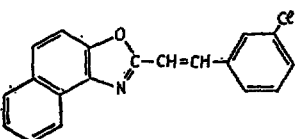
No.	Structural Form	Property and melting point	Fluorescence in benzene solution
15		slightly yellow pillar-like crystals 134—135°C.	blue
16		light yellow pillar-like crystals 122—123°C.	green-blue
17		slightly yellow needle-like crystals 158—159°C.	blue-green
18		light yellow flake-like crystals 114—114°C.	blue

TABLE 1 (Continued)

No.	Structural Formula	Property and melting point	Fluorescence in benzene solution
19		yellow needle-like crystals 159—160°C.	green-blue
20		light yellow pillar-like crystals 125—126°C.	violet-blue
21		greenish yellow pillar-like crystals 185—186°C.	blue-green
22		light yellow flake-like crystals 123—124°C.	violet-blue
23		yellow long flake-like crystals >300°C.	blue
24		light yellow needle-like crystals 219—220°C.	violet-blue

As indicated in Table 1, the novel 2-styryloxazole compounds of this invention generally have a fluorescence of blue violet to violet. They also show excellent affinity for organic textile materials from an aqueous dispersed system so that they are very useful for the optical brightening of man-made fibres, particularly polyester, polyacrylonitrile, polyamide acetalized polyvinyl alcohol, polyolefin and cellulose acetate fibres and they possess excellent light fastness. For example, compound listed No. 18 in Table 1 can be made

into an aqueous dispersed system by using an anionic surface active agent of the alkylbenzene sulphonic acid type, and when the above-mentioned man-made fibres are treated in a bath which contains an amount of this compound equal to 0.1% to 0.2% of the material to be treated, an excellent optical brightening effect can be obtained. The treatment conditions and the light fastness (according to JIS L 1045—1959, xenon light source) of man-made fibres treated with this compound are shown in Table 2.

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20

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TABLE 2

Fibre Materials	Compound concentration (%)	Treatment temperature (°C)	Treatment times (min.)	Light fastness
Polyester	0.2	120	45	4
Polyacrylonitrile	0.1	100	45	3
Polyamide	0.1	80	45	3
Celluloseacetate	0.1	80	45	3—4
Acetalized polyvinyl alcohol	0.1	80	45	3
Polypropylene	0.1	100	45	2—3

In treating organic textile materials, it is convenient to use a composition which is obtained by mixing the compound of the invention with a surface active agent. For example, a composition comprising 10 parts of a 2-styryloxazole compound according to the invention, 10 parts of a surface active agent of the alkylbenzene sulphonic acid type and 80 parts of a formaldehyde condensate of naphthalene sulphonic acid can be conveniently used.

The preparation of the 2-styryloxazole compounds of this invention and a method of using them for the optical brightening of organic textile materials are illustrated by the following Examples. Percentages and parts are by weight.

EXAMPLE 1

2,5-dimethylbenzoxazole (14.7 parts), 4-carboxybenzaldehyde (15 parts) and zinc chloride (5 parts) were thoroughly mixed together and caused to react by heating at 160—200°C. for 8 hours with stirring. The reactants were boiled and dissolved in methanol of 10 times volume. On cooling the methanol solution, 5-methyl-2-(4-carboxystyryl)-benzoxazole was precipitated as yellow crystals. When recrystallized from ethanol containing glacial acetic acid, light yellow pillar-like crystals (mp. >310°C.) were obtained.

EXAMPLE 2

2,5-dimethylbenzoxazole (14.7 parts), 4-cyano-3-chlorobenzaldehyde (18 parts) and zinc bromide (13 parts) were thoroughly mixed together and caused to react by heating at 160°C. for 6 hours with stirring. In this case the water formed by the reaction was successively driven out of the reaction system. The reactants were boiled and dissolved in 50 parts of methanol. On cooling the methanol

solution, 5-methyl-2-(4'-cyano-3'-chloro-styryl)-benzoxazole was precipitated as yellow crystals. When recrystallized from dimethyl formamide, light yellow needle-like crystals (mp. 221°C.) were obtained.

EXAMPLE 3

2,5,7-trimethylbenzoxazole (16.1 parts), 4-cyanobenzaldehyde (13.1 parts) and zinc chloride (7 parts) were mixed thoroughly and caused to react by heating at 160—200°C. for 8 hours with stirring while the water formed was successively removed from the reaction system. The reactants were then subjected to steam distillation and any unreacted starting materials were distilled out. The distillation residue was treated with hot xylene and the resulting xylene solution allowed to cool precipitating 5,7-dimethyl-2-(4'-cyanostyryl)-benzoxazole as yellow needle-like crystals. When recrystallized from ligroin containing benzene, slightly yellow needle-like crystals (mp. 207—209°C.) were obtained.

EXAMPLE 4

2-methyl- α -naphthoxazole (18.3 parts), benzaldehyde (11 parts) and zinc chloride (7 parts) were thoroughly mixed and caused to react by heating at 160—200°C. for 8 hours with stirring. To the reaction product was added hot methanol of 3 times volume and after cooling the precipitate was filtered out. The precipitate was recrystallized from a mixture of ethanol and glacial acetic acid to give light yellow pillar-like crystals (mp. >300°C.) of a double salt of 2-styryl- α -naphthoxazole and zinc chloride. On heating with water, 2-styryl- α -naphthoxazole was easily separated. Recrystallization from ligroin gave colourless needle-like crystals (mp. 124—125°C.).



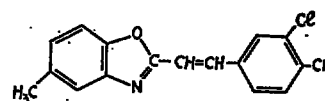
EXAMPLE 5

2 - methyl - β - naphthoxazole (28 parts), 3 - chloro - benzaldehyde (22 parts) and zinc chloride (10 parts) were mixed together and then caused to react by heating at 160—165°C. for 6 hours while the water formed was successively removed from the reaction system. The reactants were dissolved in 150 parts of isopropanol. The isopropanol solution was allowed to cool to precipitate 2 - (3¹-chlorostyryl) - β - naphthoxazole as yellow crystals. Recrystallization from methanol gave light yellow flake-like crystals (mp. 114—115°C.).

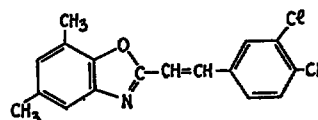
wherein A is an alkyl-, aromatic hydrocarbon- or alkylene-substituted benzene nucleus or an unsubstituted naphthalene nucleus which is condensed with the oxazole ring, and R and R¹, which may be the same or different, are each a hydrogen atom, a halogen atom, a cyano group, a carboxyl group or an ester derivative thereof, an alkyl group or an aromatic hydrocarbon group.

2. A compound as claimed in Claim 1, wherein A is a methyl- or ethyl-substituted benzene nucleus.

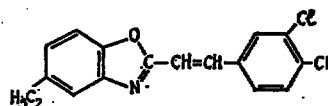
3. 5 - methyl - 2 - (3¹ - chloro - 4¹-cyanostyryl) - benzoxazole having the structural formula:



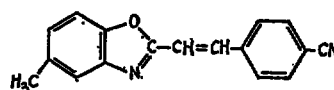
4. 5,7 - dimethyl - 2 - (3¹ - chloro - 4¹-cyanostyryl) - benzoxazole having the structural formula:



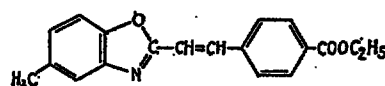
5. 5 - ethyl - 2 - (3¹ - chloro - 4¹ - cyano-styryl) - benzoxazole having the structural formula:



6. 5 - methyl - 2 - (4¹ - cyanostyryl)- benzoxazole having the structural formula:



7. 5 - methyl - 2 - (4¹ - carboxyethoxystyryl) - benzoxazole having the structural formula:

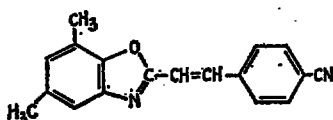


EXAMPLE 6

Cinnamic acid - (2¹ - hydroxynaphthyl - 1¹)-amide (25 parts) obtained from 1 - amino - 2-naphthol hydrochloric acid salt (20 parts) and cinnamic acid chloride (17 parts) was boiled with 10 parts of phosphorus oxychloride in 50 parts of *o* - dichlorobenzene for 8 hours. Then, the *o* - dichlorobenzene was removed by steam distillation and the crude 2 - styryl - β - naphthoxazole obtained as the distillation residue treated with ligroin. The ligroin solution was allowed to cooled to precipitate 2-styryl - β - naphthoxazole as yellow crystals. Recrystallization from ligroin gave light yellow pillar-like crystals (mp. 121.5—123°C.).

EXAMPLE 7

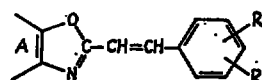
One part of 2 - (4¹ - cyanostyryl) - 5,7-dimethyl - benzoxazole having the structural formula:



was thoroughly mixed with 9 parts of a surface active agent of the alkylbenzene sulphonic acid type and 0.2 parts of the resulting mixture per 10 parts of a polyester cloth, which was to be treated, was put into 400 parts of water to form a dispersed system. In this dispersed system the polyester cloth was treated at 120°C. for 45 minutes. The treated cloth was washed with water and dried to give an excellent brightening effect when compared with un-treated cloth.

WHAT WE CLAIM IS:—

1. A 2 - styryloxazole compound represented by the general structural formula:



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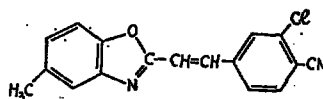
EXAMPLE 5

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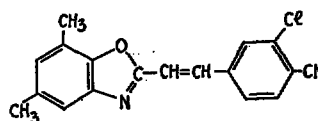
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2. A compound as claimed in Claim 1, wherein A is a methyl- or ethyl-substituted benzene nucleus.

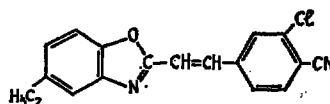
3. 5 - methyl - 2 - (3¹ - chloro - 4¹-cyanostyryl) - benzoxazole having the structural formula:



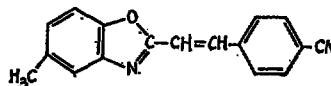
4. 5,7 - dimethyl - 2 - (3¹ - chloro - 4¹-cyanostyryl) - benzoxazole having the structural formula:



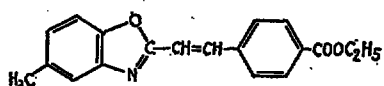
5. 5 - ethyl - 2 - (3¹ - chloro - 4¹ - cyanostyryl) - benzoxazole having the structural formula:



6. 5 - methyl - 2 - (4¹ - cyanostyryl) - benzoxazole having the structural formula:



7. 5 - methyl - 2 - (4¹ - carboxyethoxystyryl) - benzoxazole having the structural formula:

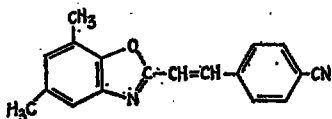


EXAMPLE 6

Cinnamic acid - (2¹ - hydroxynaphthyl - 1¹)-amide (25 parts) obtained from 1 - amino - 2-naphthol hydrochloric acid salt (20 parts) and cinnamic acid chloride (17 parts) was boiled with 10 parts of phosphorus oxychloride in 50 parts of *o* - dichlorobenzene for 8 hours. Then, the *o* - dichlorobenzene was removed by steam distillation and the crude 2 - styryl - β - naphthoxazole obtained as the distillation residue treated with ligroin. The ligroin solution was allowed to cooled to precipitate 2-styryl - β - naphthoxazole as yellow crystals. Recrystallization from ligroin gave light yellow pillar-like crystals (mp. 121.5—123°C.).

EXAMPLE 7

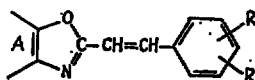
One part of 2 - (4¹ - cyanostyryl) - 5,7-dimethyl - benzoxazole having the structural formula:



was thoroughly mixed with 9 parts of a surface active agent of the alkylbenzene sulphonic acid type and 0.2 parts of the resulting mixture per 10 parts of a polyester cloth, which was to be treated, was put into 400 parts of water to form a dispersed system. In this dispersed system the polyester cloth was treated at 120°C. for 45 minutes. The treated cloth was washed with water and dried to give an excellent brightening effect when compared with un-treated cloth.

WHAT WE CLAIM IS:—

1. A 2 - styryloxazole compound represented by the general structural formula:



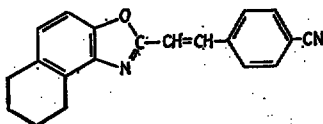


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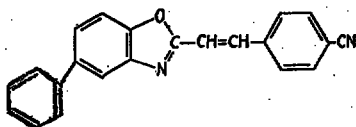
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8. 4,5 - cyclotetramethylene - 2 - (4¹-cyanostyryl) - benzoxazole having the following formula:

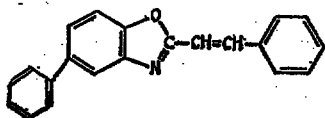


5 9. 5 - phenyl - 2 - (4¹ - cyanostyryl)-benzoxazole having the following formula:



10. 5 - phenyl - 2 - styrylbenzoxazole having the following formula:

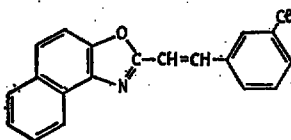
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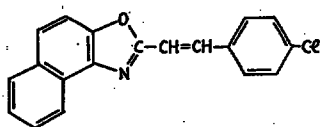
11. A compound as claimed in Claim 1, wherein A is a naphthalene nucleus.

12. 2 - (3¹ - chlorostyryl) - β - naphthoxazole having the structural formula:

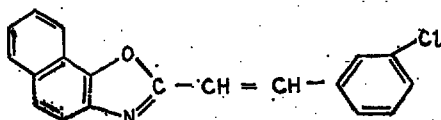
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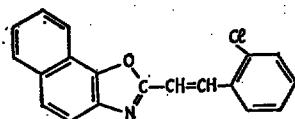
13. 2 - (4¹ - chlorostyryl) - β - naphthoxazole having the structural formula:



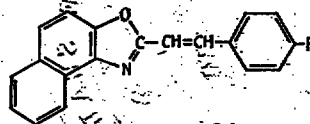
20 14. 2 - (3¹ - chlorostyryl) - α - naphthoxazole having the structural formula:



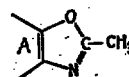
15. 2 - (2¹ - chlorostyryl) - α - naphthoxazole having the structural formula:



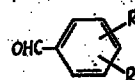
16. 2 - (4¹ - fluorostyryl) - β - naphthoxazole having the structural formula: 25



17. A method of preparing a 2-styryloxazole compound having the general structural formula defined in Claim 1, which method comprises heating a 2-methyl oxazole compound represented by the general structural formula: 30



wherein A is defined as in Claim 1, with a benzaldehyde derivative represented by the general structural formula: 35



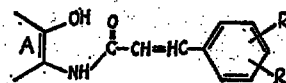
III

wherein R and R¹ are each defined as in Claim 1, to form the desired 2-styryloxazole compound. 40

18. A method according to Claim 17, wherein there are used equal molar quantities of the 2 - methyl - oxazole compound and the benzaldehyde derivative, which are mixed together and heated to a temperature in the range of from 150°C to 200°C. 45

19. A method according to Claim 17 or 18, wherein a dehydrating agent is employed. 50

20. A method of preparing a 2-styryloxazole compound having the general structural formula defined in Claim 1 which method comprises adding a dehydrating agent to a solution, in an inert organic solvent, of a cinnamic acid amide derivative represented by the general structural formula: 55



IV

wherein A, R and R¹ are defined as in Claim 1, and heating said solution to form the desired 2-styryloxazole compound. 60

21. A method according to Claim 20, wherein said cinnamic acid amide derivative is formed by N-acylating an *o*-aminophenol or *o*-aminonaphthol with a cinnamic acid halide. 20
- 5 22. A method of preparing a 2-styryloxazole compound, substantially as described in any one of the foregoing Examples 1 to 6.
23. A 2-styryloxazole compound as defined in Claim 1 wherever prepared by the method claimed in any one of Claims 17 to 22.
- 10 24. A process for the optical brightening of organic textile materials, which comprises treating an organic textile material in an aqueous dispersed system containing a 2-styryloxazole compound as claimed in any one of Claims 1 to 16, and 23.
- 15 25. A process according to Claim 24, wherein said organic textile material is formed from polyester, polyacrylonitrile, acetalized polyvinyl alcohol, polyamide or polyolefin fibres. 20
26. A process for the optical brightening of organic textile materials, substantially as described in the foregoing Example 7.
27. Optically brightened organic textile materials, whenever treated by the process claimed in Claim 24, 25 or 26. 25

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