

OPTICALLY BRIGHTENED POLYURETHANE**DESCRIPTION**

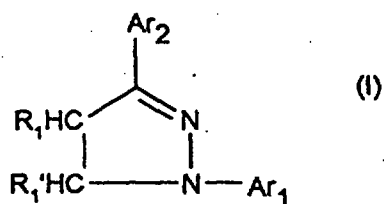
It is already known to brighten polyurethanes (PU) with optical brighteners. This is done by adding selected optical brighteners to the finished polymer and converting this mixture to the desired end product by means of an additional shaping process, for example by compression molding, spinning, extrusion or injection molding. In the case of polyurethane fiber, the optical brightener is preferably applied by means of an exhaust process.

It is also known to brighten PU by dissolving certain optical brighteners from the class of the coumarins in a polyesterpolyol and then preparing the PU by adding an isocyanate component (US 3 380 955). However, the amounts of optical brighteners used therein are extremely low and serve only to mask the yellow color. A true brightening effect is not possible here, since the brighteners used therein do not dissolve sufficiently in the PU. In contrast, for an optimum brightening effect it is necessary for the optical brightener to dissolve well both in the starting components needed to prepare PU and in the polymer itself.

It has now been found that this requirement can be met by brighteners from the class of the pyrazolines and that, using brighteners of this type, very good white effects are obtained in PU.

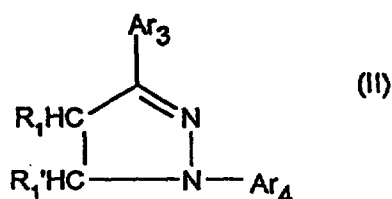
The invention provides optically brightened polyurethanes obtained by polyaddition of polyol components and isocyanate components required to prepare polyurethanes, a pyrazoline brightener being dissolved in the polyol component or isocyanate component.

The optical brighteners of the pyrazoline class which are suitable are preferably those of the formula I



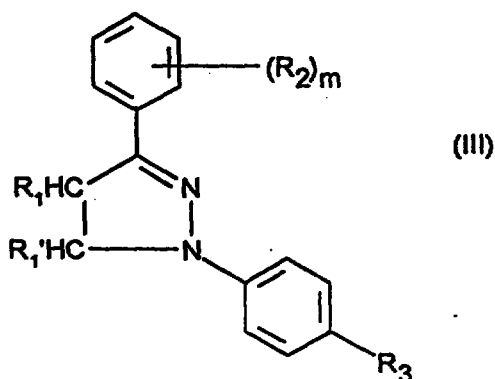
in which Ar_1 and Ar_2 independently of one another are substituted or unsubstituted aryl radicals, and R_1 and R_1' , which can be identical or different, are hydrogen, C_1 - C_4 -alkyl or phenyl.

Of particular interest are compounds of the formula



in which Ar_3 and Ar_4 independently of one another are phenyl, biphenyl or naphthyl radicals which may carry further substituents such as hydroxyl, C_1 - C_6 -alkyl, C_1 - C_6 -alkoxy, halogen, hydroxyalkyl, amino, alkylamino, acylamino, carboxyl, alkoxy carbonyl, sulfonic acid, sulfonic ester, alkylsulfonyl, arylsulfonyl, sulfonyl and sulfonamido groups, and R_1 and R_1' are as defined above.

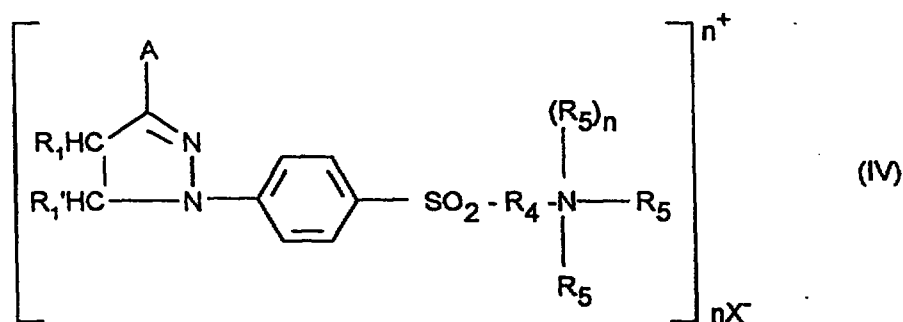
Particular mention should be made of compounds of the formula



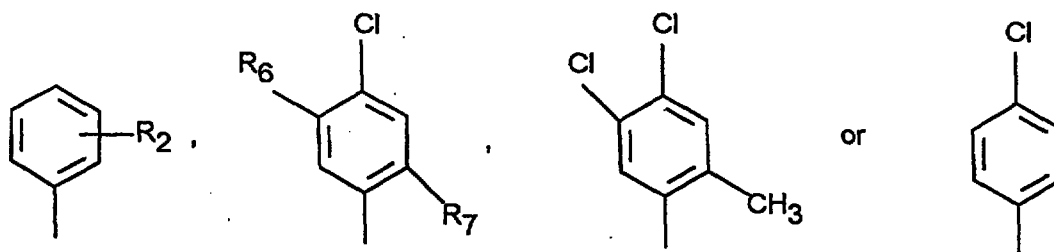
in which R_2 is hydrogen, halogen or C_1 - C_6 -alkyl, R_3 is a substituted or unsubstituted

C₁-C₆-alkoxycarbonyl, C₁-C₆-alkylsulfonyl, sulfonamido or sulfonic acid group, m is zero, 1, 2 or 3, and R₁ and R₁' are as defined above.

Particular preference is given to compounds of the formula



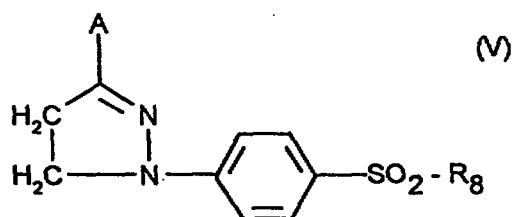
in which A is a group of the formula



R₄ is substituted or unsubstituted C₁-C₆-alkylene, C₁-C₆-alkylene-O-C₁-C₆-alkylene, C₁-C₆-alkylene-CONH-C₁-C₆-alkylene, C₁-C₆-alkylene-COO-C₁-C₆-alkylene, -NH-C₂-C₄-alkylene or -C₂-C₄-hydroxyalkylene-NH-C₂-C₄-alkylene, R₅ independently at each occurrence is hydrogen, C₁-C₆-alkyl or C₂-C₆-hydroxyalkyl or pairs of radicals R₅, together with the nitrogen atom, are a morpholino, pyrrolidino, piperidino, N-alkylpiperazino or N-hydroxyethylpiperazino group, R₆ and R₇ independently of one another are hydrogen, methyl or chlorine, R₁ and R₁' are as defined above, n is zero or 1 and X is a colorless anion.

In the compounds of the formulae I, II, III and IV, R₁ and R₁' are preferably both hydrogen or one substituent R₁ or R₁' is hydrogen and the other substituent is C₁-C₄-alkyl or phenyl.

Common pyrazoline brighteners which are particularly suitable are the compounds of the following formula



in which A is a 4-chlorophenyl group and R_8 is a group of the formula $-NH_2$, $-C_2H_4N(CH_3)_2$, $-CH_2CHCH_3N(CH_3)_2$, $-C_2H_4OC_2H_4N(CH_3)_2$ or $-CHCH_3CH_2N(CH_3)_2$ or A is a 2-methyl-4,5-dichlorophenyl group and R_8 is a group of the formula $-C_2H_4N(CH_3)_2$, $(CH_2)_x-OCOR_9$ or $(CH_2)_x-OR_{10}$, x is a number from 1 to 4, R_9 is C_1 - C_6 -alkyl, preferably C_1 - C_3 -alkyl, or C_1 - C_6 -hydroxyalkyl, preferably C_1 - C_3 -hydroxyalkyl, and R_{10} is hydrogen or C_1 - C_6 -alkyl, preferably C_1 - C_3 -alkyl.

Suitable C_1 - C_6 -alkyl radicals are unbranched and branched alkyl radicals, such as the methyl, ethyl, propyl, butyl, pentyl and hexyl radical. Corresponding comments apply to the C_1 - C_8 -alkoxy groups and to the C_1 - C_6 -alkylene groups.

The formulae I, II, III and V show the pyrazoline compounds in the form of their bases. The invention of course also embraces all pyrazoline brighteners of these formulae which are not in the base form but are in the salt form, i.e. are acid addition salts. Suitable acids for these salts are those having colorless anions, for example C_{1-3} -alkanoates, C_{1-4} -alkanephosphonates, C_{1-4} -alkanesulfonates, C_{2-3} -hydroxyalkanoates, phosphite, sulfamate, halides, methosulfate, p-toluenesulfonate, preferably those which induce good solubility in water.

Depending on the structure and the nature of the anion, the pyrazoline brighteners can be employed as concentrated aqueous or nonaqueous solutions.

These pyrazoline brighteners are dissolved in the polyol components or isocyanate components that are known and customary for the preparation of PU. This is followed by the polyaddition of these components in accordance with customary and known techniques. A suitable isocyanate component here is, in particular, tolylene

diisocyanate, diphenylmethane 4,4'-diisocyanate, naphthylene 1,5-diisocyanate, hexamethylene diisocyanate or 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane or mixtures thereof. Suitable polyol components are all those compounds which contain at least two hydroxyl groups, for example polyetherpolyols, such as, for example, polyethylene glycols, polytetrahydrofuran, polyesterpolyols such as, for example, polyethylene glycol adipate or polycarbonatepolyols. The optical brightener can also have been dissolved in a polyisocyanate or prepolymer customarily used for the preparation of PU, in the presence or absence of an organic solvent such as, for example, dimethylformamide or dimethylacetamide.

The preparation of the polyurethanes from the polyester-, polyether- and polycarbonatepolyols and the polyisocyanates takes place in accordance with the customary methods, which are known in urethane chemistry, with the addition of the customary auxiliaries and additives, such as catalysts, pigments, blowing agents, emulsifiers, surfactants, foam stabilizers, flameproofing agents, UV stabilizers, antioxidants, hydrolysis inhibitors and yellowing inhibitors. Catalysts which can be employed are tertiary amines, such as, for example, triethylamine, dimethylbenzylamine, diazabicyclooctane and also dialkyltin(IV) compounds, such as dibutyltin dilaurate or dibutyltin dichloride, for example. The reaction can take place either without solvent in the melt or in the presence of a solvent. Suitable solvents are those which can be removed later on by distillation, examples being methyl ethyl ketone, methyl isobutyl ketone, acetone, tetrahydrofuran, toluene and xylene. All or part of these solvents can be distilled off after the preparation of the polyurethane dispersion. In addition it is also possible to employ water-dilutable high-boiling solvents, for example N-methylpyrrolidone or dimethylformamide. For further details regarding the preparation of PU reference is made to the relevant literature, e.g. Gertel, Polyurethane Handbook, New York 1985. In addition to the optical brightener, the novel polyurethane may also comprise all of the additives customary in this case, for example light stabilizers of the HALS type.

Example 1

0.06 part of an optical brightener of the formula I was added to 100 parts of a

polyetherpolyol (OH number 45) and was dissolved by heating at 60 - 70°C. Subsequently, 0.15 part of triethanolamine, 0.15 part of tin dioctoate, 0.6 part of a foam stabilizer and 2.7 parts of water and 0.7 part of TiO_2 (anatase) are added. The resulting mixture is added to 35.8 parts of tolyl diisocyanate. The CO_2 which is eliminated in the course of the subsequent reaction causes the polymer to foam up. A polyurethane with excellent white effects is obtained.

Example 2

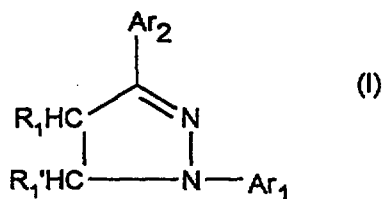
The procedure of Example 1 is repeated except that the brightener is dissolved in tolyl diisocyanate. A polyurethane with excellent white effects is obtained.

Example 3

The procedure of Example 1 is repeated but, in addition, 1 part of a HALS stabilizer @Hostavin NO 20 is incorporated into the polyol. A polyurethane with excellent white effects and high lightfastness is obtained.

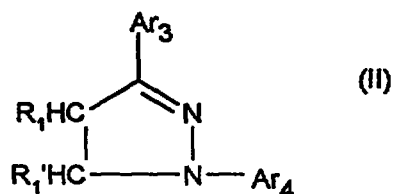
Patent claims:

1. An optically brightened polyurethane obtained by polyaddition of polyol components and isocyanate components required to prepare polyurethane, a pyrazoline brightener being dissolved in the polyol component or isocyanate component.
2. An optically brightened polyurethane as claimed in claim 1, wherein the pyrazoline brightener is of the formula I



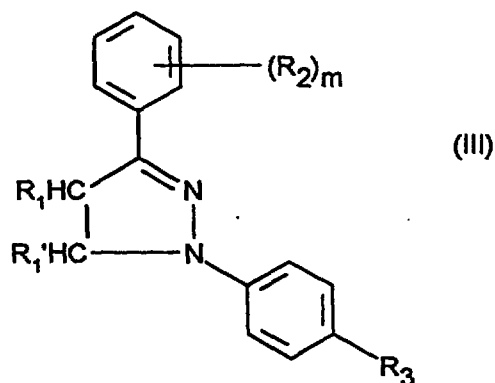
in which Ar_1 and Ar_2 independently of one another are substituted or unsubstituted aryl radicals, and R_1 and R_1' , which can be identical or different, are hydrogen, C_1 - C_4 -alkyl or phenyl.

3. An optically brightened polyurethane as claimed in claim 1, wherein the pyrazoline brightener is of the formula II



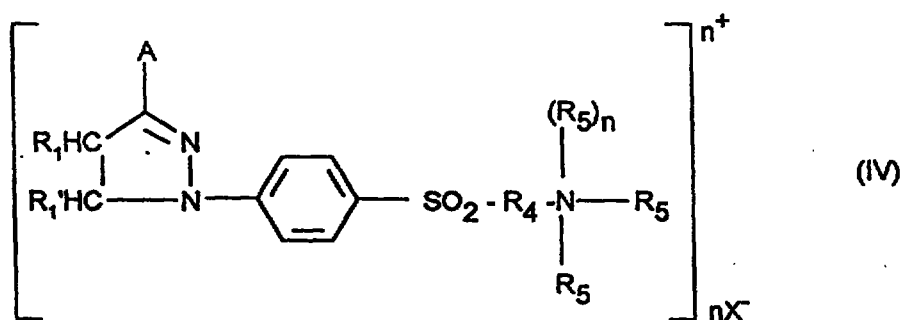
in which Ar_3 and Ar_4 independently of one another are phenyl, biphenyl or naphthyl radicals which may carry further substituents such as hydroxyl, C_1 - C_6 -alkyl, C_1 - C_6 -alkoxy, halogen, hydroxyalkyl, amino, alkylamino, acylamino, carboxyl, alkoxycarbonyl, sulfonic acid, sulfonic ester, alkylsulfonyl, arylsulfonyl, sulfonyl and sulfonamido groups, and R_1 and R_1' are as defined in claim 2.

4. An optically brightened polyurethane as claimed in claim 1, wherein the pyrazoline brightener is of the formula III

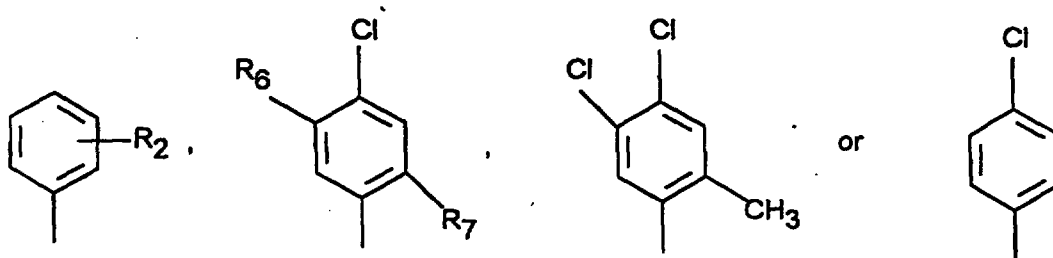


in which R_2 is hydrogen, halogen or C_1 - C_6 -alkyl, R_3 is a substituted or unsubstituted C_1 - C_6 -alkoxycarbonyl, C_1 - C_6 -alkylsulfonyl, sulfonamido or sulfonic acid group, m is zero, 1, 2 or 3, and R_1 and R_1' are as defined in claim 2.

5. An optically brightened polyurethane as claimed in claim 1, wherein the pyrazoline brightener is of the formula IV

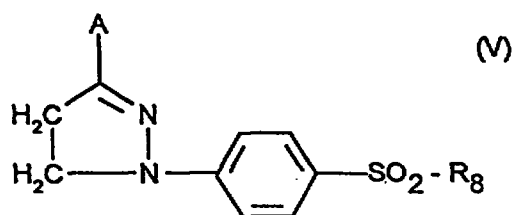


in which A is a group of the formula



R_4 is substituted or unsubstituted C_1 - C_6 -alkylene, C_1 - C_6 -alkylene-O- C_1 - C_6 -alkylene, C_1 - C_6 -alkylene-CONH- C_1 - C_6 -alkylene, C_1 - C_6 -alkylene-COO- C_1 - C_6 -alkylene, -NH- C_2 - C_4 -alkylene or - C_2 - C_4 -hydroxyalkylene-NH- C_2 - C_4 -alkylene, R_5 independently at each occurrence is hydrogen, C_1 - C_6 -alkyl or C_2 - C_6 -hydroxyalkyl or pairs of radicals R_5 , together with the nitrogen atom, are a morpholino, pyrrolidino, piperidino, N-alkylpiperazino or N-hydroxyethylpiperazino group, R_6 and R_7 independently of one another are hydrogen, methyl or chlorine, R_1 and R_1' are as defined in claim 2, n is zero or 1 and X is a colorless anion.

6. An optically brightened polyurethane as claimed in claim 1, wherein the pyrazoline brightener is of the formula V



in which A is a 4-chlorophenyl group and R_8 is a group of the formula $-NH_2$, $-C_2H_4N(CH_3)_2$, $-CH_2CHCH_3N(CH_3)_2$, $-C_2H_4OC_2H_4N(CH_3)_2$ or $-CHCH_3CH_2N(CH_3)_2$ or A is a 2-methyl-4,5-dichlorophenyl group and R_8 is a group of the formula $-C_2H_4N(CH_3)_2$, $(CH_2)_x-OCOR_9$ or $(CH_2)_xOR_{10}$, x is a number from 1 to 4, R_9 is C_1 - C_6 -alkyl, preferably C_1 - C_3 -alkyl, or C_1 - C_6 -hydroxyalkyl, preferably C_1 - C_3 -hydroxyalkyl, and R_{10} is hydrogen or C_1 - C_6 -alkyl, preferably C_1 - C_3 -alkyl.

7. An optically brightened polyurethane as claimed in claim 1, which additionally comprises a HALS light stabilizer.