

Description

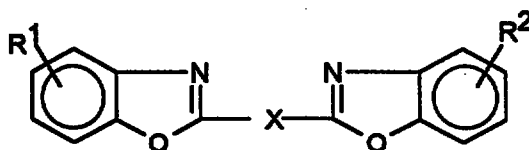
Mixtures of optical brighteners for plastics

Synergistic effects in relation to the use of mixtures of optical brighteners for brightening polyester textile materials are known and are widely used in the textile industry to obtain effect improvements and cost savings. Here the synergy effect evidently results from the special nature of the textile application process, i.e. from the application of the brightener mixture in dispersed form by the exhaust process or the pad-thermosoling process. A literature review and interpretation of the synergism is given in *Melliand Textilberichte* (65) 1984, 327-329.

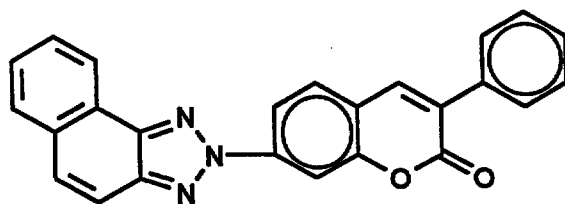
No synergism has hitherto been demonstrated in the field of plastics brightening. White effect increases through a combination of selected optical brighteners where the mixtures exhibit approximately the same or higher white effects than the better or best individual components when used in the same amounts are unknown for plastics.

It has now been found that, surprisingly, synergistic effects can be achieved in plastics too by using specific brightener types as defined hereinafter. The synergistic mixtures are of brighteners having a more reddish hue and brighteners having a more blue hue.

The invention accordingly provides optical brightener mixtures comprising one or more brighteners of the formulae 1 and 1a

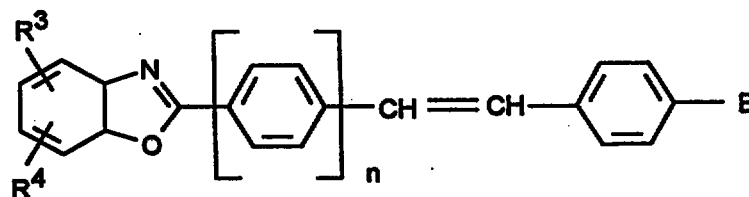


(1)



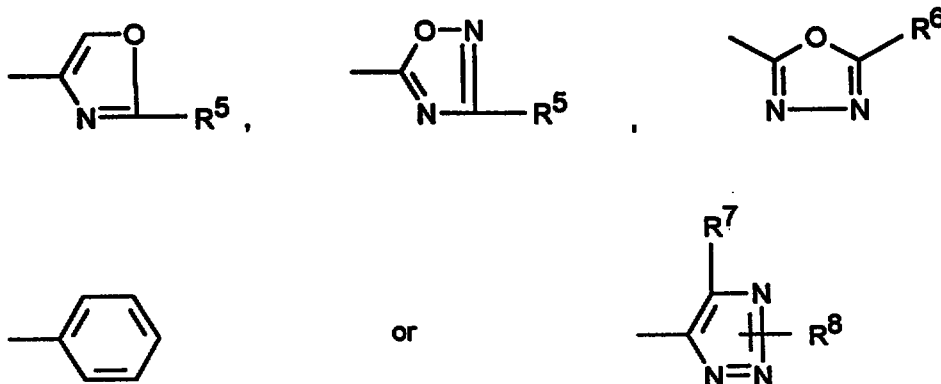
(1a)

where R^1 and R^2 are each hydrogen, C_1 - C_{10} -alkyl or carbo- C_1 - C_4 -alkoxy and X is 1,4-naphthylene, 2,5-thiophene or 2,5-furan, and one or more brighteners of the formula 2



(2)

where R^3 in position 5 is hydrogen or halogen, C_1 - C_4 -alkyl or phenyl and R^4 is hydrogen, or R^3 and R^4 in positions 5 and 6 or in positions 5 and 7 are each methyl, n is 0 or 1, and B is cyano, carbo- C_1 - C_4 -alkoxy or a group of the formula



where R^5 is C_1 - C_6 -alkyl, C_1 - C_8 -haloalkyl, C_1 - C_4 -alkoxy- C_1 - C_4 -alkyl, hydroxy- C_1 - C_4 -alkyl or a group of the formula $-(CH_2CH_2O)_n-R'$, n is 2 or 3, R' is hydrogen or C_1 - C_4 -alkyl, R^6 is phenyl, halophenyl, C_1 - C_4 -alkylphenyl or C_1 - C_4 -alkoxyphenyl, R^7 is cyano or carbo- C_1 - C_4 -alkoxy and R^8 is C_1 - C_4 -alkyl.



Any alkyl or substituted alkyl in the above-defined brighteners preferably has 1 to 4 carbon atoms. Chlorine is preferred as halogen.

The mixing ratio of brighteners (1) and/or (1a) to brightener (2) can be varied within wide limits, for example from 1 to 99 % by weight of one brightener type and the corresponding quantity of the other brightener type. Preference is given to mixtures of 20 - 80 % by weight of the one brightener type and 80 - 20 % by weight of the other.

The brightener mixtures of this invention give rise to synergistic whiteness effects in all known polymers, whether produced by addition polymerization, polyaddition or polycondensation. Examples thereof include polyolefins, polyacetates, polyamides, polystyrene and polyvinyl chloride. Copolymers of different types and proportions of monomers are also contemplated.

The synergism of a superadditive increase in whiteness is very particularly pronounced in the case of polyvinyl chloride, homopolymers of ethylene and vinyl acetate and copolymers of ethylene and vinyl acetate in which the two monomers can be present in any desired ratio. Similarly, the inclusion of a plurality of monomers in the polymerization is possible here, as are blends with other polymers.

The polymers to be brightened with the mixture of this invention can be liquid or solid in consistency, depending on their molecular weight. Of course, these polymers can be produced and formulated in the presence of customary additives, for example titania, zinc oxide, chalk, stearic acid, pigments, plasticizers, lubricants, heat and light stabilizers, antioxidants and foamers.

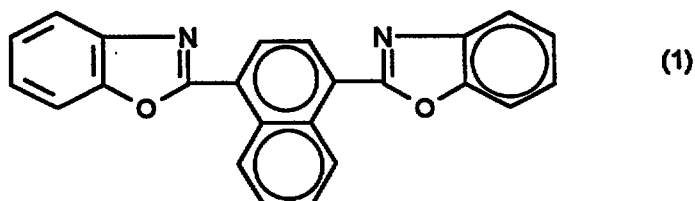
These additives give the plastic its desired consistency and lead to the end product. End products of this type are used as shoe soles, in the electrical industry (cable sheathings), in interior and furniture design, in clothing, in the cosmetics industry and the photographic industry and also as films, profiles and seals and in many other areas of everyday needs.

Besides the synergistic increase in whiteness, the brightener mixtures of this invention have the further advantage that, compared to the individual substances, they exhibit a distinctly enhanced buildup capacity. This means that, using a mixture, significantly more brightener can be dissolved in the plastic, and so higher whiteness effects achieved, than when the individual components are used.

The brightener mixture of this invention can be added prior to the polymerization by dissolving the brightener mixture in monomers, for example vinyl acetate. Another possibility is to apply the brightener mixture to the ready-produced polymer, for example by drum coating, optionally with further additives, for example plasticizers, titania, stabilizers or foamers, and subjecting the resulting mixture to a thermal process corresponding to the processing temperature of the plastic in question. This dissolves or disperses the brightener mixture of this invention in the plastic. The amount of brightener mixture to be used for white articles varies from 1 ppm to 5000 ppm. It is perfectly possible to use higher quantities if master batch preconcentrates are to be prepared for later dilution with further polymer material. Here the brightener proportion, based on the plastic to be brightened, can be 1 to 30 % by weight or more. Of course, the brightener mixture can be premixed with other additives and then added to the plastic. Small quantities (e.g. 1 - 5 ppm) of the brightener mixture of this invention produce less marked daylight white effects, which, however, are sufficient to offset the natural yellow hue of the plastic, or else can be used as indicator under UV light.

Example 1

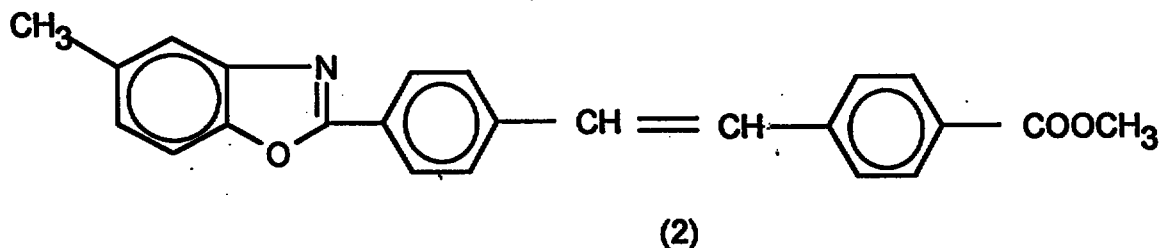
50 g of a pelletized copolymer of ethylene and vinyl acetate with a vinyl acetate content of 50 % were homogeneously mixed with a mixture consisting of 0.36 g of dioctyl phthalate, 0.25 g of TiO_2 (anatase), 0.5 g of stearic acid and 25 mg of the brightener of the formula 1



and then treated for 10 min between two heated rolls (roll stack), one roll being at 90°C and the second at 100°C. The EVA sheet to be removed is very highly optically brightened to a Ganz whiteness of 210 units.

Example 2

Example 1 was repeated using 25 mg of the compound of the formula 2 as brightener



A Ganz whiteness of 176 units was achieved.

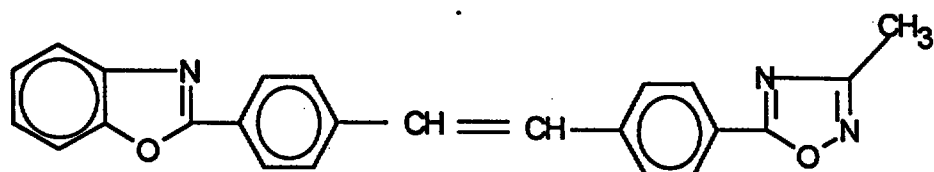
Example 3

Example 1 was repeated with a mixture consisting of 20 mg of brightener 1 of Example 1 and 5 mg of brightener 2 of Example 2 as optical brightener component, affording an excellent white effect of 215 Ganz units.



Example 4

Example 3 was repeated with 20 mg of brightener 1 of Example 1 and 5 mg of the brightener of the formula 3 as optical brightener component



(3)

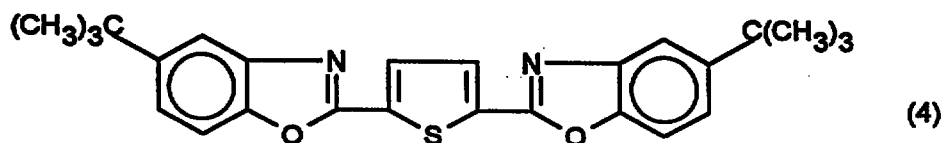
An excellent whiteness of 212 Ganz units was obtained.

Example 5

Example 3 was repeated using 25 mg of brightener 3 of Example 4 as optical brightener. The brightening effects obtained were distinctly lower than in Example 4 and have a greenish cast.

Example 6

Example 1 was repeated using a mixture consisting of 20 mg of the compound of the formula 4



(4)

and 5 mg of brightener 2 of Example 2 as optical brightener component.

The brightening effects achieved are visibly better than the effects obtained using only 25 mg of brightener 4 or only 25 mg of brightener 2 of Example 2.

Example 7

50 g of polyethylene (LDPE) pellets were uniformly drum coated with a mixture of 0.25 g of TiO_2 (rutile) and 3 mg of brightener 2 of Example 2 and also 12 mg of brightener 1 of Example 1 and then processed at 220°C in an injection molding machine. The molding materials obtained are notable for high white effects, amounting to 136 Ganz units.

Example 8

Example 7 was repeated using 15 mg of the brightener of Example 1 as brightener, affording a whiteness of 134 Ganz units.

Example 9

Example 7 was repeated using 15 mg of brightener 2 of Example 2 as brightener, affording a whiteness of 112 Ganz units.

Example 10

Example 3 was repeated using as optical brightener a mixture of 20 mg of brightener 1a and 5 mg of brightener 2 of Example 2. The brightening effects obtained are visibly better than the result from the use of 25 mg of compound 1a. Similarly, the use of 25 mg of brightener 2 of Example 2 gave poorer white effects than the mixture.

Example 11

A mixture consisting of

72.37 parts by weight of PVC powder

25.00 parts by weight of a plasticizer (dioctyl phthalate)

2.00 parts by weight of TiO_2 (rutile)

0.10 part by weight of PE wax

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and 1.50 parts by weight of a stabilizer
was treated on the roll stack at 135°C for 10 min with

- a) 300 ppm of a brightener of the formula 1 of Example 1, or
- b) a mixture of 250 ppm of brightener 1 of Example 1 and 50 ppm of brightener 2 of Example 2, or
- c) 300 ppm of the brightener of Example 2.

The rolled sheet obtained exhibited the following respective white effects according to the formula of Ganz:

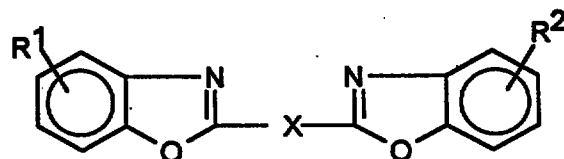
- a) 135 units
- b) 137 units
- c) 125 units.

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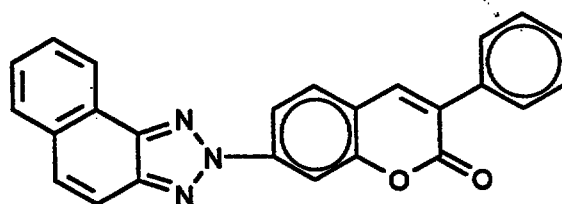


What is claimed is:

1. An optical brightener mixture comprising one or more brighteners of the formulae 1 and 1a

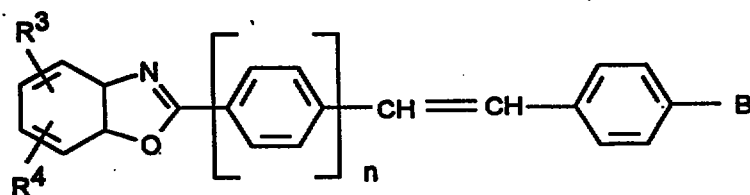


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(1a)

where R^1 and R^2 are each hydrogen, C_1 - C_{10} -alkyl or carbo- C_1 - C_4 -alkoxy and X is 1,4-naphthylene, 2,5-thiophene or 2,5-furan, and one or more brighteners of the formula 2



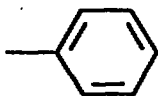
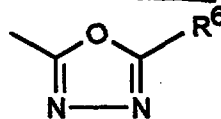
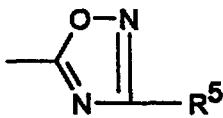
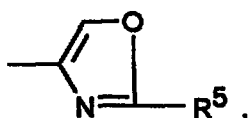
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where R^3 in position 5 is hydrogen or halogen, C_1 - C_4 -alkyl or phenyl and R^4 is hydrogen, or R^3 and R^4 in positions 5 and 6 or in positions 5 and 7 are each methyl, n is 0 or 1, and B is cyano, carbo- C_1 - C_4 -alkoxy or a group of the formula

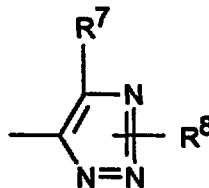


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or



where R^5 is C_1 - C_6 -alkyl, C_1 - C_8 -cycloalkyl, C_1 - C_4 -alkoxy- C_1 - C_4 -alkyl, hydroxy- C_1 - C_4 -alkyl or a group of the formula $-(CH_2CH_2O)_n-R'$, n is 2 or 3, R' is hydrogen or C_1 - C_4 -alkyl, R^6 is phenyl, halophenyl, C_1 - C_4 -alkylphenyl or C_1 - C_4 -alkoxyphenyl, R^7 is C_1 - C_4 -alkyl and R^8 is cyano or carbo- C_1 - C_4 -alkoxy.

2. The use of the optical brightener mixture of claim 1 for brightening plastics.
3. The use of the optical brightener mixture of claim 1 for brightening polyvinyl chloride and homo- and copolymers of ethylene and vinyl acetate.
4. The use of the optical brightener mixture of claim 1 for brightening plastics in an amount of 1 to 5000 ppm.
5. The use of the optical brightener mixture of claim 1 for brightening plastics, wherefor the optical brightener mixture is used in the form of a master batch having a total optical brightener content of 1 to 30 % by weight.



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