



- (51) International Patent Classification:  
*C09D 5/00* (2006.01)
- (21) International Application Number:  
PCT/EP2013/062032
- (22) International Filing Date:  
11 June 2013 (11.06.2013)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
PCT/CN2012/080233  
16 August 2012 (16.08.2012) CN
- (71) Applicant: **BASF COATINGS GMBH** [DE/DE]; Glasuritstrasse 1, 48165 Münster (DE).
- (71) Applicant (*for CY only*): **BASF SCHWEIZ AG** [CH/CH]; Klybeckstrasse 141, CH-4057 Basel (CH).
- (72) Inventors: **POPPE, Andreas**; Am tiefen Weg 8, 97753 Karlstadt (DE). **LIN, Jia**; 706, No. 2, 1458 Gu Mei Road, Shanghai, 201102 (CN). **JIN, Lei**; 602, No. 153, 458 Nan Qi Chang Road, Shanghai, 201600 (CN).

- (81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

**Published:**

— with international search report (Art. 21(3))

(54) Title: COATING COMPOSITIONS CONTAINING BENZOTRIZOL BASED UV-ABSORBERS

(57) Abstract: The present invention relates to a composition, especially an automotive coating composition containing, as an UVA, mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester, wherein the automotive coating composition contains less than 10wt. % of residual free PEG X, based on overall weight of all UVAs present in the automotive coating composition, in which X is a number in the range of more than 100 and less than 1000, and also to a process for producing a coating system, preferably an automotive coating system, comprising application of the coating composition of the present invention.



## COATING COMPOSITIONS CONTAINING BENZOTRIAZOL BASED UV-ABSORBERS

### FIELD OF THE INVENTION

The present invention relates to coating compositions containing  $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid-poly(ethylene glycol) ester as an UV-absorber, and to a process for producing a coating system, particularly an automotive coating system comprising application of the coating composition as at least one layer of the coating system.

### BACKGROUND OF THE INVENTION

UV-absorbers are well known in the state of the art for use in coatings, in particular in automotive coating systems. The UV-protection is achieved not only by the use of UV-absorbers, but normally by a mixture of various stabilizers, such as anti-oxidizing agents, hindered amine light stabilizers, phosphites, phosphonites, etc. A detailed description of all the other components which are useful in combination with UV-absorbers in automotive coatings is available, e.g. in EP 0669330A1, especially page 8 or in WO 2006082145A1, especially pages 26 to 43. Since there is quite some effort to reduce organic volatile components in automotive coatings, one of the key requirements for UV-absorbers in automotive coatings is their compatibility with water-borne coating formulations, which are more and more used in the automotive industry.

It is well known in the state of the art that UV-absorbers (abbreviated as UVAs) based on benzotriazoles are very effective as described by *Andreas Valet*, "Lichtschutzmittel für Lacke. Die Technologie des Beschichtens, Vincentz, 1996". Since these UVAs have a very unique structure and hydrophobic properties, the challenge is to render these basically very hydrophobic molecules much more hydrophilic to make them more compatible with water-borne coatings. It is also well known that the UVA-based light stabilizers can have quite some interactions - even if they are used in original equipment manufacture clear coat (abbreviated as OEM CC) - with pigments coming from the base coats, as described by *G. Haacke, E. Longordo, F. F. Andrawes, B. H. Campbell, Progress in Organic Coatings 34 (1998), 75-83*. The basic understanding and evidence that there is also quite some potential of the UVA-light stabilizer to migrate through various layers in the coating system are described by *Karlis Adamsons, Progress in Organic Coatings 45 (2002), 69-81* and also by *K Leo G. J. van der Ven, Rene T.M. Leijzer, Keimpe J. van den Berg, Pokon Ganguli, Rob Lagendijk, Progress in Organic Coatings 58 (2007) 117-121*.

Those interactions will occur also for other UVAs, such as hydroxyphenyl-s-triazines, oxalanilides, hydroxyphenylpyrimidines or hydroxybenzophenones. However, due to the fact that the benzotriazoles show a much more suitable absorption spectrum to enhance durability, as described by A. Valet "Lichtschutzmittel für Lacke", pp. 23, benzotriazoles are much more preferred for the application in automotive OEM coatings.

The interaction and migration occur due to the hydrophobic property profile of the UV-absorbers. Based on that, an improved compatibility is most likely obtained by UVAs which do exhibit amphiphilic properties. In order to improve the compatibility of the UVAs, various modifications have been developed, for example, modification of benzotriazoles with aromatic substituents, substituents based on sulfonic acid or modification based on polyethylene oxide substituents.

In the state of the art, there are quite some examples that those benzotriazole light stabilizers are commonly used in OEM clear coats. The use of these materials in base coats is also described in literatures, e.g. US 6284183 B1, Example 1, black base coat, but in practice the use of UVAs in base coats is rather limited.

In general, examples of benzotriazole based UV-absorbers include, but not limited to,

Mixtures of 95% by weight of C<sub>7-9</sub> branched and linear alkyl esters of 3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxy-benzenepropanoic acid and 5% by weight of 1-methoxy-2-propyl acetate that are commercially available under **Tinuvin 384-2** from BASF SE, Ludwigshafen, Germany, or **Eversorb 81** from Everlight (Taipei, Taiwan);

2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol, which is commercially available under **Tinuvin 900** from BASF SE or under **Eversorb 234** from Everlight; and

Mixture of mono{β-[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG 300 ester (approx. 50 wt. %), Bis{β-[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG 300 ester (approx. 38 wt. %) and PEG 300 (approx. 12 wt. %), which is commercially available under **Tinuvin 1130** from BASF SE or under **Eversorb 80** from Everlight.

However, except for **Tinuvin 1130** and **Eversorb 80**, all of the above listed UV-absorbers are very hydrophobic, which are rather incompatible with water borne coating formulations due to that hydrophobic property.

In the state of the art, another approach is described to render the benzotriazole based UV-absorbers more hydrophilic. That is based on the modification by sulfuric components which then can be converted to sulfonic acids as described in the publication EP 0323853 A2.

However, this approach implies that there will be an interaction between the UV-absorber and any electrostatically stabilized particles in the water borne base coat formulations. Even though, such kind of sulfonic acid stabilized UV-absorbers might be soluble also in solvent borne OEM CC and consequently be incorporated into the solvent borne clear coat, after spraying in a wet in wet process on the uncured base coat, there are possible ionic interactions which most likely will lead to particle destabilization due to increasing ionic strength.

The overall target of the automotive industry is to reduce cost and to provide excellent coating properties even within much lower film builds (film thickness). In this context, one challenge is to identify suitable UV-absorbers, which can be embedded into the multi-layer coating systems in a way that the coating provides excellent appearance already at very low film builds, which is most critical for the automotive Base Coat - Clear Coat wet in wet

applications. In particular, the application of OEM CC at low film builds can be very critical and in general it can be said that the overall appearance of an automotive coating system very strongly depends on the overall film build.

Also, one another option to improve the overall appearance of the coating system is to embed the UVAs in the water borne base coat (abbreviated hereinafter as WBBC) and not anymore in the OEM CC. This could be one advantage, presuming that with this step the overall appearance of the total coating system can be improved.

With the increasing demand for thin film builds of the automotive coating system and less coating consumption, there is still the need to improve the appearance of the automotive coating system, in particular at a lower film build of the clear coat, which is extremely sensitive to any incompatibility.

It was therefore an object of the present invention to provide an UV-absorber and a coating composition, in particular an automotive coating composition, containing an UV-absorber, which UV-absorber exhibits improved compatibility with water borne automotive coatings, in particular base coats and does not possess the disadvantages of the known UV-absorbers. In addition, the UV-absorbers should be soluble within automotive clear coats at least to the extent they migrate into them as well as within automotive base coats, in particular water borne automotive base coats.

## SUMMARY OF THE INVENTION

It has been surprisingly found that the object of the present invention can be achieved by use of a mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]-propionic acid}-PEG X ester in automotive coating systems as an UV-absorber with reduced amount of residual free PEG X, in which X is a number in the range of more than 100 and less than 1000.

Accordingly, the present invention provides a composition, especially an automotive coating composition, which contains as an UVA mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester, wherein the automotive coating composition contains less than 10 wt. % of residual free PEG X, based on overall weight of all UVAs present in the automotive coating composition, in which X is a number in the range of more than 100 and less than 1000.

More particularly, the present invention relates to the following aspects:

**1).** A coating composition, preferably an automotive coating composition, containing a mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester as an UV-absorber, characterized in that

the coating composition contains less than 10 % by weight of free PEG X, based on the overall weight of all UVAs in the coating composition,

wherein the free PEG X refers to unesterified poly(ethylene glycol) with a weight average molecular weight of X in g/mol and wherein X is a number in the range of from 100 < X < 1000, which comes from preparation of the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-

butyl-4-hydroxyphenyl]propionic acid}-PEG X ester with the PEG X as a starting material and remains as an impurity of the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester.

2). The coating composition according to above 1), wherein X is in the range of  $100 < X \leq 600$ .

3). The coating composition according to above 1), wherein X is in the range of  $200 \leq X \leq 400$ .

4). The coating composition according to any of above 1) to 3), wherein the composition contains less than 8 % by weight of the free PEG X, based on the overall weight of all UVAs in the coating composition.

5). The coating composition according to any of above 1) to 3), wherein the composition contains less than 10 % by weight of bis{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester, based on the overall weight of all UVAs in the coating composition.

6). The coating composition according to above 1) to 5), wherein the UV-absorber exhibits a solubility parameter of more than 10.4.

7). The coating composition according to above 1) to 5), wherein the UV-absorber exhibits a solubility parameter of more than 13.5.

8). The coating composition according to above 1) to 7), wherein the coating composition does not contain any other UV-absorbers.

9). The coating composition according to any of above 1) to 8), which is used as an OEM clear coat and/or an OEM base coat.

10). The coating composition according to above 9), which is water borne.

11). The coating composition according to above 10), which is used as a water borne OEM base coat.

12). A multilayer coating system which comprises a pigmented and/or effect coating layer and a clearcoat layer, wherein the pigmented and/or effect coating layer and/or the clearcoat layer, preferably the pigmented coating layer contains the UV absorber as defined in any of above 1) to 8).

13). A process for producing a coating system, preferably an automotive coating system, comprising application of the coating composition according to any of above 1) to 11) as at least one layer of the coating system, preferably the automotive coating system.

14). The process for producing an automotive coating system according to above 13), wherein the automotive coating composition according to any of above 1) to 11) is applied as OEM clear coat and/or an OEM base coat.

15). The process for producing an automotive coating system according to above 14), wherein the automotive coating composition according to any of above 1) to 11) is applied as the OEM base coat and the OEM clear coat of the automotive coating system does not contain any organic UVAs.

## BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a graph showing UV absorption spectra of one of the UV-absorbers of the present invention, i.e. mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG 300 ester in a concentration of 92 wt% and with a content of free PEG X of 0.3 weight % (Sample 2)), and of Tinuvin 1130 and Eversorb 80 as comparative UV-absorbers, in which the abscissa represents the wave length and the ordinate represents the absorbance. The three absorption curves from top to bottom represent the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG 300 ester (curve 1), Tinuvin 1130 (curve 2) and Eversorb 80 (curve 3), respectively.

Figure 2 is a graph showing the purities of the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG 300 ester of the present invention (one UV-absorber of the present invention), Tinuvin 1130 and Eversorb 80, as measured by HPLC. The term Monoester represent the component mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG 300 ester present in each sample, and the term Diester represents the component bis{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG 300 ester in each sample. All ratios indicated above the peaks represent Eversorb 80 : the UV-absorber of the present invention: Tinuvin 1130.

Figure 3 is a bar graph showing the results of LW-Wavescan at different CC film builds for each sample prepared in the Formulation Examples. In this graph, at each CC film build, the bars arranged from left to right represents Reference 1, Reference 2, Reference 3, Formulation 1, Formulation 2 and Formulation 3 respectively.

Figure 4 is a bar graph showing the results of SW-Wavescan at different CC film builds for each sample prepared in the Formulation Examples. In this graph, at each CC film build, the bars arranged from left to right represents the Reference 1, Reference 2, Reference 3, Formulation 1, Formulation 2 and Formulation 3 respectively.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a coating composition containing mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester as an UV-absorber, characterized in that

the coating composition contains less than 10 % by weight of free PEG X, based on the overall weight of all UVAs present in the automotive coating composition,

wherein the free PEG X refers to unesterified poly(ethylene glycol) with a weight average molecular weight of X in g/mol and wherein X is a number in the range of from  $100 < X < 1000$ , which comes from preparation of the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester with the PEG X as a starting material and remains as an impurity of the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester.

In a preferable embodiment, the coating composition of the present invention contains less than 8 % by weight of the free PEG X based on the overall weight of UVAs in the automotive coating composition, more preferably less than 5 % by weight, still preferably less than 4% by weight, and even preferably less than 1% by weight, for example 0.3% by weight.

In a further preferable embodiment, the coating composition of the present invention contains less than 10 % by weight of bis{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester, based on the overall weight of all UVAs in the coating composition.

In a still preferable embodiment, the compatibility of the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester is above 10.4, preferably above 13.5, and more preferably below 15, measured as solubility parameter.

The coating composition of the present invention is preferably an automotive coating composition.

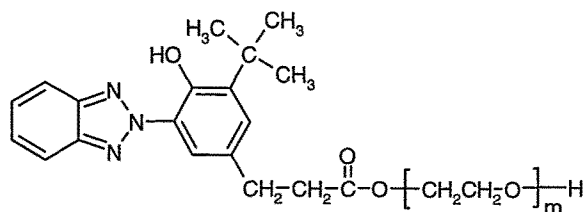
It will be understood that the “PEG-X” occurs in the terms mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester and bis{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester represents the moieties derived from the free PEG-X as defined hereinabove during the ester formation.

It will also be understood that the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester means the materials have the same structures as the monoesters obtained from the esterification of  $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid with free PEG X. However, the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X esters according to the present invention are not limited to those derived from esterification reaction.

The bis{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester optionally present in the coating composition of the present invention represents a byproduct during the preparation of the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester.

### UV-absorbers

The compounds that are used as the UV-absorber of the present invention *per se* are known in the state of the art, i.e. mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester in which X is in the range of from  $100 < X < 1000$ , which may be represented by the following formula:



Wherein m is an average number of the oxyethylene repeating unit derived from the PEG

X in which X is in the range of from  $100 < X < 1000$ .

In the state of the art, mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X esters are used as a mixture with bis{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X esters and free PEG X, which mixture is obtained from the preparation reaction to obtain the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X esters. As an example, the mixture under **Tinuvin 1130** and **Eversorb 80** may be mentioned, in which the contents of free PEG X and bis{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X esters are relatively high. However, the use of the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X esters in which X is in the range of from  $100 < X < 1000$  without byproducts or at least with reduced amounts of byproducts, as an UV-absorber in automotive coating composition are not known in the state of the art.

In a preferable embodiment, the UV-absorber of the present invention is mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X esters in which X is in the range of from 200 to 600 or less, more preferably 200 to 400.

The mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X esters as described above can be obtained by various methods known in the state of the art.

The mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X esters of the present invention may be obtained by separation from the commercially available mixtures containing the reaction product of  $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid with PEG X wherein X is a number in the range of from  $100 < X < 1000$ , preferably  $200 \leq X \leq 600$ , most preferably  $200 \leq X \leq 400$ , such as Tinuvin 1130 (available from BASF SE) or Eversorb 80 (available from Everlight) or any other products which may be available by suppliers not mentioned here.

Alternatively, the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X esters of the present invention may be prepared according to the methods known in the state of the art, for example in WO 02/24668 A1 wherein the preparation of mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG PEG 300 ester are described, or in US 7915322 B2.

It is also possible to prepare mono methyl ester of  $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid first and then transfer it into the PEG X monoester (such as PEG 200 monoester, PEG 300 monoester, PEG 600 monoester or similar, etc.) by conventional transesterification procedures. The mono methyl ester of  $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid may be synthesized by the procedures as described in WO 02/24668A1, especially Example 19 or by enzymatic synthesis methods as described by *M. Schroeder, L. Pereira, S. Rodriguez Couto, A. Erlacher, K.-U. Schoening, A. Cavaco-Paulo, G. M. Guebitz, Enzyme and Microbial Technology 40 (2007), 1748-1752.*

Moreover, the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X (e.g. PEG 200) esters of the present invention may also be prepared as described in US 7915322 B2, especially Example 5, except that no step of adding methacrylic acid is



carried out.

Any purification processes known in the state of the art, for example column chromatography, may be used in order to reduce the content of impurities, especially of the free PEG X, to obtain the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X esters with reduced amounts of impurities as used in the present invention, i.e. the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester with less than 10 % by weight of the free PEG X impurity.

Preferably, the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester is prepared as described in WO 02/24668A1, and then separated by column chromatography as described in Example 5 of US 7915322 B2. In order to improve the purity of the resulting mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X, the purification process of column chromatography might be repeated once or two time to reduce the amount of residual free PEG X even below 1 wt. %.

The resulting mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X esters of the present invention may be characterized with HPLC or UV-spectroscopy. Both methods can indicate the purity and also the effective UV-absorption of the purified material.

The hydrophilicity of the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X (e.g. PEG 200) ester UV-absorbers may be measured easily in the laboratory by applying the so called solubility parameter. The exact procedure to measure this parameter is described in *K. W. Suh, J. M. Corbett, Journal of Applied Polymer Science, Vol. 12, pp 2359-2370 (1968)*. Additionally, a more detailed description of the calculation as well as the sample volumes for the titrations is described in WO 2008/148555 A1

Preferably, the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X (e.g. PEG 200) ester UV-absorbers used in the automotive coating composition of the present invention exhibits a solubility parameter of more than 10.4 and below 15, more preferably more than 13.5. The most preferable range of the solubility parameter is in the range between 13.5 and 15.

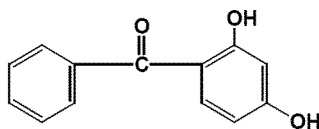
In general, a higher numerical value of a solubility parameter corresponds to a more hydrophilic property profile of the molecules, while a lower numerical value means a rather hydrophobic profile. Consequently, one option to increase the solubility parameters is to introduce hydrophilic substituents into the molecule. As described in the introduction, the standard benzotriazole UVAs are rather hydrophobic which is represented by a solubility parameter of 9.41 for a standard grade.

In addition to the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester UV-absorbers, the automotive coating composition of the present invention may contain one or more other UV-absorber(s) commonly used in an automotive coating composition in the state of the art. However,

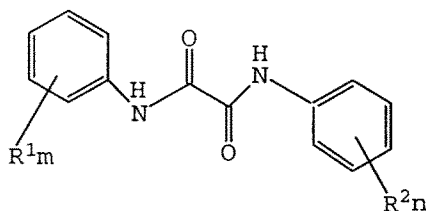
preferably there is no other organic UV-absorbers than the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X as described above present in the automotive coating composition of the present invention. By limiting the number of different UVAs in a coating system, also the danger that some of the materials are not compatible with each other is reduced. Incompatibilities of different UVAs are likely to result in poor appearance of the final cured coating film.

Nevertheless, according to the present invention, the UV-absorbers capable to be modified with a PEG X polymeric chain are not limited to the benzotriazole types as described above. In particular also the following types can be modified with a PEG X polymeric chain to render them hydrophilic:

1) Benzophenone(s) and in particular their derivatives such as Hydroxybenzophenones, e.g., 2,4-dihydroxybenzophenone:

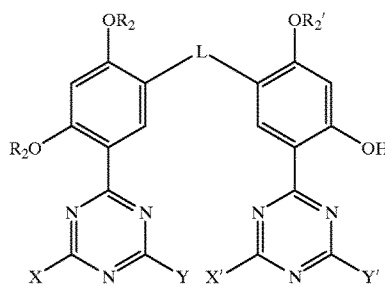
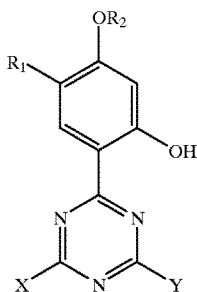


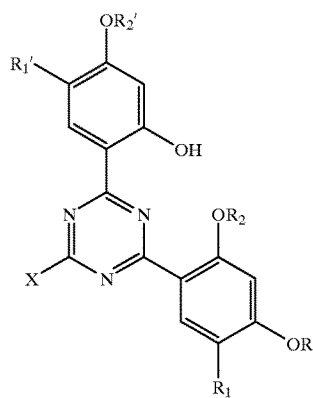
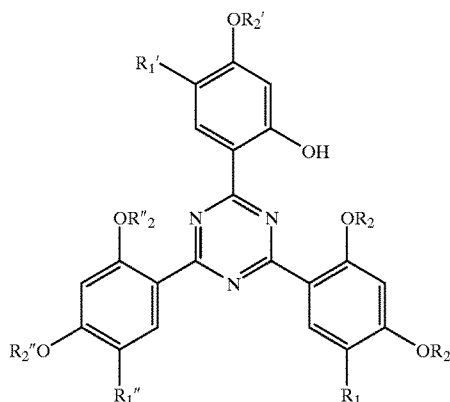
2) Oxalanilides and their derivatives such as mentioned in EP 0727318A1, a non-limiting example is:



wherein  $R^1m$  and  $R^2n$  are defined as in EP 0727318 A1 (see lines 47, page 2 to line 8, page 3, especially, the Table in page 3), provided that at least one of  $R^1$  and  $R^2$  is hydroxyl group.

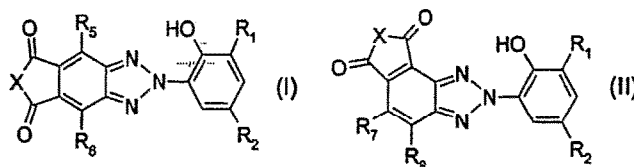
3) Hydroxyphenyl-S-Triazines and their derivatives, as for reference they are described in the state of the art in US 6191199 B1, non-limiting examples are listed as follows:





wherein the variables in the above formulae are defined as in US 6191199 B1 (*see line 10, column 4 to line 41, column 8*).

4) Specially modified benzotriazoles, in particular such as those mentioned in WO 2006/082145A1:



wherein the substituents are defined as in WO 2006/082145A1.

The esterification of phenolic hydroxyl is known in the state of the art and can be done for the above Benzophenones, Oxalanilides and Triazines. According to the acidity of the phenolic hydroxyl, suitable catalysts may be employed. For the specially modified Benzotriazoles, the same approach as described herein is applicable.

Such modified UV-absorbers with PEG X may be used instead of or in addition to the mono { $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester UV-absorbers of the present invention in the automotive coating composition.

### **Other components in the automotive coating composition**

In addition to the UV-absorbers as described above, the composition of the present invention, preferably the automotive coating composition comprises other components conventionally used in such compositions.

One of the latest and more general overviews of the compositions of these coatings is given in "Automotive Paints and Coatings", edited by Hans-Joachim Streitberger and Karl – Friedrich Dössel, Wiley – VCH, 2008.

The details of base coat compositions are disclosed on page 175 – 189, and the clear coat technology is described in detail on pages 189 – 206.

Also in "Coatings Formulation", edited by Ulrich Poth and Bodo Müller, Vincentz Network, 1<sup>st</sup> edition, May 2006, a comprehensive overview about the different ingredients for, both the solvent borne and water borne base coats which are cured at elevated temperatures and also the OEM clear coat formulations can be found.

More specifically, detailed examples for water borne base coats can be found in the following patent disclosures: EP 0 089 497 A1, EP 0 256 540 A1, EP 0 260 447 A1, EP 0 297 576 A1, WO 96/12747, EP 0 523 610 A1, EP 0 228 003 A1, EP 0 397 806 A1, EP 0 574 417 A1, EP 0 531 510 A1, EP 0 581 211 A1, EP 0 708 788 A1, EP 0 593 454 A1, DE 43 28 092 A1, EP 0 299 148 A1, EP 0 394 737 A1, EP 0 590 484 A1, EP 0 234 362 A1, EP 0 234 361 A1, EP 0 543 817 A1, WO 95/14721, EP 0 521 928 A1, EP 0 522 420 A1, EP 0 522 419 A1, EP 0 649 865 A1, EP 0 536 712 A1, EP 0 596 460 A1, EP 0 596 461 A1, EP 0 584 818 A1, EP 0 669 356 A1, EP 0 634 431 A1, EP 0 678 536 A1, EP 0 354 261 A1, EP 0 424 705 A1, WO 97/49745, WO 97/49747, EP 0 817 684 A1, WO 97/14721, WO 97/49747, WO 97/49745, WO 96/12747.

For a more detailed description, suitable typical ingredients for water borne basecoat formulations will be illustrated hereinafter.

Deionized water at content from 40 – 90 wt. % depending on the particular materials may be contained in the water borne basecoat formulations.

In addition, binders are used in the formulations.

The binders contain functional groups which render them dispersible in water and/or soluble in water. These are alternatively

- functional groups which can be converted into cations by neutralizing agents and/or quaternizing agents, or
- functional groups which can be converted into anions by neutralizing agents, and/or anionic groups, and/or
- nonionic hydrophilic groups, especially poly(alkylene ether) groups.

Examples of suitable functional groups which can be converted into cations by neutralizing agents and/or quaternizing agents are primary, secondary or tertiary amino groups, secondary sulfide groups or tertiary phosphine groups, especially tertiary amino groups or secondary sulfide groups.

Examples of suitable cationic groups are primary, secondary, tertiary or quaternary ammonium groups, tertiary sulfonium groups or quaternary phosphonium groups, preferably quaternary ammonium groups or tertiary sulfonium groups, but especially tertiary sulfonium groups.

Examples of suitable functional groups which can be converted into anions by neutralizing agents are carboxylic, sulfonic or phosphonic acid groups, especially carboxylic acid groups.

Examples of suitable anionic groups are carboxylate, sulfonate or phosphonate groups, especially carboxylate groups.

Examples of suitable neutralizing agents for functional groups convertible into cations are inorganic and organic acids such as sulfuric acid, hydrochloric acid, phosphoric acid, formic acid, acetic acid, lactic acid, dimethylolpropionic acid or citric acid.

Examples of suitable neutralizing agents for functional groups convertible into anions are

ammonia, amines such as trimethylamine, triethylamine, tributylamine, or amino alcohols, dibutylamine, dimethylaniline, diethylaniline, triphenylamine, dimethylethanolamine, diethylethanolamine, methyldiethanolamine, 2-aminomethylpropanol, dimethylisopropylamine, dimethylisopropanolamine or triethanolamine, for example. Preferred neutralizing agents used are dimethylethanolamine, dibutylamine and/or triethylamine.

The complementary reactive functional groups described above may be incorporated into the binders by the customary and known methods of polymer chemistry. This can be done, for example, by incorporating monomers which carry the corresponding reactive functional groups, and/or by means of polymer-analogous reactions. Examples of suitable olefinically unsaturated monomers containing reactive functional groups by means of which these groups may be introduced into (meth)acrylate copolymers are monomers which carry per molecule at least one hydroxyl, amino, alkoxymethylamino, carbamate, allophanate or imino group, such as hydroxy alkyl esters of acrylic acid, methacrylic acid or another  $\alpha,\beta$ -olefinically unsaturated carboxylic acid which are derived from an alkylene glycol which is esterified with the acid, or which are obtainable by reacting the  $\alpha,\beta$ -olefinically unsaturated carboxylic acid with an alkylene oxide such as ethylene oxide or propyleneoxide, especially hydroxy alkyl esters of acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, maleic acid, fumaric acid or itaconic acid in which the hydroxy alkyl group contains up to 20 carbon atoms, such as 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 3-hydroxybutyl, 4-hydroxybutylacrylate, methacrylate, ethacrylate, crotonate, maleate, fumarate or itaconate; or hydroxycycloalkyl esters such as 1,4-bis(hydroxymethyl)cyclohexane, octahydro-4,7-methano-1H-indenedimethanol or methylpropanediol monoacrylate, monomethacrylate, monoethacrylate, monocrotonate, monomaleate, monofumarate or monoitaconate; reaction products of cyclic esters, such as  $\epsilon$ -caprolactone, for example, and these hydroxyalkyl or hydroxycycloalkyl esters; olefinically unsaturated alcohols such as allyl alcohol polyols such as trimethylolpropane monoallyl or diallyl ether or pentaerythritol monoallyl, diallyl or triallyl ether; reaction products of acrylic acid and/or methacrylic acid with the glycidyl ester of an  $\alpha$ -branched monocarboxylic acid having 5 to 18 carbon atoms per molecule, especially a Versatic® acid, or, instead of the reaction product, an equivalent amount of acrylic acid and/or methacrylic acid which subsequently, during or after the polymerization reaction, is reacted with the glycidyl ester of an  $\alpha$ -branched monocarboxylic acid having 5 to 18 carbon atoms per molecule, especially a Versatic® acid; aminoethyl acrylate, aminoethyl methacrylate, allylamine or N-methyliminoethyl acrylate; N,N-di(methoxymethyl)aminoethyl acrylate or methacrylate or N,N-di(butoxymethyl)aminopropyl acrylate or methacrylate.

Typically, as one particular binder component, melamine resins are used to achieve crosslinking. Those resins are polycondensation resins formed from melamine (1,3,5-triazine-2,4,6-triamine) and a maximum of 6 mol of formaldehyde per mole of melamine. Some or all of the resulting methylol groups may be etherified with one or more different alcohols. Thus, melamine resins may have different degrees of methylation and different degrees of etherification.

The degree of methylation of a melamine resin describes how many of the possible methylation sites of the melamine have been methylated, i.e., how many of the total of six hydrogen atoms of the primary amino groups of melamine (i.e., of 1,3,5-triazine-2,4,6-triamine) have been replaced by a methylol group. A fully methylated mononuclear melamine resin, accordingly, has six methylol groups per triazine ring, such as hexamethylolmelamine, for example. The methylol groups may independently of one another also be in etherified form.

Typically, basecoat materials contain preferably 0% to 20% by weight of melamine resin.

Additionally, Polyester Binders may be employed. By polyester binders are meant polyester resins and polyester-polyurethanes. The basecoat materials contain 0% to 30 % by weight polyester binders (PE). Suitable polyester binders may be saturated or unsaturated, especially saturated. Unsaturated polyester binders are those which contain at least one polymerizable carbon-carbon double bond. Saturated polyester binders are those which contain no polymerizable carbon-carbon double bond.

As polyester binders it is preferred to use polyester resins. Polyester resins can be prepared by esterifying organic dicarboxylic acids or their anhydrides with organic diols, or may derive from a hydroxycarboxylic acid or a lactone. With particular preference the polyester resins are prepared by esterifying organic dicarboxylic acids or their anhydrides with organic diols. The particularly preferred polyester resins therefore comprise structural units which originate from aliphatic, cycloaliphatic and/or aromatic dicarboxylic and/or polycarboxylic acids and from diols and/or polyols. In order to prepare branched polyester resins it is possible to a small extent also to use polyols or polycarboxylic acids having a functionality of greater than 2. The dicarboxylic and/or polycarboxylic acids and diols and/or polyols may be linear or branched aliphatic, cycloaliphatic or aromatic dicarboxylic and/or polycarboxylic acids or diols and/or polyols.

Examples of diols suitable for preparing the polyester resins include alkylene glycols, such as ethylene glycol, propylene glycol, butylene glycol, butane-1,4-diol, hexane-1,6-diol, neopentylglycol, and other diols, such as dimethylolcyclohexane. It is also possible, however, to add small amounts of polyols, such as trimethylolpropane, glycerol or pentaerythritol, for example. The acid component of the polyester is composed primarily of low molecular weight dicarboxylic acids or their anhydrides having 2 to 44, preferably 4 to 36, carbon atoms in the molecule. Examples of suitable acids include o-phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, cyclohexanedicarboxylic acid, succinic acid, adipic acid, azelaic acid, sebacic acid, maleic acid, fumaric acid, glutaric acid, hexachloroheptanedicarboxylic acid, tetrachlorophthalic acid and/or dimerized fatty acids. Instead of these acids it is also possible to use their anhydrides, where they exist. In the formation of polyester polyols it is also possible to use relatively small amounts of carboxylic acids having 3 or more carboxyl groups, examples being trimellitic anhydride or the adduct of maleic anhydride with unsaturated fatty acids.

Further binders that are used typically are, for example, random, alternating and/or block, linear and/or branched and/or comb (co)polymers of ethylenically unsaturated monomers, or polyaddition resins and/or polycondensation resins. For further details of these terms, refer to Rompp Lexikon Lacke und Druckfarben, Georg Thieme Verlag, Stuttgart, New York, 1998, page 457, "Polyaddition" and "Polyadditionsharze (Polyaddukte)" [Polyaddition Resins (Polyadducts)], and also pages 463 and 464, "Polykondensate" [Polycondensates], "Polykondensation" [Polycondensation], and "Polykondensationsharze" [Polycondensation resins], and also pages 73 and 74, "Bindemittel" [Binders]. As particular examples for "Polyaddition" resins, Polyurethane dispersions are mentioned. Those Polyurethane dispersions are manufactured in addition reactions in process solvents. Typically, as educts, polyisocyanates, especially diisocyanates are employed together with polyols, especially diols or triols based on polyether or polyester. A more detailed description of the suitable raw materials and processes to prepare Polyurethane dispersions is described in "Automotive Paints and Coatings", edited by Hans-Joachim Streitberger and Karl – Friedrich Dössel, Wiley – VCH, 2008, pp. 231- 241 and in EP 0401565 A1, EP 0522420 A1, EP 0522419 A2 and EP 0730613 A1. The organic polyisocyanate can be an aliphatic polyisocyanate, including a cycloaliphatic polyisocyanate or an aromatic polyisocyanate. Useful aliphatic polyisocyanates include aliphatic diisocyanates such as ethylene diisocyanate, 1,2-diisocyanatopropane, 1,3-diisocyanatopropane, 1,6-diisocyanatohexane, tetramethylenediisocyanate, lysine diisocyanate, methylene bis(4-cyclohexylisocyanate), 4,4'-Dicyclohexylmethanediisocyanate and isophorone diisocyanate. Useful aromatic diisocyanates and araliphatic diisocyanates include the various isomers of toluene diisocyanate, meta-xylylene diisocyanate and para-xylylene diisocyanate, also 4-chloro-1,3-phenylene diisocyanate, 1,5-tetrahydro-naphthalene diisocyanate, 4,4'-dibenzyl diisocyanate and 1,2,4-benzene triisocyanate. In addition, the various isomers of alpha,alpha,alpha',alpha'-tetramethyl xylylene diisocyanate can be used. Also useful as the polyisocyanate are isocyanurates such as DESMODUR® 3300 from Bayer and biurets of isocyanates such as DESMODUR® N100 from Bayer.

Examples of suitable polyols are diols and triols, especially diols. Normally, triols are used alongside the diols in minor amounts in order to introduce branches into the polyester polyols.

Suitable diols are ethylene glycol, 1,2- or 1,3-propanediol, 1,2-, 1,3- or 1,4-butanediol, 1,2-, 1,3-, 1,4- or 1,5-pentanediol, 1,2-, 1,3-, 1,4-, 1,5- or 1,6-hexanediol, neopentyl glycol mono(hydroxypivalate), neopentyl glycol, diethylene glycol, 1,2-, 1,3- or 1,4-cyclohexanediol, 1,2-, 1,3- or 1,4-cyclohexanedimethanol, 2,2,4-trimethyl-1,3-pentanediol, 1-ethyl-2-butyl-1,3-propanediol or the positional isomers of diethyloctanediols. Moreover, the polyols and diols described in US 2004/0234487 A1, [0100 - 0109], as well as polyols and diols based on polyesters and/or polyethers as described in US 2004/0234487 A1, [0110 - 0113] can be used. Typically, basecoats contain 0 – 30 % by weight of the aforementioned further binders.

Additionally, as a pigmented coating composition, the basecoat material comprises at least one pigment.

Pigments are colorants in powder or platelet form which unlike dyes are insoluble in the surrounding medium (cf. Rompp Lacke und Druckfarben, page 451, entry heading "Pigmente" [Pigments]).

Preferably the pigment is selected from the group consisting of organic and inorganic, color-imparting, effect-imparting, color- and effect-imparting, magnetically shielding, electrically conductive, corrosion-inhibiting, fluorescent, and phosphorescent pigments. Preference is given to using the color and/or effect pigments. With particular preference the basecoat material comprises at least one effect pigment, more particularly at least one metal flake pigment. Together with the effect pigment or pigments, the basecoat may further comprise at least one, or two or more, color pigments.

Examples of suitable effect pigments, which may also impart color, are metal flake pigments, such as commercial aluminum bronzes and commercial stainless steel bronzes, and also nonmetallic effect pigments, such as, for example, pearlescent pigments and interference pigments, platelet-shaped effect pigments based on iron oxide, or liquid-crystalline effect pigments. For further details refer to Rompp Lexikon Lacke und Druckfarben, page 176, entry heading "Effekt pigments" [Effect pigments] and pages 380 and 381, entry headings "Metalloxid-Glimmer-Pigmente" [Metal oxide-mica pigments] to "Metallpigmente" [Metallic pigments].

Regarding effect pigments, use is made in particular of commercial aluminum bronzes. In this context, both untreated types, which are available commercially, for example, under the name Stapa® from Eckart and treated types, especially silanized types, which are described, for example, in WO 01/81483 and are available commercially, for example, under the name Hydrolan® from Eckart, are used.

Typically the metal flake pigment has a thickness in the range between 200 to 2000 nm and typically has an average particle size between 10 to 50 and more typically 13 to 25  $\mu\text{m}$  (ISO 13320-1 by Cilas (instrument 1064)).

Suitable organic and/or inorganic color pigments are the pigments typically employed in the paint industry. Examples of such suitable inorganic color pigments are white pigments such as titanium dioxide, zinc white, zinc sulfide or lithopones; black pigments such as carbon black, iron manganese black or spinel black; chromatic pigments such as chromium oxide, chromium oxide hydrate green, cobalt green or ultramarine green, cobalt blue, ultramarine blue or manganese blue, ultramarine violet or cobalt violet and manganese violet, red iron oxide, cadmium sulfoselenide, molybdate red or ultramarine red; brown iron oxide, mixed brown, spinel phases and corundum phases or chromium orange; or yellow iron oxide, nickel titanium yellow, chromium titanium yellow, cadmium sulfide, cadmium zinc sulfide, chromium yellow or bismuth vanadate.

Examples of suitable organic color pigments are monoazo pigments, disazo pigments, anthraquinone pigments, benzimidazole pigments, quinacridone pigments, quinophthalone pigments, diketopyrrolopyrrole pigments, dioxazine pigments, indanthrone pigments, isoindoline pigments, isoindolinone pigments, azomethine pigments, thioindigo pigments,



metal complex pigments, perinone pigments, perylene pigments, phthalocyanine pigments or aniline black.

For further details refer to Rompp Lexikon Lacke und Druckfarben, Georg Thieme Verlag, 1998, pages 180 and 181, entry headings "Eisenblau-Pigmente" [Iron blue pigments] to "Eisenoxidschwarz" [Black iron oxide], pages 451 to 453, entry headings "Pigmente" [Pigments] to "Pigmentvolumenkonzentration" [Pigment volume concentration], page 563, entry heading "Thioindigo-Pigmente" [Thioindigo pigments], page 567, entry heading "Titandioxid-Pigmente" [Titanium dioxide pigments], pages 400 and 467, entry heading "Natürlich vorkommende Pigmente" [Naturally occurring pigments], page 459, entry heading "Polycyclische Pigmente" [Polycyclic pigments], page 52, entry headings "Azomethinpigmente" [Azomethine pigments], "Azopigmente" [Azo pigments], and page 379, entry heading "Metallkomplex-Pigmente" [Metal complex pigments].

The amount of the pigments may vary very widely and is guided primarily by the depth of color and/or intensity of effect that are to be brought about, and also by the dispersibility of the pigments in basecoat materials. In the case of solid-color basecoat materials, based in each case on the total weight of the basecoat material, the pigment content is typically between 0.5 to 60% by weight. Solid-color basecoat materials are basecoat materials which contain no metallic or effect pigments. In the case of metallic coating materials, based in each case on the total weight of the basecoat material, the pigment content is typically between 0.1% and 40% by weight.

The basecoat material contains at least one organic solvent typically in an amount of from 1 % to 30 % by weight, based on the total weight of the basecoat composition.

Suitable organic solvents are all solvents which are typically used in the paint industry, examples being alcohols, glycol ethers, esters, ether esters, and ketones, aliphatic and/or aromatic hydrocarbons, such as, for example, acetone, methyl isobutyl ketone, methyl ethyl ketone, butyl acetate, 3-butoxy-2-propanol, ethyl ethoxypropionate, butylglycol, butylglycol acetate, butanol, ethylhexanol, dipropylene glycol methyl ether, butyl glycolate, n-methylpyrrolidone, n-ethylpyrrolidone, dimethylsulfoxid, xylene, toluene, Shellsol T, Pine Oel 90/95, Solventnaphtha®, Shellsol® A, Solvesso, benzine 135/180, Isopar L, Isopar V and the like.

So that a polymeric, chemically resistant network can form from the monomeric and/or oligomeric constituents when baking temperatures are lowered and/or baking times are made shorter, the basecoat material may comprises catalyst(s). Suitable catalysts are the known catalysts which are typically used for crosslinking with melamine resins, such as, for example, sulfonic acid catalysts or phosphoric acid derivatives. The catalyst or catalysts are used in amounts of typically 0.5% to 5% by weight, based on the total weight of the basecoat material.

Besides the components described above and the UV absorbers of the present invention, the basecoat material may comprise customary and known auxiliaries and additives in typical amounts, preferably 0% to 40% by weight, more typically 0.5% to 30% by weight, based in

each case on the total weight of the basecoat material, of at least one auxiliary or additive.

Suitable auxiliaries or additives are the known auxiliaries and additives that are typically used in the paint industry. Examples of suitable auxiliaries and additives are organic and inorganic fillers, such as talc, and/or dyes (organic substances that are black or chromatic and are soluble in the surrounding medium (cf. Rompp Lacke and Druckfarben, page 221, entry heading "Farbmittel" [Colorants])), and also further customary auxiliaries and additives, such as, for example, antioxidants, deaerating agents, wetting agents, dispersants, emulsifiers, rheological assistants such as flow control agents, thickeners, antisag agents, and thixotropic agents, such as layered silicates, waxes, polyacrylate or polyurethane based thickeners and wax-like compounds, slip additives, reactive diluents, free-flow aids, siccatives, biocides, additives for improving the substrate wetting, additives for improving the surface smoothness, matting agents, free-radical scavengers, light stabilizers, corrosion inhibitors, flame retardants or polymerization inhibitors, as described in detail in the book "Lackadditive" [Additives for Coatings] by Johan Bieleman, Wiley-VCH, Weinheim, New York, 1998. Preferred auxiliaries and additives are rheological assistants, deaerating agents, wetting agents, dispersants, waxes and wax-like compounds, and free-radical scavengers. Particularly preferred auxiliaries and additives are wetting agents, and waxes and wax-like compounds.

Suitable clear coat material for producing the clear coat of the multilayer coating of the invention may comprise the transparent coating compositions that are typically employed as solvent borne transparent coating compositions, which may be formulated either as one-component coating compositions or as two-component or multi-component coating compositions.

The transparent coating compositions (clear coat materials) preferably have a solids fraction in the range between 40 % and 70 % by weight. The transparent coating compositions used may be curable thermally and/or by means of radiation, in particular by means of UV radiation.

The transparent coating compositions typically comprise at least one binder with functional groups and also at least one crosslinker having a functionality which is complementary to the functional groups of the binder. Examples of such complementary functionalities are in particular the following pairings (a/b) that are in each case complementary to one another: (carboxyl / epoxy), (amine or thiol or hydroxyl / blocked or free isocyanate or alkoxylated amino groups or transesterifiable groups), ((meth)acryloyl / CH-acidic or amine or hydroxyl or thiol), (carbamate / alkoxylated amino groups), and ((meth)acryloyl / (meth)acryloyl) and (hydroxyl / methoxysilane. Additionally clear coats based on a silane self-crosslinking mechanism as described in patent WO 2007033786 A1 can be used.

Use is made in particular of transparent coating compositions based on polyurethane resins and/or polyacrylate resins and/or polyester resins, preferably with hydroxyl, amino, carbamate, carboxyl, methoxysilane, (meth)acryloyl and/or thiol groups, in combination with the corresponding crosslinkers, more particularly in combination with isocyanates, amino

resins, anhydrides, and the like.

Besides the UV absorbers of the present invention, the binder and crosslinker, the transparent coating compositions may comprise customary auxiliaries and additives, such as, for example, catalysts for crosslinking, defoamers, adhesion promoters, additives for improving substrate wetting, additives for improving surface smoothness, matting agents, light stabilizers, corrosion inhibitors, biocides, flame retardants or polymerization inhibitors, as described in detail in the book "Lackadditive" by Johan Bieleman, Wiley-VCH, Weinheim, New York, 1998.

For automotive OEM clear coats, more specifically, a detailed description of suitable ingredients, in particular rheology modifiers can be found in US 6652915 B1, EP 2188341, EP 2102263 B1, and US 6403699.

The production of the coating materials is described in detail in the literature, A. Goldschmidt, H.-J. Streitberger, "BASF Handbuch Lackiertechnik", Vincentz, 2002, pp. 197 – 329.

The present invention also relates to a process for producing a coating system, in particular an automotive coating system, comprising application of the coating composition of the present invention as at least one layer of a coating system, in particular an automotive coating system.

In a preferable embodiment, the coating composition of the present invention is applied as an automotive OEM clear coat or an automotive OEM base coat or both.

In another preferable embodiment, the automotive coating composition of the present invention is applied as the OEM base coat and the OEM clear coat does not contain any organic UVAs.

The steps and respective conditions for applying an automotive coating composition to obtain the automotive coating system are known in the state of the art.

That is to say, the process for producing the automotive coating system may be carried out in accordance with any well-known process for producing an automotive coating system in the state of the art, provided that the automotive coating composition of the present invention is applied as at least one layer of the coating system.

For example, the process of the present invention is carried out by applying a basecoat material provided with color and/or effect pigments, especially an aqueous basecoat material, to the substrate surface, drying the applied basecoat film at a temperature between 15°C and 100°C, afterwards applying to the dried basecoat film a transparent coating material (clear coat) and subsequently baking the basecoat film and clear coat film together, preferably at a temperature between 70°C and 160°C. Suitable substrates include all surfaces of articles to be coated which are amendable to curing of the coating films present thereon using heat. Besides special composite materials, such as fiber reinforced plastics, glass and/or carbon fiber reinforced plastics or similar materials, it is in particular possible to coat primed or unprimed/pretreated (flamed) or non - pretreated plastics, such as for example ABS, AMMA, ASA, CA, CAB, EP, UF, CF, UF, PPE, POM, PE, PA, HDPE, LDPE, UHMWPE, PET,

PMMA, PP, PP-EPDM, PVC, SAN, SMC (abbreviations according to DIN 7728T1).

Depending on the aforementioned substrates, there is a variety of techniques available to apply the coating materials. As for car bodies, spray application is the preferred application method. A detailed description of variants and different spray application techniques can be found in the literature, A. Goldschmidt, H.-J. Streitberger, "BASF Handbuch Lackiertechnik", Vincentz, 2002, pp. 494 – 644. A very detailed description of the application processes can also be found in "Automotive Paints and Coatings", edited by Hans-Joachim Streitberger and Karl – Friedrich Dössel, Wiley – VCH, 2008, pp. 259 - 305.

However, in particular for plastic parts, the automotive coatings might also be applied by alternative methods, such as dipping.

In case foils are coated and afterwards used in the automotive industry by laminating plastic or other car body parts, also rolling applications can be employed.

Additionally, the invention is directed to a process for producing a multilayer coating system comprising a pigmented and/or effect coating layer and a clear coat layer on a surface of primed or unprimed substrates, wherein the pigmented and/or effect coating layer and/or the clear coat layer, preferably the pigmented and/or effect coating layer contains the UV absorber of the present invention as defined hereinbefore. A multilayer coating system which is obtained according to this process is also a subject of the present invention.

The invention will be further illustrated by the following examples, which set forth particularly advantageous embodiment. While the Examples are provided to illustrate the present invention, they are not intended to limit it.

## EXAMPLES

### 1. Preparation Examples

In the scope of this patent application, three different samples of benzotriazole based UVAs have been prepared according to WO 02/24668A1 and purified according to the procedures described in US 7915322 B2.

#### Example 1

1) mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG 200 ester

#### Example 2

2) mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG 300 ester

#### Example 3

3) mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG 600 ester

The samples 1), 2) and 3) have been prepared respectively in Examples 1 to 3 according to the well known procedure described in Example 19 of WO 02/24668A1, and then separated by column chromatography as described in Example 5 of US 7915322 B2. The resulting

residual free PEG X contents have been analyzed by means of HPLC using a standard for calibration, the following results have been obtained:

Table 1 – Residual contents of free PEG X in the reaction mixtures of various UVAs

	Reference, Eversorb 80, commercial grade,	Sample 1), Mono { $\beta$ -[3-(2H- benzotriazol-2-yl)-5-t- butyl-4-hydroxy- phenyl]propionic acid}-PEG 200 ester	Sample 2), Mono { $\beta$ -[3-(2H- benzotriazol-2-yl)-5-t- butyl-4-hydroxy- phenyl]propionic acid}-PEG 300 ester	Sample 3), Mono { $\beta$ -[3-(2H- benzotriazol-2-yl)-5-t- butyl-4-hydroxy- phenyl]propionic acid}-PEG 600 ester
Respective free PEG X content (residual), in wt. %	14.5	7.2	0.3	3.7

To evaluate the hydrophilicity, respective measurement of the solubility parameters of the UV-absorbers prepared in the above Examples and two commercially available UV-absorbers was conducted and the results are listed in Table 2 below:

Table 2 - Solubility parameter of various UVAs

	Reference, Tinuvin 384-2	Reference, Eversorb 80	Sample 1)	Sample 2)	Sample 3)
Solubility parameter*	9.41	10.26	10.45	13.71	>15

\* determined according to K. W. Suh, J. M. Corbett, *Journal of Applied Polymer Science*, Vol. 12, pp 2359-2370 (1968)

It can be seen clearly that the property profiles of the mono { $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X esters are by far more hydrophilic in their properties and thus expected to be much better in regard to their compatibility with water borne coatings, compared with the commercially available UVAs as References.

However, in the course of the investigation of the solubility parameters, it clearly turned out that the Sample 3) — mono { $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG 600 ester have already the highest solubility parameter which can be measured by the described experimental set – up.

Based on these findings, it is then also expected that use of the monoester UV-absorbers of the present invention with less free PEG X in the coating compositions will result in superior appearance, compared to the commercially available mixtures such as Tinuvin 1130 or Eversorb 80, as the compatibility of the former is higher.

On the other hand, the capability of these mono { $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X esters to absorb UV-light in an appropriate manner is a mandatory requirement. Thus, the UV-absorption of mono { $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG 300 (Sample 2)) has also been proven by measurement.

As shown in figure 1, it turned out that there is no difference between the basic shape of the absorption spectrum of the UV-absorber of the present invention compared to the less pure commercial grades Tinuvin 1130 and Eversorb 80. The difference of the absolute values

can be explained by the enhanced purity of the mono  $\{\beta\text{-}[3\text{-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}\}$ -PEG 300 ester and thus higher concentration of UV-absorbing groups per molecule.

## 2. Formulation Examples - Preparation of an automotive OEM Base Coat

In this Example, six samples in total were prepared by mixing all components in the ratios by weight as listed in the Table 3 below, including one sample without any organic UVA (Reference 1), two samples using the conventional UVAs (Reference 2 and 3) and three samples using the UVAs of the present invention (Formulations 1 to 3).

In each sample, a silver shaded water borne base coat, commercially available from BASF Shanghai Coatings, product code FW797055 CB GREYSTONE was used. As it is confirmed by the producer, FW797055 CB GREYSTONE does not contain any organic UVAs, such as benzotriazoles or similar derivatives.

Table 3

	Reference 1 without UVA,	Reference 2 using hydrophobic UVA	Reference 3 using a mixture of hydrophilic UVAs	Formulation 1 using purified hydrophilic UVA with low Mw	Formulation 2 using purified hydrophilic UVA with medium Mw	Formulation 3 using purified hydrophilic UVA with high Mw
FW79-7055 CB GREYSTONE	99	99	99	99	99	99
Butyl glycol	1	0.8	0.8	0.8	0.8	0.8
Tinuvin 384-2		0.2				
Eversorb 80			0.2			
Sample 1)				0.2		
Sample 2)					0.2	
Sample 3)						0.2
sum	100	100	100	100	100	100

## 3. Application Examples

The resulting formulations have been homogenized carefully and used as the base coats for the application in a typical automotive coating system.

The formulations were applied by the pneumatic application known in the state of the art. This was carried out by employing metal test panels which had each been coated with a customary and known, cathodically deposited, thermally cured electrocoat, a customary and known, thermally cured solvent borne primer surfacer (product code FC60715A UNIB 5910 GREY, commercially available from BASF Shanghai Coatings, Guanghua Lu 521). After application of the base coat from above Formulation Examples, a flash off was applied for drying at 80°C for 10 minutes. Afterwards, the basecoat film and the clear coat (StarGloss, commercially available from BASF Shanghai Coatings, Guanghua Lu 521, product code FF71045A STARGLOSS 5910) film were cured jointly at 140°C for 24 minutes. The resulting basecoat had a film thickness of 12  $\mu\text{m}$ , while the clear coat was applied in a wedge to evaluate the wetting as well as the appearance at low film builds (20  $\mu\text{m}$ , 30  $\mu\text{m}$ ) as well as

at standard film builds (40  $\mu\text{m}$  and 50  $\mu\text{m}$ ).

#### 4. Appearance evaluation

To evaluate the appearance, measurements have been carried out by using a wavescan equipment which is commercially available from BYK-Gardner. The lower the measurement values are obtained, the better the appearances are.

The measurement of the appearance is carried out by employing a device from BYK, “Wavescan Dual” which is based on a laser measurement under an incident angle of 60°. The device is moved over the surface and the results are recorded depending on the size of the structures. In this context, the SW – values refer to structures in the range between 0.3 and 1.2 mm, the LW values refer to structures in the range of from 1.2 to 12 mm. A detailed description of the device employed, the measurement method and details about the length scales of the structures dealt with can be found in the literature: BYK – Gardner Instrumente, “Qualitätskontrolle für Lacke”, 2008, Glanz/Appearance, available at BYK Gardner, Lausitzer Strasse 8, 82538 Geretsried, Germany.

It can be seen from Figure 3 and Figure 4 that the appearances of the coatings resulted from Formulations 1 to 3 of the present invention are the most striking ones. The measured results can also be proven by visual inspection. The result can be explained by the superior compatibility of the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester having reduced content of free PEG X with the overall coating system compared to any of the commercial products such as Eversorb 80.

The chain length of the PEG moiety also has an effect on the appearance.

For the Wavescan at long wave (LW), as can be clearly seen from Figure 3, the longer the chain and consequently the more hydrophilic the total UVA, the better the LW appearance values at all film builds. Particularly, this effect is more significant at rather low film builds, such as 20  $\mu\text{m}$ .

For the Wavescan at short wave (SW), as can be seen from Figure 4, a similar effect is observed, except for the formulation 3 using mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG 600 ester with 3.7 wt.% of free PEG 600 which exhibits slightly worse result compared to the formulation 2 using mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG 300 ester. The higher the film builds, the worse the results are obtained for the more hydrophilic grade. That indicates too hydrophilic UVAs will harm the appearance at short wave, since a similar poor result for the SW wavescan values is also observed for the commercial grade Eversorb 80, which contains quite some amounts of very hydrophilic PEG 300 residues. All the numerical results are summarized in Table 4.

Table 4: Summary of the Wavescan Results

	Reference 1	Reference 2	Reference 3	Formulation 1	Formulation 2	Formulation 3
LW - 20 $\mu$ m	23,6	21,8	20,8	17,8	14	13,6
SW - 20 $\mu$ m	21,4	20,4	17,5	16,2	13,5	14,7
LW - 30 $\mu$ m	8,6	8,3	5,6	5,1	4,1	3,7
SW - 30 $\mu$ m	13,5	13,9	14,2	14,9	13,7	14,5
LW - 40 $\mu$ m	2,8	3,1	2,4	2,5	2,1	2,1
SW - 40 $\mu$ m	14,6	15	15,5	15,5	16,2	16,3
LW - 50 $\mu$ m	2,2	2,3	1,8	2	1,8	1,8
SW - 50 $\mu$ m	15,3	15,5	16,6	15,6	16,4	17,2

Taking into consideration that the overall coating system needs to exhibit the optimum appearance, an UVA which is as pure as possible having an moderate hydrophilicity is most favorable for the application, since it can balance an superior LW-appearance at low film build and a good-acceptable SW-appearance at higher film builds. It has surprisingly been found that such optimum balanced property profile is obtained by using the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester with reduced content of free PEG X as an UV-absorber wherein X being a number in the range of from more than 100 to less than 1000, especially from 200 and 600.

In addition, with use of the automotive coating composition of the present invention, PEG 300 may be omitted which might deteriorate the long term weathering and in particular humidity performance of the cured coating films, and also be rather harmful for the overall appearance of the automotive coating system. Moreover, the bis-ester may also be omitted, which is rather likely to increase the incompatibility due to its high molecular weight, which is well known in the state of the art due to entropic effects.



**Claims:**

1. A coating composition, preferably an automotive coating composition, containing a mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester as an UV-absorber, characterized in that

the coating composition contains less than 10 % by weight of free PEG X, based on the overall weight of all UVAs in the coating composition,

wherein the free PEG X refers to unesterified poly(ethylene glycol) with a weight average molecular weight of X in g/mol and wherein X is a number in the range of from  $100 < X < 1000$ , which comes from preparation of the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester with the PEG X as a starting material and remains as an impurity of the mono{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester.

2. The coating composition according to claim 1, wherein X is in the range of  $100 < X \leq 600$ .

3. The coating composition according to claim 1, wherein X is in the range of  $200 \leq X \leq 400$ .

4. The coating composition according to any of claims 1 to 3, wherein the composition contains less than 8 % by weight of the free PEG X, based on the overall weight of all UVAs in the coating composition.

5. The coating composition according to any of claims 1 to 3, wherein the composition contains less than 10 % by weight of bis{ $\beta$ -[3-(2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyphenyl]propionic acid}-PEG X ester, based on the overall weight of all UVAs in the coating composition.

6. The coating composition according to claim 1, wherein the UV-absorber exhibits a solubility parameter of more than 10.4.

7. The coating composition according to claim 1, wherein the UV-absorber exhibits a solubility parameter of more than 13.5.

8. The coating composition according to claim 1, wherein the coating composition does not contain any other UV-absorbers.

**9.** The coating composition according to claim 1, which is used as an OEM clear coat and/or an OEM base coat.

**10.** The coating composition according to claim 9, which is water borne.

**11.** The coating composition according to claim 10, which is used as a water borne OEM base coat.

**12.** A multilayer coating system which comprises a pigmented and/or effect coating layer and a clear coat layer, wherein the pigmented and/or effect coating layer and/or the clear coat layer, preferably the pigmented coating layer contains the UV absorber as defined in any of claims 1 to 8.

**13.** A process for producing a coating system, preferably an automotive coating system, comprising application of the coating composition according to any of claims 1 to 11 as at least one layer of the coating system, preferably the automotive coating system.

**14.** The process for producing an automotive coating system according to claim 13, wherein the automotive coating composition according to any of claims 1 to 11 is applied as OEM clear coat and/or an OEM base coat.

**15.** The process for producing an automotive coating system according to claim 14, wherein the automotive coating composition according to any of claims 1 to 11 is applied as the OEM base coat and the OEM clear coat of the automotive coating system does not contain any organic UVAs.

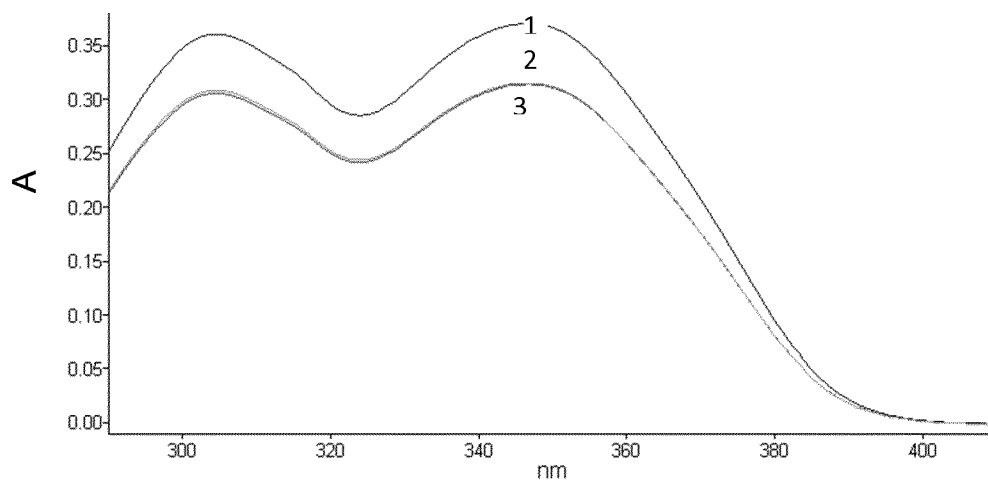


Figure 1

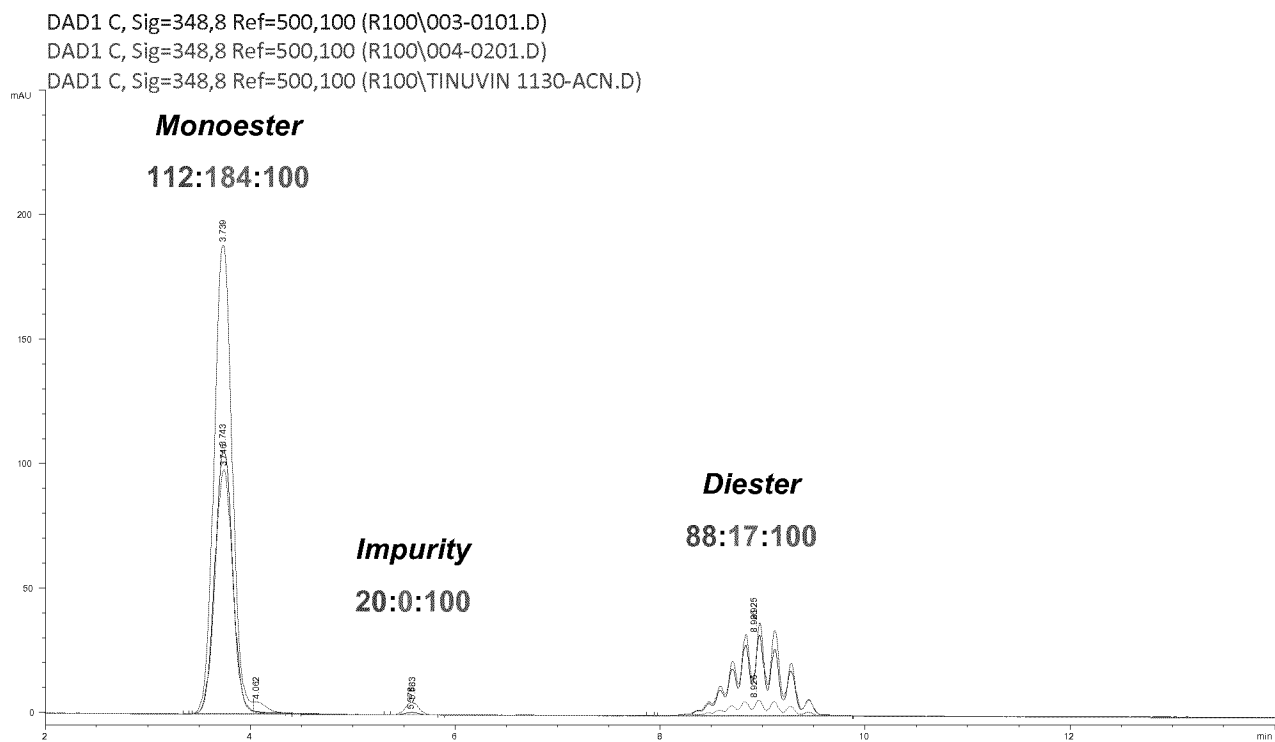


Figure 2

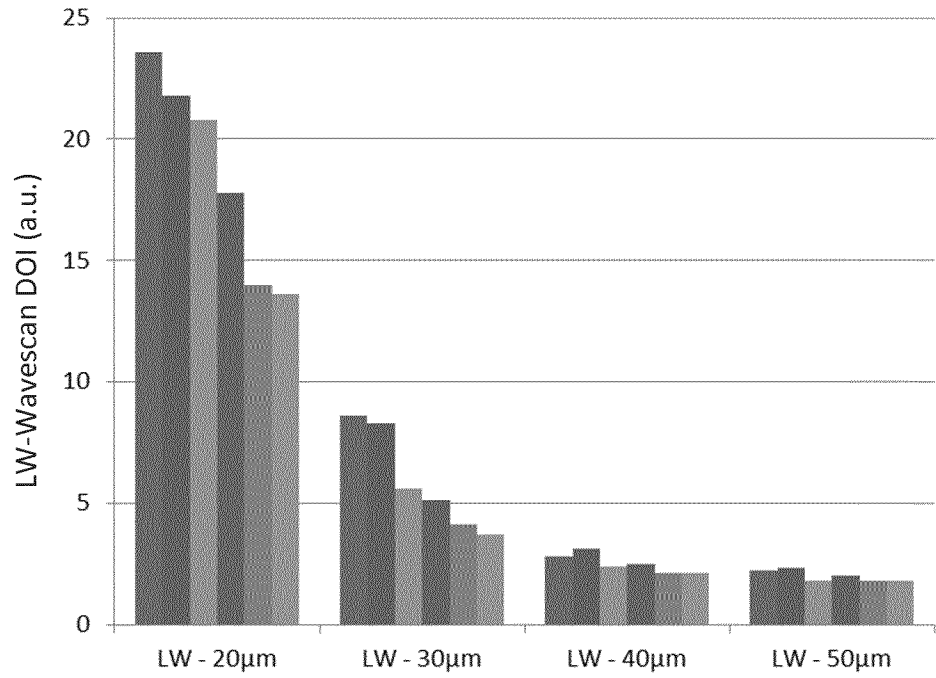


Figure 3

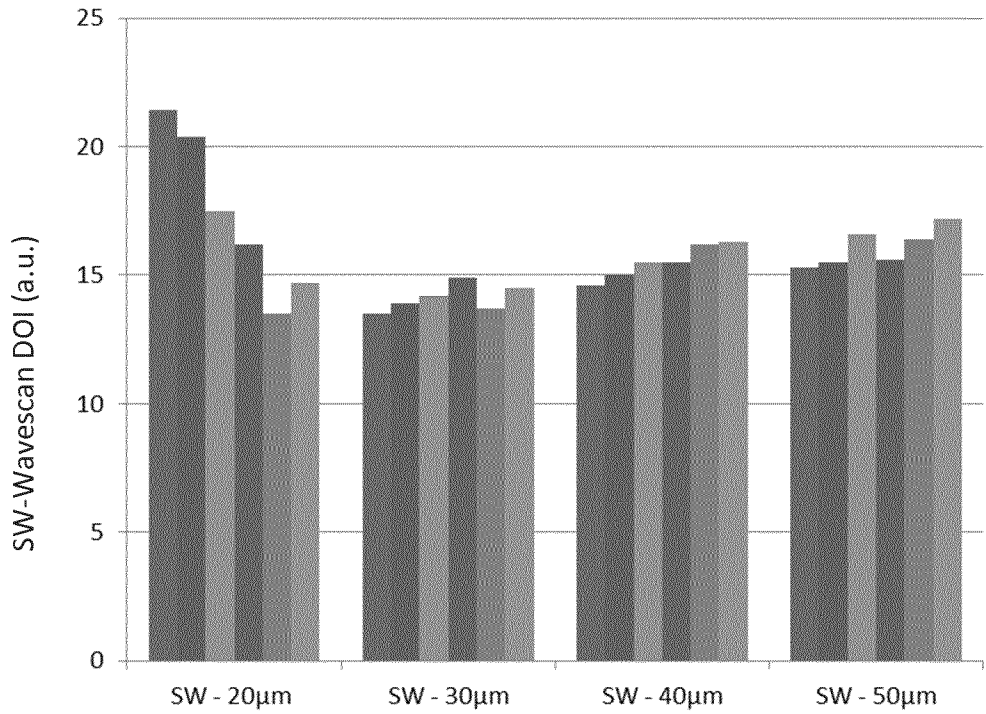


Figure 4

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2013/062032

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C09D5/00  
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
C09D

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

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

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>CHRISTIAN SCHALLER ET AL: "Organic vs inorganic light stabilizers for waterborne clear coats: a fair comparison", JOURNAL OF COATINGS TECHNOLOGY AND RESEARCH, SPRINGER US, BOSTON, vol. 9, no. 4, 29 November 2011 (2011-11-29), pages 433-441, XP035071710, ISSN: 1935-3804, DOI: 10.1007/S11998-011-9380-8 Fig 1-7 (BTZ-PEG)</p> <p style="text-align: center;">----- -/--</p>	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

7 October 2013

Date of mailing of the international search report

15/10/2013

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040,  
Fax: (+31-70) 340-3016

Authorized officer

Kositza, Matthias

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2013/062032

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	C. SCHALLER ET AL: "Hydroxyphenyl-s-triazines: advanced multipurpose UV-absorbers for coatings", JOURNAL OF COATINGS TECHNOLOGY AND RESEARCH, vol. 5, no. 1, 1 March 2008 (2008-03-01), pages 25-31, XP55068986, ISSN: 1547-0091, DOI: 10.1007/s11998-007-9025-0 Fig 1, 7 (BTZ-2) -----	1-15
X	WO 00/66666 A1 (BASF COATINGS AG [DE]; OTT GUENTHER [DE]; WOLTERING JOACHIM [DE]; STUE) 9 November 2000 (2000-11-09) example 2, page 1 lines 8-13 (use of TINUVIN 1130 together with additional UV-absorber TINUVIN 292) -----	1-15
X	WO 2009/026138 A1 (CSD INC [US]; AKHTAR PARVEZ [US]; FITZWATER JOHN [US]; GREENBERG NORMA) 26 February 2009 (2009-02-26) Table II (use of TINUVIN 1130 together with additional UV absorber TINUVIN 292) -----	1-15

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/062032

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0066666	A1	09-11-2000	BR 0010233 A 08-01-2002
		DE 19920141 C1 25-01-2001	
		EP 1189996 A1 27-03-2002	
		ES 2188537 T3 01-07-2003	
		JP 2002542942 A 17-12-2002	
		US 6509096 B1 21-01-2003	
		US 2003059553 A1 27-03-2003	
		WO 0066666 A1 09-11-2000	
-----			
WO 2009026138	A1	26-02-2009	US 2008268140 A1 30-10-2008
		WO 2009026138 A1 26-02-2009	
-----			