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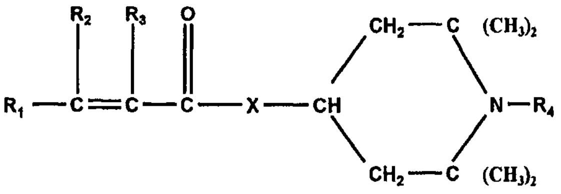

(I)

$$R_1-C(R_2)=C(R_3)-C(=O)-X-CH<(CH_2-C(CH_3)_2)_2>N-R_4$$

(57) Abstract

A stabilizing agent for polymer materials, such as polyethylene, and a polymer material containing it are disclosed. The stabilizing agent comprises a copolymer of ethylene or propylene (A) and a vinyl compound (B) with the formula (I), wherein X=O, NH or NR_5; R_1, R_2 and R_3 independently each = H, C_1–C_8 alkyl, C_1–C_8-alkenyl or C_1–C_8 substituted aryl; R_4=H, C_1–C_8 alkyl, C_6–C_{12} cycloalkyl, C_1–C_{10} acyl, C_1–C_{10} acyloxy or C_1–C_8 alkyl ether; R_5=C_1–C_8 alkyl; the copolymer contains at least 1 mol% of (B); and the copolymer has an MFR_2 of 1- 1000 g/10 min.

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STABILIZING AGENT

Field of the invention

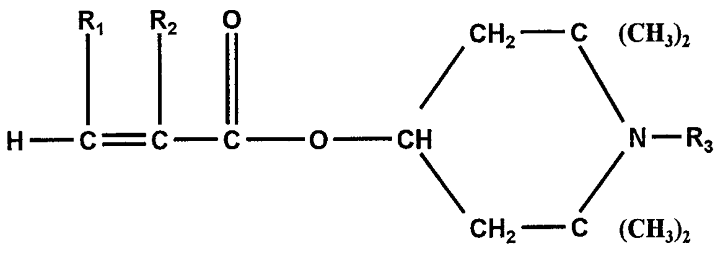
The present invention relates to a stabilizing agent for polymer materials and to a polymer material containing the stabilizing agent.

Background of the invention

Polymer materials, e.g. polyolefin materials such as ethylene polymers generally have rather poor resistance to the influence of different environmental conditions such as light, heat and weather.

To improve the physical properties of polymer materials and to increase their resistance to the influence of environmental conditions, various stabilizing additives are usually added in a total amount of about 0.05 – 5 % by weight, preferably about 0.1 – 4 % by weight. These additives include antioxidants such as sterically hindered phenols, aromatic amines, organic phosphites, and thio compounds; and light stabilizers such as hindered amine light stabilizers (HALS). Usually a „cocktail“ of at least two different stabilizing agents, e.g. a HALS compound and a hindered phenol compound is added to the polymer material. However, known stabilizing additives often have an insufficient stabilizing effect or become unsatisfactory due to bleeding of the additive from the polyolefin material. A stabilizing additive that effectively protects polymer materials against the influence of environmental conditions and which is not prone to bleeding from the polymer material would therefore be desirable.

One such stabilizing additive is disclosed in EP-A-0 468 418 and consists of a copolymer of ethylene (A) and a vinyl compound (B) represented by the general formula:



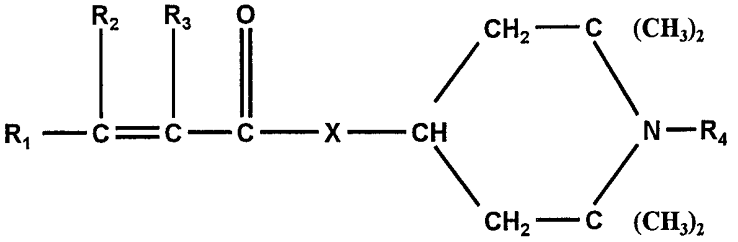
wherein R_1 and R_2 are each an independent hydrogen atom or a methyl group, R_3 is a hydrogen atom or an alkyl group of 1 – 4 carbon atoms; a ratio of (B) to the sum of (A) and (B) is less than 1 mol%; a proportion of the amount of vinyl compounds (B), which are not successively bonded to like units (B) in the chain, but bonded to unlike units (A) on both sides thereof, to the total amount of (B) units in the copolymer is at least 83 %; and an MFR of the copolymer ranges from 0.1 to 200 g/10 min.

In EP-A-0 468 418 it is submitted that decreased light stability of hindered amine copolymer additives is caused by the block structure comprising at least two vinyl moieties successively bonded having hindered amines in the side chain or unreacted residual ester groups. The most important feature of EP-A-0 468 418 is therefore said to be that the proportion of the amount of vinyl compounds (B) which are not successively bonded at all to like units (B) in the chain to the total amount of (B) is at least 83 %. Consequently, the ratio of the vinyl compound (B) to the sum of ethylene (A) and the vinyl compounds (B) is less than 1 mol%.

Summary of the invention

It has now been surprisingly discovered that, contrary to the teachings of EP-A-0 468 418 it is possible to obtain an effective stabilizing agent of a copolymer of ethylene or propylene (A) and a vinyl compound (B) with the formula (I) below where the ratio of the vinyl compound (B) to the sum of ethylene or propylene (A) and the vinyl compound (B) is at least 1 mol%. This stabilizing copolymer additive can be used as a master batch to stabilize polymer materials, particularly polyolefin materials such as ethylene polymers against the influence of oxygen, light and heat.

More particularly, the present invention provides a stabilizing agent for polymers, characterised in that it comprises a copolymer of ethylene or propylene (A) and a vinyl compound (B) with the formula (I):



(I)

wherein X = O, NH or NR_5; R_1, R_2 and R_3 independently each = H, $C_1 - C_8$ alkyl, $C_1 - C_8$ alkenyl or $C_1 - C_8$ substituted aryl; R_4 = H, $C_1 - C_8$ alkyl, $C_6 - C_{12}$ cycloalkyl, $C_1 - C_{10}$ acyl, $C_1 - C_{10}$ acyloxy or $C_1 - C_8$ alkyl ether; R_5 = $C_1 - C_8$ alkyl; the copolymer contains at least 1 mol% of (B); and the copolymer has an MFR_2 of 1 – 1000 g/10 min.

The present invention also provides a polymer material comprising the stabilizing agent defined above as a combined light and heat stabilizing agent.

Other distinguishing features and advantages of the invention will appear from the following specification and the appended claims.

Detailed description of the invention

In the stabilizing agent of the present invention preferred vinyl monomer compounds (B) of formula (I) are those where $X = O$; R_1 and R_2 are H; R_3 is H or CH_3; and R_4 is H, $C_1 - C_8$ alkyl, preferably methyl, or $C_1 - C_9$ acyl, preferably acetyl or acetoxyl. The most preferred vinyl monomer compound (B) at present is 2,2,6,6-tetramethyl-4-piperidinyl methacrylate, i.e. R_1 and R_2 are H and R_4 is H or $C_1 - C_4$ alkyl and R_3 is CH_3 in formula (I).

As stated above, a characterising feature of the present invention is that the copolymer stabilizing agent includes the comonomer (B) in an amount of at least 1 mol %, preferably at least 1.2 mol%, and more preferably at least 1.5 mol%. The upper limit of the amount of comonomer (B) is preferably 4 mol%, and it is particularly preferred that the amount of (B) is 1.5 – 4 mol%. This means that compared to EP-A-0 468 418 the amount of the comonomer (B) is higher and that many of the comonomer units (B) will be bonded to other comonomer units (B). This is contrary to the teachings of EP-A-0 468 418, which stresses that at least 83 % of the comonomer units (B) must be bonded to unlike units (A). Actually, at the present invention it appears that within the above defined ranges for the comonomer (B) a better stabilizing effect is obtained on the polyolefin material the higher the content of the comonomer (B) of the stabilizing agent. This is quite surprising in the light of the teachings of EP-A-0 468 418.

The „melt flow rate“ (MFR) of the copolymer stabilizing agent of the invention is determined in accordance with ISO 1133 and is equivalent to the term „melt index“ earlier used. The melt flow rate is determined at a loading of 2.16 kg (MFR_2). Generally, the MFR_2 of the copolymer stabilizing agent of the invention lies in the range of 1 to 1000 g/10 min, preferably 10 – 400 g/10 min.

The monomer (B) of formula (I) can be prepared by known methods such as disclosed in EP-A-0 468 418. Similarly, the copolymer stabilizing agent of the present invention can be prepared by known methods such as copolymerisation, e.g. as disclosed in EP-A-0 468 418 or transesterification of e. g. EMA (ethylene/methyl acrylate copolymer) copolymers, e.g. as disclosed in EP-A-0 293 253 or US 4,413,096.

As mentioned earlier, a particular aspect of the present invention is a polymer material incorporating the above defined stabilizing agent. Generally and in connection with the present invention, the expression "polymer material" refers to macromolecular or high molecular weight materials of natural or, preferably synthetic origin. As examples of such polymer materials may be mentioned polyolefins, particularly α-olefin polymers and especially ethylene and propylene polymers; polyacrylate polymers such as polymethyl(meth)acrylate polymers; polyester polymers such as polyethyleneterephthalate polymers; polyamide polymers such as Polyamide 6 and Polyamide 6/6; polyurethanes; halogen containing polymers such as polyvinyl chloride and polyvinylidene chloride; aromatic polymers such as polystyrene; polycarbonate polymers; etc. For a more exhaustive list of suitable polymer materials reference is made to the above mentioned EP-A-0 468 418.

Particularly preferred polymer materials to be stabilized by the incorporation of the above defined stabilizing copolymer are polyolefins such as $C_1 - C_8$ olefin polymers, preferably ethylene or propylene polymers, most preferably ethylene polymers. The polymer may be a homopolymer of the olefin or a copolymer of the olefin with one or more comonomers which are copolymerisable with the olefin. In the copolymer the olefin should constitute the major part of the mass. The term "copolymer" is intended to include graft copolymers.

Ethylene polymers, including ethylene homopolymers and ethylene copolymers, are particularly preferred polyolefin materials to be stabilized with the stabilizing copolymer of the present invention. Copolymers of ethylene may include up to about 50 % by weight, preferably about 1 – 35 % by weight of one or more comonomers which are copolymerisable with ethylene. Such comonomers are well known to those skilled in the art and no extensive enumeration will be required, but as examples, mention can be made of vinylically unsaturated monomers, such as $C_3 - C_8$ α-olefins, for instance propene, butene; vinylically unsaturated monomers containing functional groups, such as hydroxyl groups, alkoxy groups, carbonyl groups, carboxyl groups and ester groups. Such comonomers may consist of e.g. (meth)acrylic acid and alkyl esters thereof, such as methyl-, ethyl-, and butyl(meth)acrylate; vinylically unsaturated, hydrolysable silane compounds, such as vinyl trimethoxy silane; vinyl acetate, etc.

Low density polyethylene (LDPE), i.e. polyethylene prepared by radical polymerisation at a high pressure is a preferred ethylene polymer at present.

The stabilizing agent should be incorporated homogeneously into the polymer material and this is preferably done by compounding the polymer material and the stabilizing agent in the form of a master batch. The stabilizing agent master batch may consist of the copolymer stabilizing agent only or it may comprise the copolymer stabilizing agent together with another master batch polymer such as polyethylene. The master batch may also include other additives, including other stabilizing agents to be incorporated into the polyolefin material. However, the stabilizing agent of the present invention provides combined light and heat/oxidation stabilization. This means that the stabilizing agent of the present invention may be used as a UV stabilizer as well as an antioxidant. It is thus possible for the stabilizing agent of the present invention to replace the stabilization "cocktails" generally used so far. This implies advantages with regard to costs as well as environmental aspects and human health.

The amount of the stabilizing agent in the master batch is not critical, but in order to conveniently give the amounts of stabilizing agent in the polymer material defined below, the master batch usually comprises the stabilizing agent in an amount such as to give 2 – 25 % by weight of comonomer units (B) in the master batch.

With regard to the amount of the copolymer stabilizing agent added to a polymer material, such as an ethylene polymer, this is dependent on the content of the comonomer (B) in the stabilizing agent. Thus, decisive for the amount of copolymer stabilizing agent added is the overall amount of comonomer (B) and not the amount of the copolymer stabilizing agent as such. Generally, it is preferred to incorporate the copolymer stabilizing agent in such an amount that the comonomer (B) comprises 0.01 – 0.80 % by weight, more preferably 0.05 – 0.60 % by weight of the polymer material.

Although the stabilizing agent of the present invention may be used as a stabilizing agent for various polymer materials as defined above, it is particularly useful as a stabilizing agent for ethylene polymers and propylene polymers. The stabilizing agent is preferably used as a stabilizing agent for ethylene polymers, and particularly good results have been obtained when stabilizing low density polyethylene (LDPE) as well as high density polyethylene (HDPE).

Having explained the present invention above, it will now be further illustrated by way of some non-limiting examples.

Example 1

This example illustrates the enhanced resistance against thermo-oxidative degradation provided by the stabilizing agent of the present invention.

The base resin used for the degradation tests was an LDPE polymer with a melt flow rate (MFR_2) of 2 g/10 min, determined according to ISO 1133, and a density of 0.920 g/cm^3.

Three stabilizing agents were tested, one stabilizing agent A according to the present invention, and two reference stabilizing agents B and C, respectively.

The stabilizing agent A according to the present invention was a copolymer of ethylene and a vinyl compound of formula (I) with $X = O$; $R_1 = R_2 = R_4 = H$; and $R_3 = CH_3$. The stabilizing agent A contained about 1.4 mole% of the vinyl compound of formula (I) as determined by NMR (6.3 vinyl compound units/1000 carbon atoms). The MFR_2 of stabilizing agent A was about 200 g/10 min.

The reference stabilizing agent B was a copolymer similar to that of stabilizing agent A, except that it contained only about 0.5 mole% (2.3 vinyl compound units/1000 carbon atoms) of the vinyl compound of formula (I). The MFR_2 of stabilizing agent B was also about 200 g/10 min.

The reference stabilizing agent C was a well-known oligomeric HALS stabilizing agent available under the trade name Chimassorb 944 from Ciba-Geigy.

The amount of stabilizing agent added to the base resin was such that the same molar concentration of stabilizing groups were obtained in the base polymer in each case.

The test samples were prepared by blending the two components (base resin and stabilizing agent) in a Brabender Plasticorder operating at 140°C and 40 rpm. When preparing test samples of stabilizing agent C a master batch was first prepared containing 1.2 % by weight of stabilizing agent C, and then the master batch was diluted with more base resin to a concentration of 0.06 % by weight stabilizing agent C. The same procedure was used for stabilizing agents A and B, although the concentration in % by weight was adjusted to obtain the same concentration in mole% of stabilizing groups for all three test samples.

The test samples were then pressed in a hot press at 125°C to thin films with a thickness of 0.1 – 0.2 mm for ageing tests. The ageing was performed at 90°C in a cellular oven, Elastocon EB01. An air flow of 0.8 liters/min was used for the ageing tests.

The ageing was monitored by FT-IR and SEC (Size Exclusion Chromatography) measurements. The FT-IR measurements were made on a Perkin-Elmer FT-IR 2000 for determinimg the thermo-oxidative degradation in terms of carbonyl index (CI). The carbonyl index is the peak height of the absorption at 1717 cm^{-1} divided by the peak height of an internal reference at 2019 cm^{-1}. The SEC measurements were made on a Waters 150 CV type apparatus operating at 135°C and using trichlorobenzene as the mobile phase. The equipment was calibrated with narrow polystyrene standards and linear polyethylene samples according to the principle of universal calibration. The weight average molar mass (Mw) values obtained have not been corrected for long chain branches.

The results of the FT-IR measurements are shown in Figure 1 and the results of the SEC measurements are shown in Figure 2.

As is evident from both Figure 1 and Figure 2, stabilizing agent A according to the present invention with the highest amount of HALS comonomer has an outstanding performance compared both to stabilizing agent B and stabilizing agent C.

Example 2

This example illustrates the enhanced resistance against degradation caused by ultraviolet radiation (UV degradation) provided by the stabilizing agent of the present invention.

Three different stabilizing agents were tested: (i) stabilizing agent I according to the present invention which corresponded to stabilizing agent A in Example 1; (ii) stabilizing agent II (reference) which corresponded to stabilizing agent C in Example 1; and (iii) stabilizing agent III (reference) which was a low molecular weight HALS stabilizing agent known to provide good stability against UV degradation and commercially available under the trade name Tinuvin 770 from Ciba-Geigy.

The samples for the UV degradation test were prepared in the same way as described in Example 1. The UV degradation tests were performed at 65°C on an Atlas Wheatherometer equipped with a Xenon lamp operating in the wavelength intervall of 290 – 400 nm under 50 % relative humidity. The temperature given is the one a black body would have when placed in the test chamber and not the actual temperature of the tested specimens. The tests were performed according to ISO 4892-2.

The UV degradation was monitored by carbonyl index (CI) and molar mass (Mw) measurements.

For the UV degradation tests the CI values are based on the peak at about 1712 cm^{-1} divided by the internal reference at 2019 cm^{-1}. The molar mass (Mw) was determined in the same way as described in Example 1. The results are shown in Figure 3 and Figure 4.

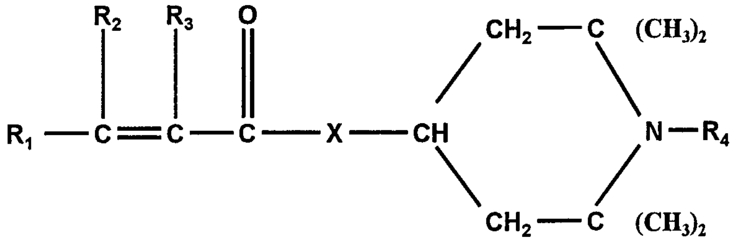
As is evident from Figure 3, the samples stabilized with stabilizing agent III (Tinuvin 770) reached a very high CI value and showed a substantial decrease in Mw after 2500 hrs of ageing, i.e. the stabilizing effect of stabilizing agent III against UV degradation was poor. The same effect also applies for stabilizing agent II (Chimassorb 944), although to a lesser extent. Stabilizing agent I according to the present invention, however, shows excellent performance with regard to stabilization against UV degradation.

The results of Examples 1 and 2 show that the stabilizing agent according to the present invention is an excellent combined light and heat stabilizing agent.

Having thus described and exemplified the invention with reference to preferred embodiments, it is obvious to the skilled person that it is possible to modify the invention within the scope of the invention as defined by the appended claims.

CLAIMS

1. A stabilizing agent for polymers, characterised in that it comprises a copolymer of ethylene or propylene (A) and a vinyl compound (B) with the formula (I):



(I)

wherein X = O, NH or NR_5; R_1, R_2 and R_3 independently each = H, $C_1 - C_8$ alkyl, $C_1 - C_8$ – alkenyl or $C_1 - C_8$ substituted aryl; R_4 = H, $C_1 - C_8$ alkyl, $C_6 - C_{12}$ cycloalkyl, $C_1 - C_{10}$ acyl, $C_1 - C_{10}$ acyloxy or $C_1 - C_8$ alkyl ether; R_5 = $C_1 - C_8$ alkyl; the copolymer contains at least 1 mol% of (B); and the copolymer has an MFR_2 of 1 – 1000 g/10 min.

2. A stabilizing agent as claimed in claim 1, wherein the copolymer contains at least 1.2 mol% of (B).

3. A stabilizing agent as claimed in claim 1 or 2, wherein the copolymer contains 1.5 – 4 mol% of (B).

4. A stabilizing agent as claimed in any one of claims 1 – 3, wherein the MFR is 10 – 400 g/10 min.

5. A polymer material comprising the stabilizing agent according to any one of claims 1 – 4 as a combined light and heat stabilizing agent.

6. A polymer material as claimed in claim 5, wherein the amount of the stabilizing agent is such that (B) comprises 0.01 – 0.80 % by weight of the polymer material.

7. A polymer material as claimed in claim 6, wherein the amount of (B) is 0.05 – 0.60 % by weight of the polymer material.

8. A polymer material as claimed in any one of claims 5 – 7, wherein the polymer material is a polyolefin.

FIG I

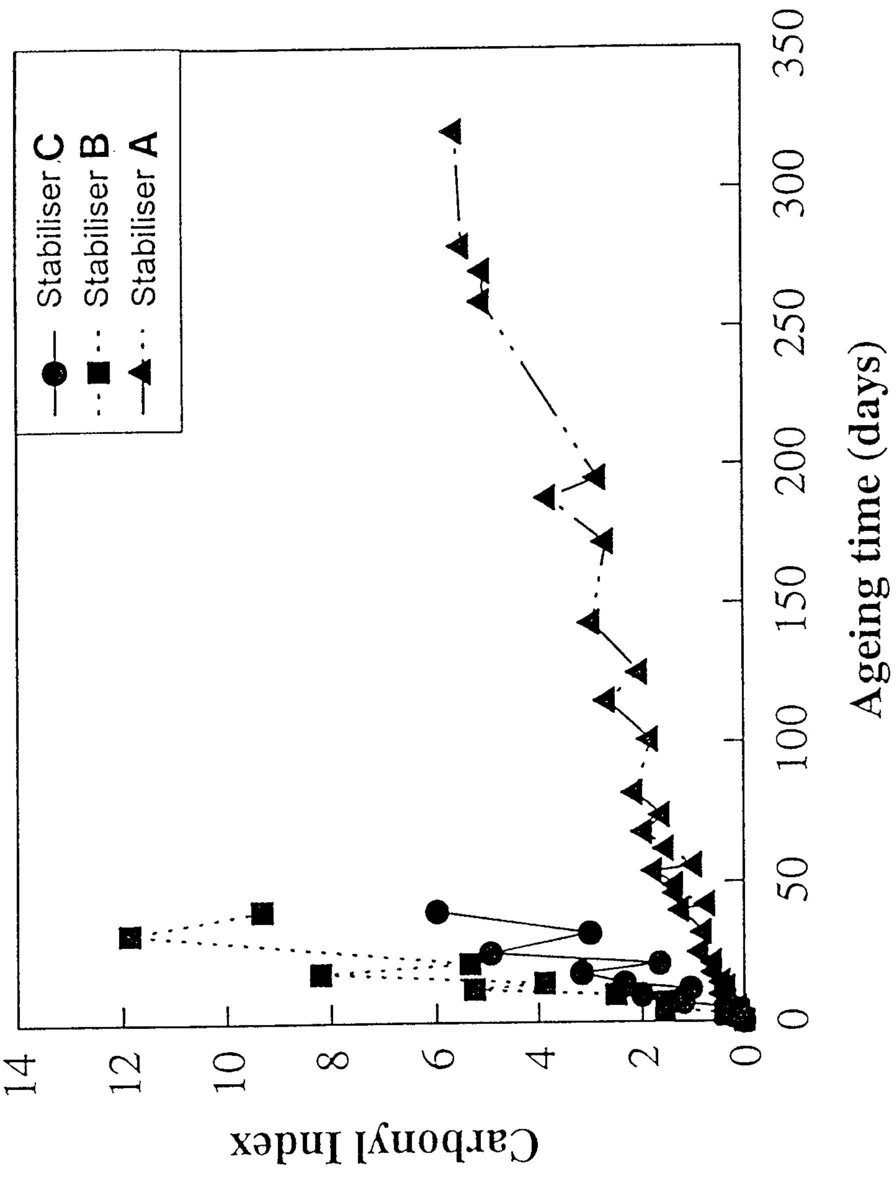

Carbonyl Index
0
2
4
6
8
10
12
14
Ageing time (days)
0
50
100
150
200
250
300
350
Stabiliser C
Stabiliser B
Stabiliser A

FIG 2

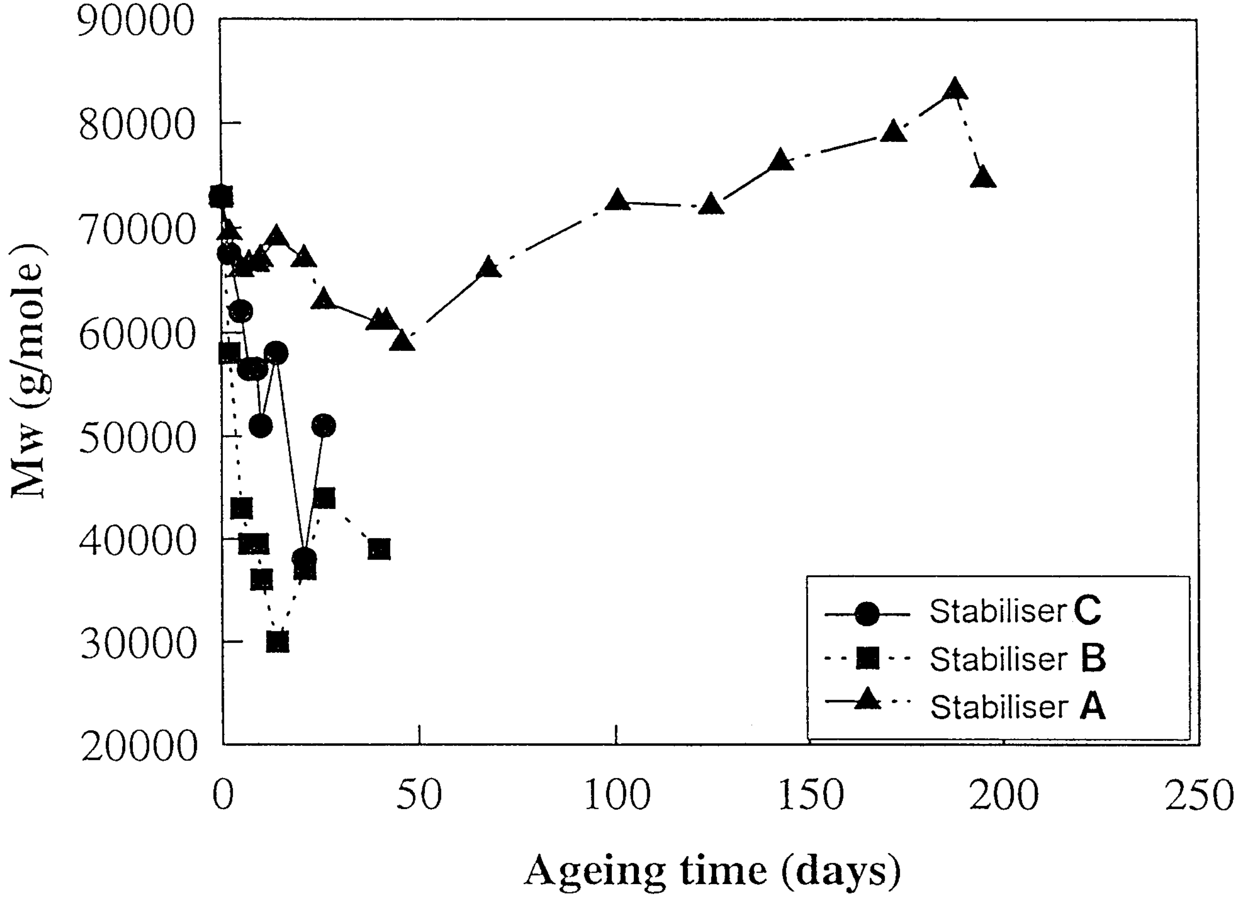

90000
80000
70000
60000
50000
40000
30000
20000
Mw (g/mole)
0
50
100
150
200
250
Ageing time (days)
Stabiliser C
Stabiliser B
Stabiliser A

FIG 3

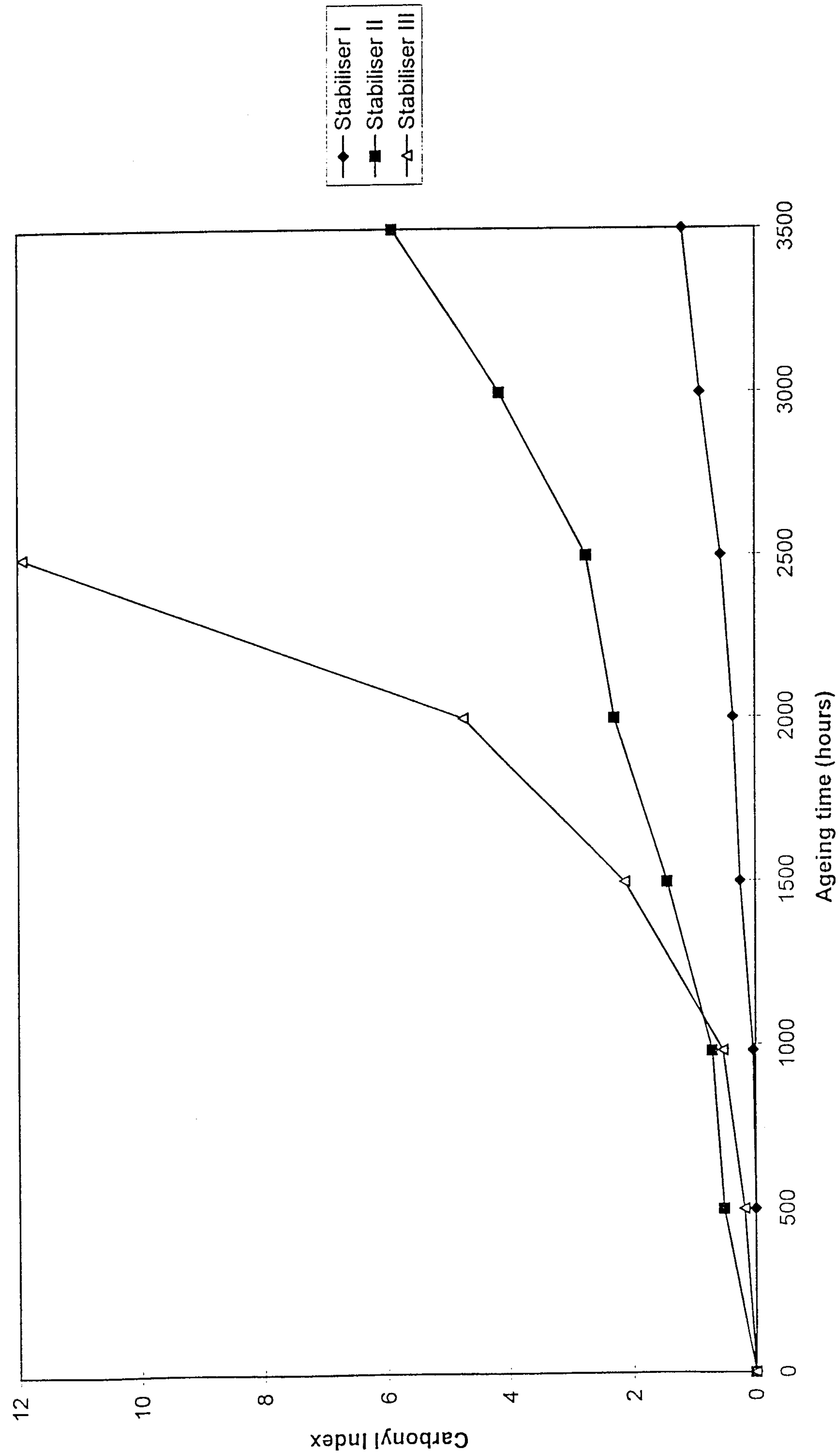
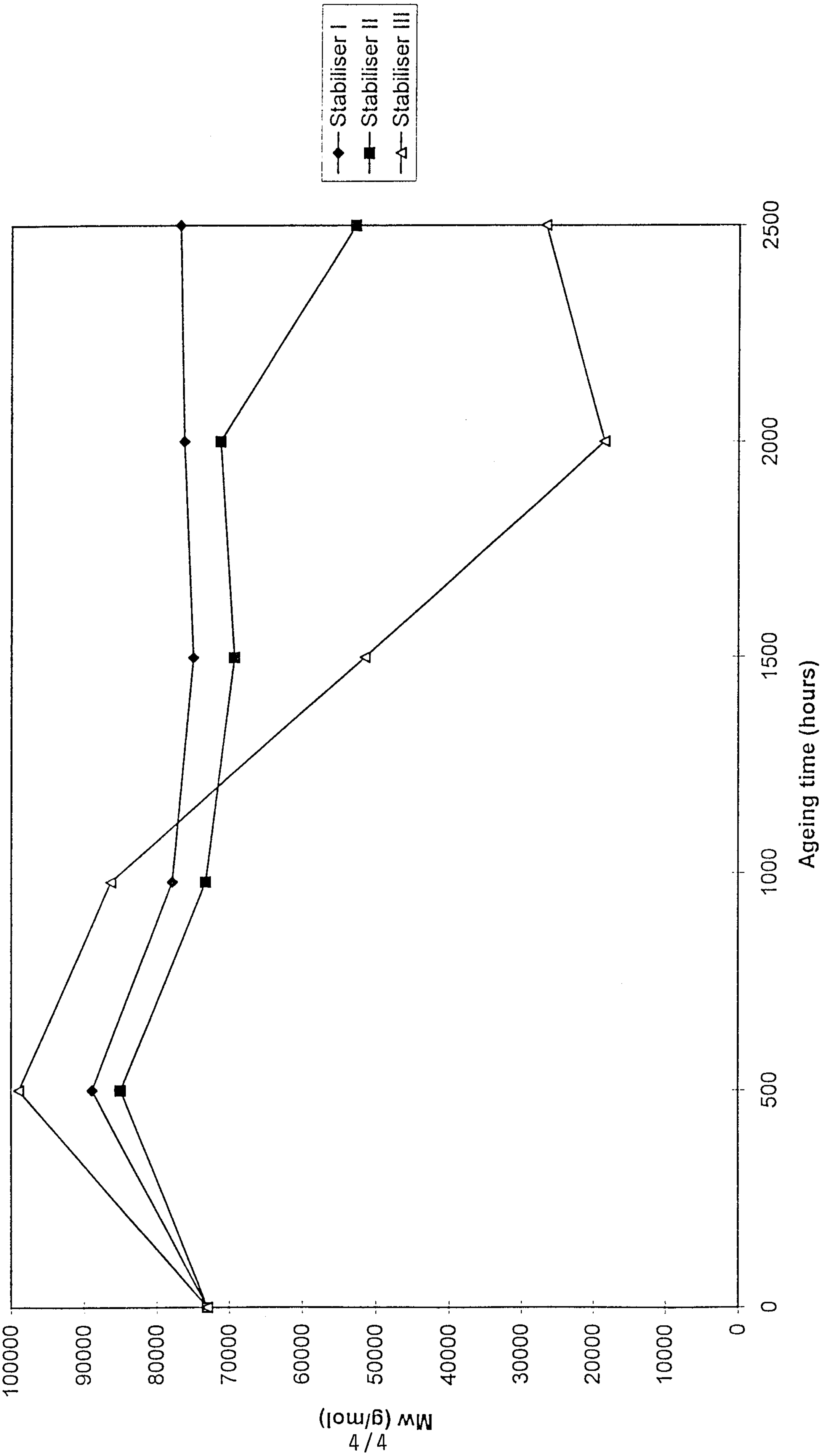

Stabiliser I
Stabiliser II
Stabiliser III
Carbonyl Index
0
2
4
6
8
10
12
Ageing time (hours)
0
500
1000
1500
2000
2500
3000
3500

FIG 4


Stabiliser I
Stabiliser II
Stabiliser III
Mw (g/mol)
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
0
500
1000
1500
2000
2500
Ageing time (hours)

INTERNATIONAL SEARCH REPORT

tional Application No
PCT/EP 99/07695

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F210/02 C08F210/06 C08L23/00 //(C08F210/02,220:34, 220:60)

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)
IPC 7 C08F C08L

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 294 949 A (KARRER FRIEDRICH) 13 October 1981 (1981-10-13) examples 82,83	1,2,5-8
X	EP 0 063 544 A (CIBA GEIGY AG) 27 October 1982 (1982-10-27) claims 8,11	1-4,7-9
A	EP 0 468 418 A (MITSUBISHI PETROCHEMICAL CO) 29 January 1992 (1992-01-29) cited in the application the whole document	1-8

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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Date of the actual completion of the international search 15 February 2000	Date of mailing of the international search report 24/02/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Friederich, P

INTERNATIONAL SEARCH REPORT

Information on patent family members

I ional Application No
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