

PATENT SPECIFICATION

(11) 1234 128

NO DRAWINGS

- (21) Application No. 8522/69 (22) Filed 17 Feb. 1969
 (31) Convention Application No. 2371 (32) Filed 19 Feb. 1968 in
 (33) Switzerland (CH)
 (45) Complete Specification published 3 June 1971
 (51) International Classification C 07 c 103/32
 (52) Index at acceptance
 C2C 220 227 22Y 30Y 342 34Y 364 365 366 368 36Y
 586 58Y 591 62X 63X 658 65X 793 797 79Y
 KM KW
 C3F 331 413 621
 C3P 10A 10C17 10C20C 10D1A 7A 7C12X 7C17 7C18
 7C20B 7C20C 7C20D1 7C20D3 7D1A 7D1C
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(54) OXALIC ACID DERIVATIVES

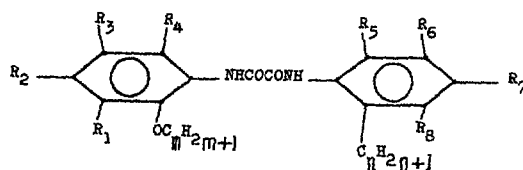
(71) We, SANDOZ LTD., of Lichtstrasse 35, Basle, Switzerland; a Swiss Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to new asymmetric diaryloxalamides and their use as stabilizers and ultra violet (hereinafter referred to as UV) light absorbers for plastics.

It is known that certain asymmetric diaryloxalamides may be used as UV light absorbers for plastics. The known compounds of this class, however, are either relatively difficultly soluble in the plastics, especially polyolefins, or alternatively contain one or more high molecular weight organophile radicals with a hydrocarbon portion containing more than 8 carbon atoms which reduce the effectiveness of the diaryloxalamides as UV light absorbers.

It has now been found that asymmetric diaryloxalamide compounds of the formula I below have a good solubility in polymers, especially in polyolefins, which compounds do not contain any of the above mentioned high molecular weight organophile radicals in their molecule.

The present invention provides compounds of the formula I



in which each of

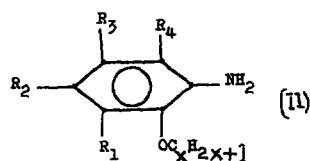
$R_1, R_2, R_3, R_4, R_5, R_6, R_7$ and R_8 represents H, Cl, Br, $-\text{C}_n\text{H}_{2n+1}$, $-\text{C}_n\text{H}_{2n-1}$ or $-\text{O}-\text{C}_n\text{H}_{2n+1}$ or an $-\text{O}-\text{aryl}$, alkaryl, aralkyl or aryl radical with up to 8 carbon atoms,

m represents a whole number from 1 to 8 inclusive, and

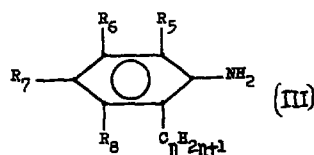
n represents a whole number from 1 to 4 inclusive, with the proviso that the radicals $R_1, R_2, R_3, R_4, R_5, R_6, R_7$ and R_8 , within their definition, may be similar or dissimilar and n need not necessarily have the same value in all of the radicals where n occurs.

The present invention also provides a process for the production of the compounds of formula I, which process is characterized in that 1 mol of oxalic acid or 1 mol of a functional derivative (for example an ester, acid halide or ester halide, e.g. the acid chloride, acid bromide or an ester chloride) thereof is reacted, simultaneously or consecutively, with 1 mol of a compound of the formula II

[Price 25p]



in which R_1 to R_4 are as defined above and x is zero or a whole number from 1 to 8 inclusive, and 1 mol of a compound of the formula III



in which R_5 to R_8 and n are as defined above, in such a way that amidation of the oxalic acid or its functional derivative is effected to the highest degree possible, and that the resulting product is alkylated with an alkylation agent containing the above radical $-C_{2n+1}H_{2n+1}$ when said product contains a phenolic hydroxyl radical.

The compounds of formula I are very stable against the effect of heat, absorb UV light rays, and are easily soluble in polymers especially polyolefins.

The present invention thus also provides a polymer especially polyethylene or other polyolefin, composition containing dissolved therein a UV light stabilizer constituted by a compound of the formula I above. Preferably the amount of said compound I in said polymer composition should be from 0.1 to 0.5% by weight. Furthermore, it is also within the scope of the present invention to add to the polymer composition comprising the dissolved UV light stabilizer of the formula I one or more additional UV light stabilizers, e.g. a nickel salt UV light stabilizer, a nickel complex UV light stabilizer or a sterically hindered phenol UV light stabilizer.

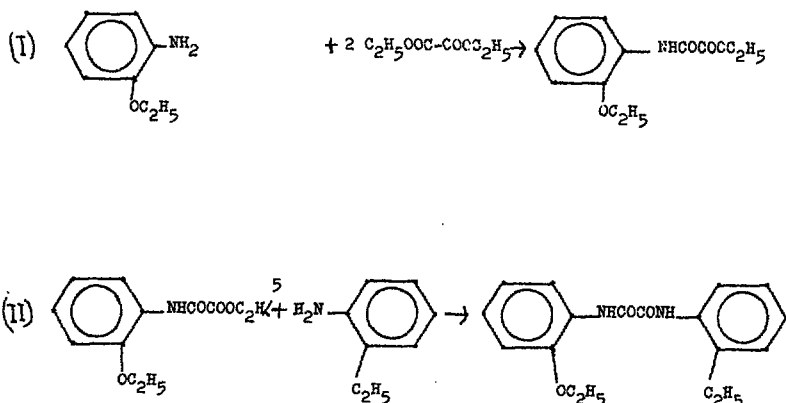
By means of two concrete cases, the following Examples 1 and 2 explain how the diaryloxalamides of the formula I may be produced, the temperatures being stated in degrees Centigrade and the quantities in parts by weight. In Table 1, given after Examples 1 and 2, further compounds of formula I and two similar ones (i.e. the 11th and 22nd compounds in Table 1, which are also included in the present invention) are listed all of which are produced in accordance with the method set forth in Example 1 or 2. The compounds of formula I and the 11th and 23rd compounds in Table 1 as produced by the specifically described method may be incorporated in polymers without purification or may first be purified. Polymers containing a compound of formula I or the 11th and 23rd compound in Table 1 in an amount of from 0.1 to 0.5% by weight are protected against heat and especially against UV light rays; specifically, pressed sheets of polyethylene containing such an amount of said compound are clear in appearance and protected against the harmful effect of UV light rays to an extent sufficient for practical purposes.

Examples A to E illustrate specific methods of using specified compounds of formula I. In Table 2 there are mentioned, for purposes of comparison, a number of diaryloxalamides and their properties which diaryloxalamides do not have the formula I and are therefore outside the scope of the present invention. In both Tables, E signifies the molar extinction coefficient. This was determined with light of a wave length λ with an alcoholic solution of the oxalamide. λ is also the most strongly absorbed wave length expressed in $m\mu$.

The solubility of the oxalamides in ethyl alcohol and benzine (boiling point 100 to 120° C., $D_4^{20}=0.727$) was determined at 20 to 22° in milligrams per litre.

In the Examples reference is made to a Xenotest apparatus and to a Fadeometer; these are manufactured by Atlas Electric Devices Company of Chicago 10, Illinois, U.S.A., the Fadeometer being sold under the designation "Typ FOA—R Serie No. FO 2770".

EXAMPLE 1

Production of *o*-ethoxy-*o'*-ethyl-oxalic acid bis-anilide

I. *o*-Phenetidine and oxalic acid diethyl ester are mixed in molar ratio 1:2, i.e. 1 mol excess of the ester. About 3 to 4 ml, per mol of amine, of ethereal boron trifluoride as catalyst are added to the resulting mixture and heating while stirring is effected to a bath temperature of 130°. After a short time, dissolution takes place. When ethanol reflux commences, a vacuum (about 200 mm of Hg) is applied to the mixture so as to remove the ethanol and stirring at the same temperature is continued for a further one and a half hours. The resulting dark brown solution is stirred for a further ten minutes with decolorizing charcoal at the same temperature and filtering is then effected with the addition of a filtration auxiliary.

Distillation at reduced pressure is then effected in order to remove excess oxalic acid diethyl ester.

On cooling, the resulting ester amide crystallizes out completely; melting point 65 to 71°, yield: 85 to 90%.

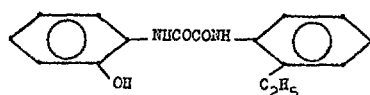
By recrystallization from alcohol the colourless, pure product of melting point 76 to 77° is obtained. However, this purification is unnecessary and the crude product may be used for reaction with a further amine, e.g. as shown at section II hereof.

II. The ester amide produced as at I hereof and 2-ethylaniline in molar quantities are heated for four hours to a bath temperature of 170° with the addition of a little ethereal boron trifluoride as catalyst. The resulting alcohol is removed at reduced pressure (200 mm of Hg) during the reaction. After the reaction is complete, the resulting dark mash is poured into a dish and allowed to cool, whereby a hard mass results which is first comminuted and subsequently triturated with alcohol in a trituration dish, suctioned off and washed with alcohol.

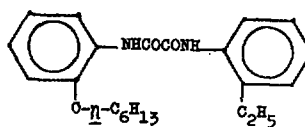
The resulting crude product melts at 121 to 131°. By recrystallization from benzene pure colourless *o*-ethoxy-*o'*-ethyl-oxalic acid bis-anilide is obtained with a melting point of 132—135° and a yield of about 65%.

EXAMPLE 2

By using *o*-aminophenol instead of *o*-phenetidine in Example 1 there is obtained the compound of the formula



1 mol of this compound together with 25 mol of acetone, 1.5 mol of potassium carbonate and 1.2 mol of *n*-hexylbromide are heated for 60 hours to 55° while stirring. Subsequently the acetone is distilled off in a vacuum, the residue is washed several times with water and recrystallization from alcohol is effected. The compound of the formula



is obtained with a yield of approximately 90% in the form of white crystals of melting point 71 to 72°. The absorption maximum in alcoholic solution is around 300 to 310 m μ , the extinction coefficient amounts to 13700. At 20° the solubility in alcohol is about 16.5 grams per litre and in benzene about 23 grams per litre.

TABLE I

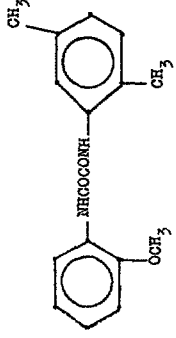
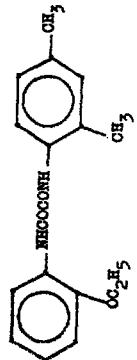
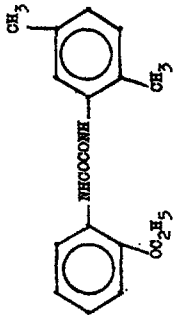
Constitution	m.p.	lambda	E	Solubility in	
				ethanol	benzine
	152—153°	300	13400	1900	2100
	143—145°	300	14200	1700	1250
	132—135°	300	14700	3900	5000
	133—135°	302	15500	2400	2400
	137—138°	302	15600	2240	2300

TABLE 1 (Continued)

Constitution	m.p.	lambda	E	Solubility in	
				ethanol	benzine
	117—118°	305	12400	4100	4500
	100—104°	320	9600	6000	6400
	118—119°	320	10400	3900	1350
	71—72°	300	1370	16500	23000
	70—72°	300	13000	16000	21000

TABLE I (Continued)

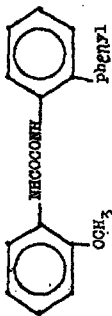
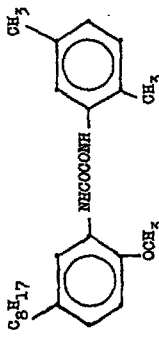
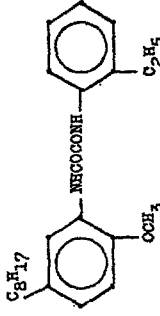
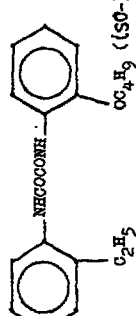
Constitution	m.p.	lambda	E	Solubility in	
				ethanol	benzine
	143—146°	302	16700	2170	1670
	149—151°	305	12300	13800	13300
	103—104°	305	12100	7100	16400
	101—102°	303	12600	5000	11000

TABLE 1 (Continued)

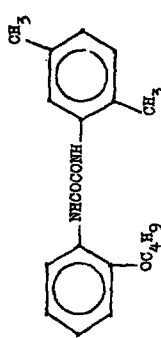
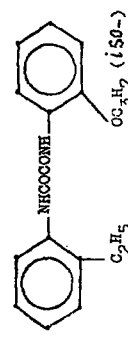
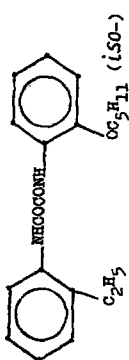
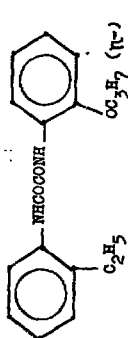
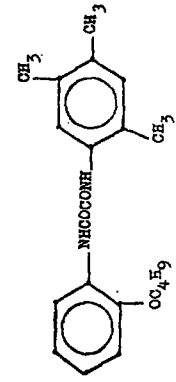
Constitution	m.p.	lambda	E	Solubility in	
				ethanol	benzine
	113—114°	301	13000	3300	5150
	87—88°	300	12700	10300	14300
	98—99°	300	12900	7400	18100
	78—79°	302	13400	13700	22900
	126—128°	304	14000	1430	2500

TABLE I (Continued)

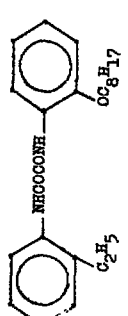
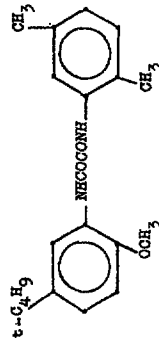
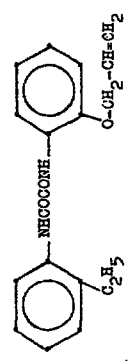
Constitution	m.p.	lambda	E	Solubility in	
				ethanol	benzine
	74—75°	300	13500	3700	12700
	141—142°	305	12500	2800	4700
	87—88°	300	13600		

TABLE 1 (Continued)

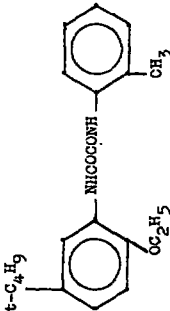
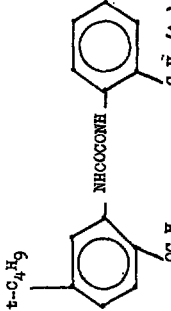
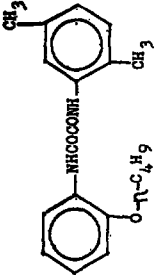
Constitution	m.p.	lambda	E	Solubility in	
				ethanol	benzine
	126—128°	305	11900	7450	13000
	120—122°	310	14700	16000	30500
	113—114°	301	13000	3300	5200

TABLE 1 (Continued)

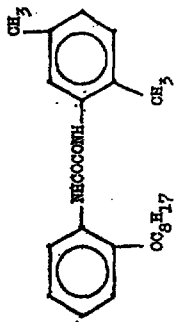
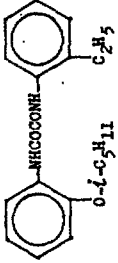
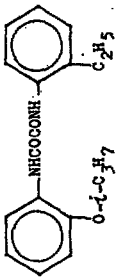
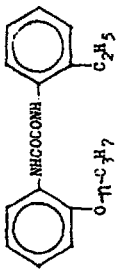
Constitution	m.p.	lambda	E	Solubility in	
				ethanol	benzine
	83—84°	300	13700	1800	10000
	98—99°	300	12900	7400	18000
	87—88°	300	12700	10300	14300
	78—79°	302	13400	13700	23000

TABLE 2

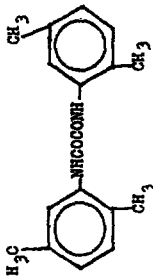
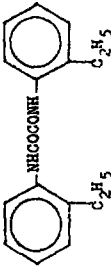
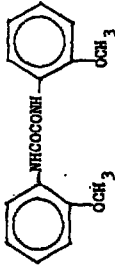
Constitution	m.p.	lambda	E	Solubility in	
				ethanol	benzene
	260—261°	278	12500	82	84
	183—184°	276	12800	450	400
	252—253°	305	16800	53	80
	267—269°	295	20000	4	4

TABLE 2 (Continued)

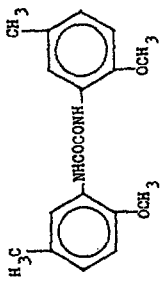
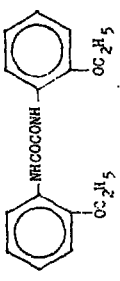
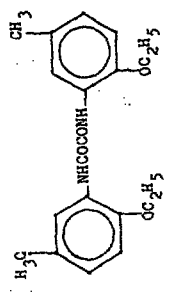
Constitution	m.p.	lambda	E	Solubility in	
				ethanol	benzine
	227—229°	315	16800	150	140
	173—174°	310	18100	470	360
	268—269°	2 95	20900	4	24
	184—186°	315	16800	100	150
	205—207°	287	21800	80	60

TABLE 2 (Continued)

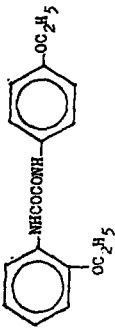
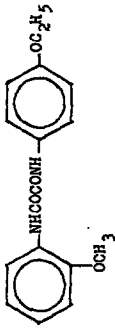
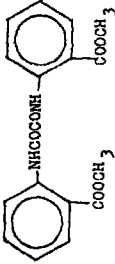
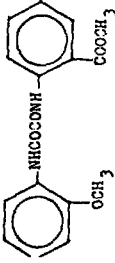
Constitution	m.p.	lambda	E	Solubility in	
				ethanol	benzine
	187—188°	298	17400	500	90
	161—163°	304	18600	675	105
	251—252°	315	20100	50	5
	188—190°	315	17700	400	130

TABLE 2 (Continued)

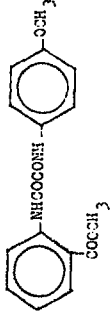
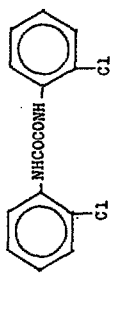
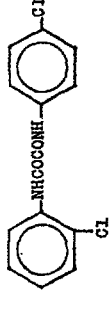
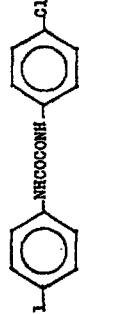
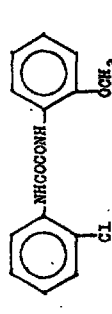
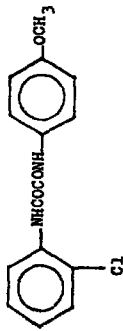
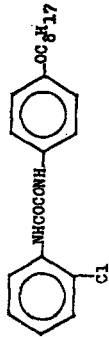
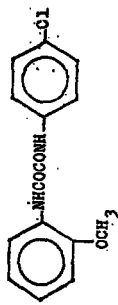
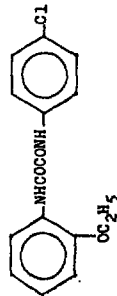
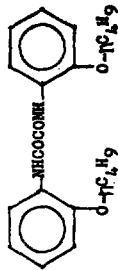
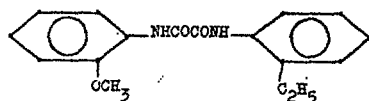
Constitution	m.p.	lambda	E	Solubility in	
				ethanol	benzine
	188—190°	315	18400	190	15
	202—203°	280	17000	150	330
	212—213°	280	19800	180	80
	297—298°	280	22500	63	4
	197—199°	300	14300	500	400

TABLE 2 (Continued)

Constitution	m.p.	lambda	E	Solubility in	
				ethanol	benzine
	171—172°	290	16500	590	140
	150—151°	290	17400	320	500
	215—216°	290	17500	390	60
	187—188°	298	17400	500	90
	122—123°	308	16700	650	1520

Example A

Polyethylene is mixed in a suitable mixer at 150° with 0.2% of its weight of the compound of the formula

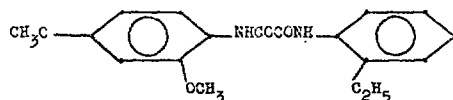


5 and the mixture is then pressed into sheets of a thickness of 0.25 mm.

5

Example B

Polypropylene is mixed in the usual way at 180° with 0.1 weight per cent of the compound of the formula

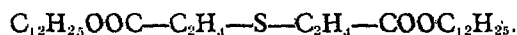


10 and the mixture pressed into sheets of 0.3 mm thickness. After irradiation for 200 hours in a Fadeometer (i.e. an apparatus containing a carbon-arc lamp that emits radiation approximating sunlight) these sheets remain unaltered, whereas a sheet without the above oxalamide shows hair cracks and is brittle. An excellent stabilization of polypropylene is obtained when there is added, in addition to the 0.2% of the above oxalamide, 0.5% of dilaurylthiodipropionate

10

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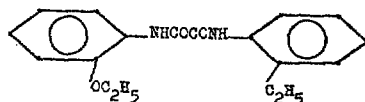


Especially effective as co-stabilizers are nickel salts or complexes, for example nickel stearate; or sterically hindered phenols, for example 2,6-di-*tert*.-butyl-4-methyl-phenol.

Example C

20 0.5% of the compound of the formula

20

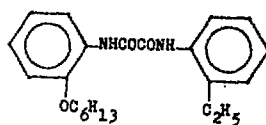


25 are worked into polyvinylchloride at 180°. Sheets made from the resulting mixture by pressing show no change after irradiation for 2000 hours in the Xenotest (i.e. an apparatus provided with a xenon lamp). By measuring the UV light absorption in irradiated and unirradiated samples it can be ascertained that the concentration of the UV light absorber is still practically unchanged.

25

Example D

3% by weight of the compound of the formula



30 are added to a commercially available nitro lacquer, i.e. a 20% solution of cellulose nitrate containing about 12% nitrogen in the usual solvent mixture consisting of toluene, butyl acetate, ethyl acetate and butyl alcohol, said 3% being based on the weight of the cellulose nitrate. Fir wood which has been painted with this lacquer does not darken in colour on exposure to light even after a long period, whereas similarly painted pieces of fir wood with nitro lacquer not containing the above oxalamide darken in colour when similarly exposed.

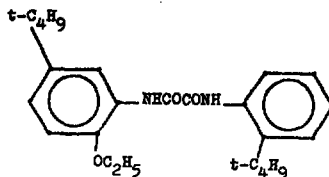
30

35

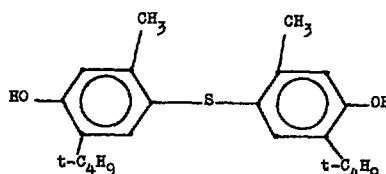
35

Example E

Polyethylene is mixed with 0.3% of the compound of formula



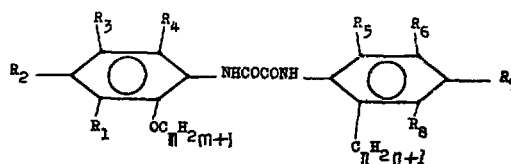
0.4% of the compound of formula



and 0.2% of tri-nonylphenyl phosphite at 180° and pressed into sheets of 0.2 mm thickness; the resulting structures are very well protected against light, heat and oxidation.

WHAT WE CLAIM IS:—

1. A compound of the formula I



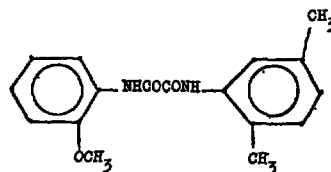
in which each of

$R_1, R_2, R_3, R_4, R_5, R_6, R_7$ and R_8 represents H, Cl, Br, $-C_nH_{2n+1}$, $-C_nH_{2n-1}$ or $-O-C_nH_{2n+1}$ or an $-O$ -aryl, aryl, alkaryl or alkaryl radical with up to 8 carbon atoms,

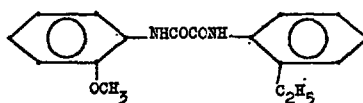
m represents a whole number from 1 to 8 inclusive, and

n represents a whole number from 1 to 4 inclusive, with the proviso that the radicals $R_1, R_2, R_3, R_4, R_5, R_6, R_7$ and R_8 , within their definition, may be similar or dissimilar and n need not necessarily have the same value in all of the radicals where n occurs.

2. A compound of the formula

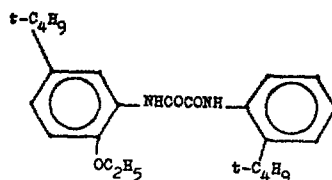


3. A compound of the formula

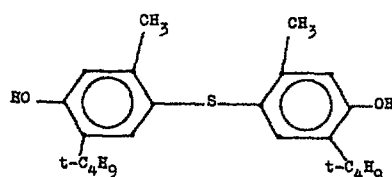


**Example E**

Polyethylene is mixed with 0.3% of the compound of formula



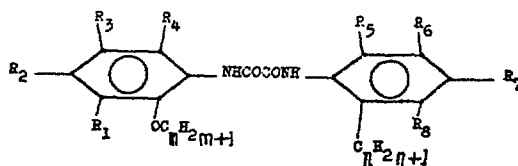
0.4% of the compound of formula



and 0.2% of tri-nonylphenyl phosphite at 180° and pressed into sheets of 0.2 mm thickness; the resulting structures are very well protected against light, heat and oxidation.

WHAT WE CLAIM IS:—

1. A compound of the formula I



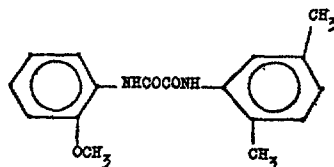
in which each of

$R_1, R_2, R_3, R_4, R_5, R_6, R_7$ and R_8 represents H, Cl, Br, $-C_nH_{2n+1}$, $-C_nH_{2n-1}$ or $-O-C_nH_{2n+1}$ or an $-O$ -aryl, aryl, aralkyl or alkaryl radical with up to 8 carbon atoms,

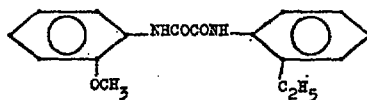
n represents a whole number from 1 to 8 inclusive, and

n represents a whole number from 1 to 4 inclusive, with the proviso that the radicals $R_1, R_2, R_3, R_4, R_5, R_6, R_7$ and R_8 , within their definition, may be similar or dissimilar and n need not necessarily have the same value in all of the radicals where n occurs.

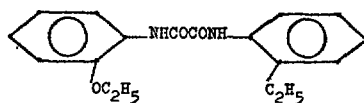
2. A compound of the formula



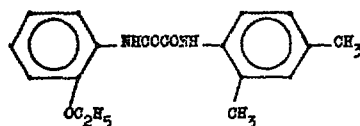
3. A compound of the formula



4. A compound of the formula



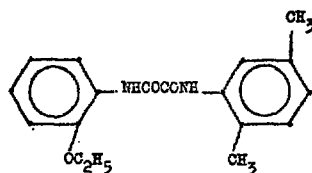
5. A compound of the formula



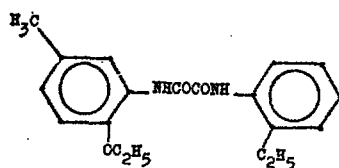
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6. A compound of the formula

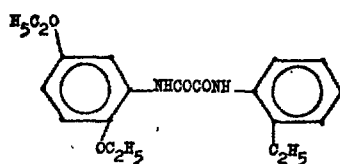
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7. A compound of the formula



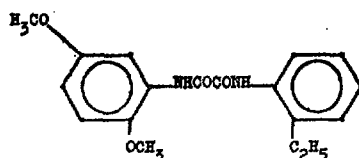
8. A compound of the formula



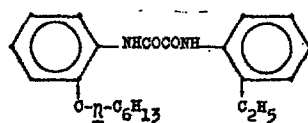
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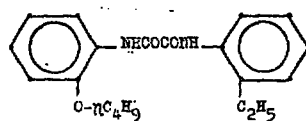
9. A compound of the formula



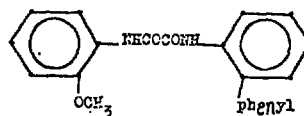
10. A compound of the formula



11. A compound of the formula



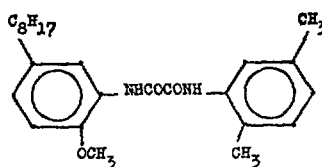
12. A compound of the formula



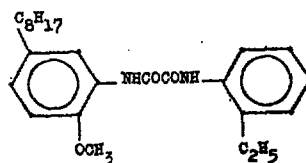
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13. A compound of the formula

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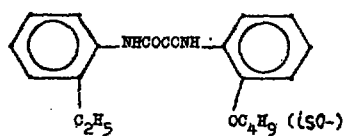


14. A compound of the formula



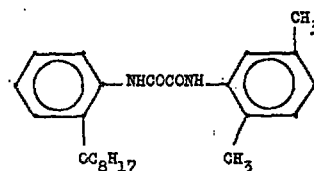
15. A compound of the formula

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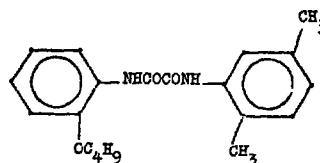


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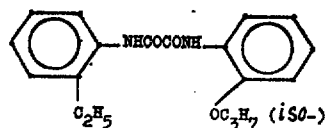
16. A compound of the formula



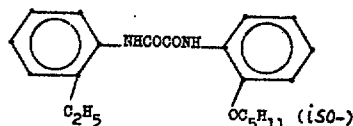
17. A compound of the formula



18. A compound of the formula



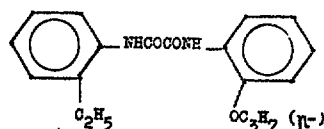
19. A compound of the formula



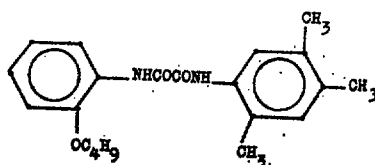
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20. A compound of the formula

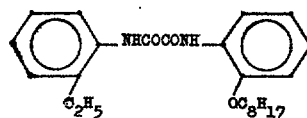
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21. A compound of the formula



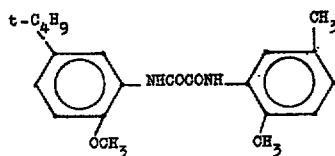
22. A compound of the formula



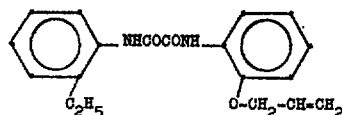
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23. A compound of the formula



24. A compound of the formula

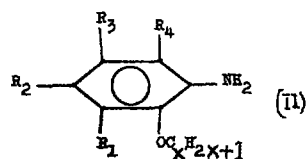


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25. A process for the production of a compound of the formula I defined in Claim 1, which process is characterized in that 1 mol of oxalic acid or 1 mol of a functional derivative thereof is reacted, simultaneously or consecutively, with 1 mol of a compound of the formula II

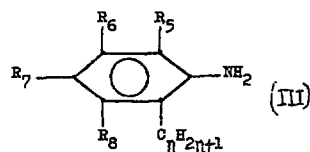
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in which

R_1 to R_4 are as defined above and
 x is zero or a whole number from 1 to 8 inclusive,
 and 1 mol of a compound of the formula III



in which

R_5 to R_8 and n are as defined above, in such a way that amidation of the oxalic acid or its functional derivative is effected to the highest degree possible, and that the resulting product is alkylated with an alkylation agent containing the above radical $-C_mH_{2m+1}$ when said product contains a phenolic hydroxyl radical.

26. A process according to Claim 25 substantially as herein described with reference to either one of the two Examples.

27. A polymer composition containing dissolved therein a UV light stabilizer constituted by a compound of the formula I as claimed in Claim 1, 12 or 24.

28. A polyethylene composition containing dissolved therein a UV light stabilizer constituted by a compound of the formula I as claimed in Claim 1, 12 or 24.

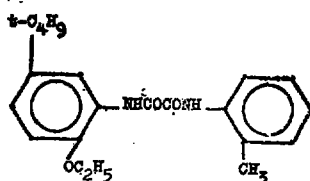
29. A composition according to Claim 27 or 28, in which said compound is present in an amount of from 0.1 to 0.5% by weight.

30. A composition according to Claim 27 or 28, in which there is additionally present a further UV light stabilizer.

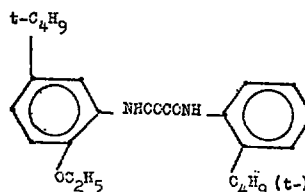
31. A composition according to Claim 27 or 28, in which there is additionally present a further UV light stabilizer selected from nickel salt UV light stabilizers, nickel complex UV light stabilizers and sterically hindered phenol UV light stabilizers.

32. A composition according to any one of Claims 27 to 31, in which said compound of formula I has the formula set forth in any one of Claims 2 to 24.

33. A compound of the formula



34. A compound of the formula



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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1971.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

