

PATENT SPECIFICATION

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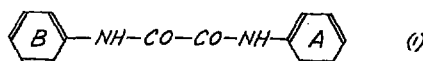
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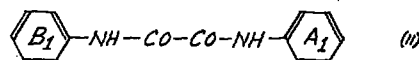
(54) PROCESS FOR THE PRODUCTION OF ALKYLATED N,N'-DIPHENYLOXAMIDES

(71) We, SANDOZ LTD., of Lichtstrasse 35, Basle/Switzerland, a Body Corporate organised according to the laws of Switzerland, 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:—

This invention relates to a process for the production of alkylated N,N'-diphenyloxamides of the formula



in which one or both of the nuclei A and B is or are substituted by 1 to 4 secondary or tertiary alkyl radicals having 3 to 20 carbon atoms and is or are otherwise unsubstituted or is or are further substituted by hydroxyl groups and/or hydrocarbon radicals having 1 to 20 carbon atoms which are bound to the nucleus directly or through an oxygen or sulphur atom. It relates also to certain compounds of that formula. The new process includes alkylating by the alkylation, in the presence of sulphuric acid, of 1 mol of a compound of formula



in which one or both of the nuclei A₁ and B₁ may contain hydroxyl groups and/or hydrocarbon radicals having 1 to 20 carbon atoms which may be bound through oxygen or sulphur atoms, with 1 to 4 mols of an olefin having 3 to 20 carbon atoms, or a secondary or a tertiary alcohol. Employing this reaction, N,N'-diphenyloxamides alkylated by a branched alkyl group or groups in the nucleus are obtained in very good yield. This is surprising since in the analogous reaction of other N-phenylamides, for example N-phenylacetamide, no or very little nucleo-alkylated amide is obtained. The difference is probably due to the fact that the amides of formula (II), in contrast to other amides such as N-phenylacetamide, are stable under the reaction conditions.

A considerable number of starting compounds of the general formula (II) are known. New members of the series can be easily synthesized by generally known methods. Each of the nuclei A₁ and B₁ in the general formula (II) may be unsubstituted or substituted. The following substituents are suitable: the hydroxyl group, which preferably occurs once only in a benzene, nucleus, straight or branched alkyl radicals such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert. butyl, iso-amyl, octyl, nonyl, dodecyl and octadecyl, cycloalkyl radicals such as the cyclohexyl radical, aryl radicals, in particular phenyl, aralkyl radicals such as the benzyl radical,

alkoxy radicals such as methoxy, ethoxy, iso-propoxy, n-butoxy, n-hexoxy, n-octoxy, dodecyloxy and octadecyloxy, alkylmercapto radicals such as methylmercapto, ethylmercapto, butylmercapto, hexylmercapto and octylmercapto, aryloxy radicals such as phenoxy, and arylmercapto such as phenylmercapto. The preferred substituents on the nuclei A₁ and B₁ of the starting compounds of formula (II) are hydroxyl groups, alkyl groups having 1 to 4 carbon atoms, alkoxy and alkylmercapto groups having 1 to 8 carbon atoms.

The alkylating agent may be chosen from the following: propene, 1-butene, 2-butene, iso-butylene, 2-methyl-1-butene, 2-methyl-2-butene, 3-methyl-1-butene, 1-pentene, 2-ethyl-1-butene, 3,3-dimethyl-1-butene, 1-hexene, 3-methyl-1-pentene, 4-methyl-2-pentene, 2,4-dimethyl-2-pentene, 4,4-dimethyl-1-pentene, 2-heptene, 3-methyl-1-hexene, tripropylene, tetrapropylene, di-iso-butylene, tri-iso-butylene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-eicosene, iso-propanol, secondary butanol, tertiary butanol, 2-methyl-2-butanol, 2-pentanol, 3-pentanol, 2,3-dimethyl-2-butanol, 2-methyl-2-pentanol, 2-methyl-3-pentanol, 3-methyl-3-pentanol, 2,4-dimethyl-2-pentanol, 3-heptanol, 2-methyl-2-hexanol, 3-methyl-3-hexanol, 5-methyl-3-hexanol, 3-ethyl-4-hexanol, 2,2-dimethyl-3-hexanol, 3,4-dimethyl-3-hexanol, 2-methyl-2-heptanol, 6-methyl-2-heptanol, 4-octanol, 2,3,4-trimethyl-3-pentanol, 2-methyl-2-octanol, 3-methyl-4-octanol, 5-nonanol, 3,6-dimethyl-3-octanol, 4-methyl-4-nonanol, 2,6,8-trimethyl-4-nonanol, 2-nonadecanol.

The olefins and the secondary or tertiary alcohols containing 3 to 12 or more, especially 3 to 9, carbon atoms are given preference as alkylating agents so that the final products of formula (I) bear preferably 1 to 4 secondary or tertiary alkyl radicals having 3 to 12 or in particular 3 to 9 carbon atoms.

In the present process sulphuric acid can be used both as a catalyst and as a condensing agent. In order to be sufficiently effective it must be employed in highly concentrated form, i.e. of more than 90%, preferably 95—100% strength. Very low percentage oleum containing e.g. up to 5% sulphur trioxide, is also suitable. In order to prevent the decomposing action of the sulphuric acid on the oxamides to the greatest possible extent, it is advisable to damp the activity of the acid by adding a diluent such as formamide, dimethyl formamide, ammonium sulphate, or one of the sulphates of alkylamines or primary alcohols. A highly suitable diluent or damping agent of this type is methanol, which is converted into methylsulphuric acid by sulphuric acid. When secondary or tertiary alcohols are employed as alkylating agents, water is split off in the reaction; it is therefore advisable to add slowly further 100% sulphuric acid in the course of the reaction so that the freed water does not dilute the sulphuric acid too heavily. It is best to choose the amount and the concentration of sulphuric acid so that its total water content at the end of the reaction (from the methanol present, when used, and/or from the alcohol used for alkylating) does not exceed 15%. If oleum is used, it is advisable to set the reaction mixture with a diluent, e.g. a primary alcohol such as methanol, in a quantity sufficient to preclude sulphonation of the diphenyl oxamide. It is desired to use oleum with e.g. 5—10% sulphur trioxide as catalyst, a primary alcohol such as methanol must be used to prevent sulphonation.

The decomposing action of sulphuric acid can be reduced by lowering the reaction temperature. The reaction can be carried out at temperatures ranging from about -30°C to +50°C, the preferred temperature range being -10°C to +15°C.

If Friedel-Crafts catalysts such as borofluoride etherate in place of sulphuric acid are employed for the reaction, the yields are substantially lower and the products of greatly inferior purity. Good results are obtained when, jointly with sulphuric acid, a second catalyst is employed, such as phosphoric acid, polyphosphoric acid, aluminium chloride, borofluoride, hydrogen fluoride or zinc chloride. However, the results obtained with sulphuric acid as sole catalyst are so good that the joint use of other, substantially dearer catalysts does not normally offer any advantages.

The compounds obtained by the new process described herein are accessible by way of a known process. In this process aniline or aniline derivatives are reacted with compounds yielding the oxalyl radical. The intermediates required for this route of synthesis are often difficult of access and expensive. In comparison, the present process provides a far more favourable route to compounds of formula (I).

The compounds of formula (I) are suitable for use as protective agents against the action of visible light and ultra-violet radiation for organic materials sensitive to this action. The starting compounds of formula (II) employed in this process are also protective agents against light, but their value as such is greatly enhanced by the process as the compounds alkylated in the benzene nucleus provide far more effective protection against light and radiation. For instance, it has been found that 2-ethyl-5'-tert. butyl-2'-ethoxy-N,N'-diphenyloxamide protects polyvinyl chloride and polypropylene

more effectively from ultra-violet radiation than 2-ethyl-2'-ethoxy-N,N'-diphenyloxamide.

Another advantage of the compounds of formula (I) is that they are more highly soluble in some of the organic materials that require protection of this nature, for instance polyalkylenes, and once fixed in the material are more resistant to migration than the oxamides used as starting compounds in the process.

The present invention relates further to the use of the oxamides of formula (I) as ultra-violet absorbers. For this purpose they are either incorporated in the materials for protection or applied to the surface of the material to form a protective film. By absorbing the detrimental ultra-violet rays they safeguard light-sensitive materials from degradation.

The oxamides produced by the present process can also be incorporated in suntan creams and lotions to absorb the ultra-violet radiation which causes erythema. But the suitable applications in plastics technology are far more numerous than in cosmetics and medicine. These oxamides can be used as protective additives in or on cellulose acetate, cellulose acetatebutyrate, polyethylene, polypropylene, polyvinyl chloride, polyvinyl chloride acetate, polyamides, polystyrene, ethyl cellulose, cellulose nitrate, polyvinyl alcohol, silicon rubber, cellulose propionate, melamine-formaldehyde resins, urea-formaldehyde resins, allyl casting resins, polymethyl methacrylate, polyesters and polyacrylonitrile. They can also be used to protect natural products such as rubber, cellulose, wool and silk. The material to be protected may be present in the form of film, sheet, rod, strip or panels, powders, granules, fibres or other solid forms, or as solutions, emulsions or dispersions.

The disclosed protective agents are incorporated in or applied to the materials by the known methods. One important method of application consists in mixing the oxamide of formula (I) with the polymer, e.g. polypropylene granules, in a kneader or other suitable machine, with subsequent extrusion. In this way homogeneous mixing is achieved, which is important for satisfactory protection. The moulding material containing the agent can be extruded in various forms, such as film, tubing or filament which may be woven into textile fabric. In this method of application the UV-absorber is incorporated in the polymer before it is converted into textiles. Alternatively, formed textile fibres and fabrics can be treated with the compounds of formula (I), which in this case are applied from superfine dispersion in an aqueous or other suitable medium. This method is suitable for textiles of polyester and cellulose acetate fibres. The compounds of formula (I) need not necessarily be added to the final polymers. They can if desired be incorporated in the monomers or prepolymers prior to the reaction giving the final polymer.

Besides clear films and the other aforementioned products, the oxamides produced by the disclosed process are suitable for stabilizing opaque, semi-opaque and translucent materials with a surface which is subject to degradation by ultra-violet radiation. Examples are foamed plastics, opaque films and coatings, opaque papers, transparent and opaque coloured plastics, fluorescing pigments, automobile and furniture polishes, creams, lotions and the like, whether opaque, clear or translucent.

The compounds of formula (I) can be employed in combination with other UV-absorbers or with stabilizers. These mixtures of active substances often have a synergistic action and protect the treated materials simultaneously against ultra-violet radiation, heat and oxidative degradation.

In order to obtain protection against ultra-violet radiation it is essential to incorporate the new compounds in the material or to coat the material with them. Light-sensitive foods such as fruit, cooking fats and butter can be protected by storage in plastic film or sheet containing a compound of formula (I).

The present invention relates further to the materials which contain one of the new compounds of formula (I) for protection against ultra-violet radiation. As stated in the foregoing, the oxamides can be incorporated in the materials at any stage of processing using the known methods; the amounts used may vary within wide limits, e.g. from 0.01 to 5%, preferably 0.05 to 1%, relative to the weight of the material for protection.

In the following Examples mp stands for the melting point, the parts and percentages are by weight and the temperatures in degree centigrade. The compounds produced in Examples 7, 16, 18, 21 and 29 are claimed *per se* as novel compounds.

Examples of the Process of Production

Example 1

1000 Parts of 100% sulphuric acid are run into 170 parts of methanol with vigorous stirring and cooling to -5° to 0° . Then 312 parts of 2-ethyl-2'-ethoxy-N,N'-

diphenyloxamide are slowly added at -10° to -5° , followed slowly at the same temperature by 90 parts of tertiary butanol. The temperature is increased to $+5^{\circ}$ and the mixture reacted at this temperature for 6 hours with stirring. Subsequently it is extracted three times using 500 parts of chlorobenzene each time. The combined extracts are washed with 10% sodium carbonate solution, the chlorobenzene removed by steam distillation, and the distillation residue filtered and dried. A practically white crystalline mass is obtained in a yield of about 360 parts. It is readily pulverizable and its melting range is $107-126^{\circ}$. Its composition and constitution, as determined by gas chromatography, infra-red and nuclear resonance spectroscopy, is as follows: approximately 80% 2-ethyl-5'-tert.butyl-2'-ethoxy-N,N'-diphenyloxamide and approximately 20% 2-ethyl-4,5-(di-tert.butyl)-2'-ethoxy-N,N'-diphenyloxamide, with a very small amount of the starting oxamide.

If sulphuric acid of about 97% instead of 100% strength is used and 60 parts of tertiary butanol in place of 90, an approximately 93—95% monobutylation product is obtained, from which can be obtained by re-crystallization, e.g. from iso-propanol, the pure 2-ethyl-5'-tert.butyl-2'-ethoxy-N,N'-diphenyloxamide, which melts at $136-138^{\circ}$.

Alternatively, the amount of 100% sulphuric acid can be increased to 1200 parts and that of tertiary butanol to 150 parts, on which a product is formed containing 60—70% 2-ethyl-4,5'-di-(tert.butyl)-2'-ethoxy-N,N'-diphenyloxamide, which crystallizes from cyclohexane and in the pure form melts at $91-92^{\circ}$.

The alkylated products obtained are more highly soluble at 20° in benzene of boiling point $100-120^{\circ}$ than the starting compound:

	N,N'-diphenyloxamide	Solubility at 20°		
		mg/l	%	
A	2-ethyl-2'-ethoxy (starting compound)	5000	0.5	
B	2-ethyl-2'-ethoxy-5'-tert.butyl-	12,000	1.2	
C	2-ethyl-2'-ethoxy-4,5'-di-(tert.butyl)-	>100,000	>10	
80% B	}	15,000	1.5	
20% C				

Example 2

The procedure is as in Example 1, except that 70 parts of iso-butylene are added to the solution of the starting compound in methanol-sulphuric acid in place of tertiary butanol. A product is obtained which has virtually the same composition as that of Example 1.

Example 3

In place of tertiary butanol, the procedure of Example 1 is carried out with 150 parts of di-iso-butylene, the final product being obtained as a soft crystalline mass. It consists of approximately 70% 2-ethyl-5'-tert.octyl-2'-ethoxy-N,N'-diphenyloxamide and about 30% 2-ethyl-4,5'-di-(tert.octyl)-2'-ethoxy-N,N'-diphenyl-oxamide.

Example 4

300 Parts of 100% sulphuric acid are added to flow slowly with thorough stirring at -10° to -15° into a mixture of 60 parts of 2-methyl-2'-ethoxy-N,N'-diphenyloxamide, 60 parts of tertiary butanol and 30 parts of formamide. Stirring is continued for 10 hours at -10° to -5° . The mixture is run on to ice and the precipitated product filtered, washed well with water, and vacuum dried. 87 parts of a soft crystalline mass are obtained, from which 2-methyl-5'-tert.butyl-2'-ethoxy-N,N'-diphenyloxamide, melting point $126-128^{\circ}$, can be isolated by re-crystallization from dioxan.

Example 5

From the isomeric compound 4-methyl-2'-ethoxy-N,N'-diphenyloxamide 4-methyl-5'-tert.butyl-2'-ethoxy-N,N'-diphenyloxamide, melting point $148-149^{\circ}$, is obtained in analogy with Example 4.

Example 6

At -10 to -5° 750 parts of 100% sulphuric acid are added slowly with good stirring and cooling to a mixture of 145 parts of 2-ethoxy-N,N'-diphenyloxamide, 150 parts of tertiary butanol and 100 parts of methanol. Stirring is continued for 6 hours at -5° to 0° . The reaction mixture is discharged on to ice and the precipitated crude product filtered and washed with water. Its melting range is $93-113^{\circ}$. Its composition

determined by gas chromatography, infra-red and nuclear resonance spectroscopy is about 65% 5-tert.butyl-2-ethoxy-N,N'-diphenyloxamide and about 35% 5,4'-di-(tert.butyl)-2-ethoxy-N,N'-diphenyloxamide. These two compounds melt at 117—118° and 136—137° respectively.

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Example 7

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The reaction is carried out as in Example 1 using 2-ethyl-2'-(n-octyloxy)-N,N'-diphenyloxamide in place of 2-ethyl-2'-ethoxy-N,N'-diphenyloxamide. It gives 2-ethyl-5'-tert.butyl-2'-(n-octyloxy)-N,N'-diphenyloxamide, melting point 70—71°.

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Example 8

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In a reaction vessel 30 parts of methanol are stirred, then 10 parts of ammonium sulphate are added. After cooling to -5 to 0° 210 parts of 100% sulphuric acid are added at this temperature, followed by 57 parts of 2,4-dimethyl-2'-hydroxy-N,N'-diphenyloxamide. In the next hour 40 parts of tertiary butanol are gradually added at -5° to -10°. The reaction mixture is stirred further for 8 hours at 0—5°. It is unloaded on to ice, giving a precipitate which is filtered, washed with sodium carbonate solution and water till free of sulphate ions, vacuum dried, and ground. 75 parts of crude 2,4-dimethyl-3',5'-di-(tert.butyl)-2'-hydroxy-N,N'-diphenyloxamide in the form of a colourless powder are obtained, which after re-crystallization from iso-propanol melts at 152—155°.

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Example 9

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The procedure of Example 8 is followed, with the addition of 32 parts of isobutylene in place of tertiary butanol. The same final product is obtained.

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In the following Examples 10 to 15 the given starting compounds are reacted with tertiary butanol or iso-butylene as in Examples 8 and 9 to yield the named products which are distinguished by their melting points.

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Example 10

2 - Ethyl - 2' - hydroxy - N,N' - diphenyloxamide → 2 - ethyl - 5' - tert.butyl - 2'-hydroxy-N,N'-diphenyloxamide, m.p. 160—163°.

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Example 11

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2 - Ethyl - 2' - hydroxy - N,N' - diphenyloxamide → 2 - ethyl - 3',5' - di - (tert.butyl)-2'-hydroxy-N,N'-diphenyloxamide, m.p. 103—106°.

Example 12

2 - Hydroxy - N,N' - diphenyloxamide → 5,4' - di - (tert.butyl) - 2 - hydroxy-diphenyloxamide, m.p. 162—164°.

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Example 13

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2,5 - Dimethyl - 2' - hydroxy - N,N' - diphenyloxamide → 2,5 - dimethyl - 3'5'-di-(tert.butyl)-2'-hydroxy-N,N'-diphenyloxamide, m.p. 173—174°.

Example 14

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2 - Hydroxy - 3' - ethylmercapto - N,N' - diphenyloxamide → 3,5 - di - (tert.butyl)-2-hydroxy-3'-ethylmercapto-N,N'-diphenyloxamide, m.p. 176—180°.

Example 15

2,2' - Dihydroxy - N,N' - diphenyloxamide → 3,5,3',5' - tetra - (tert.butyl) - 2,2'-dihydroxy-N,N'-diphenyloxamide, m.p. 222—226°.

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In the following Examples 16 to 18 the starting compounds used in Examples 10 and 11 are reacted with the stated branched olefins to give the products named.

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Example 16

Di - iso - butylene → 2 - ethyl - 5' - tert.octyl - 2' - hydroxy - N,N' - diphenyloxamide, m.p. 104—106°.

Example 17

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Tripropylen → 2 - ethyl - 5' - tert.nonyl - 2' - hydroxy - N,N' - diphenyloxamide, m.p. 80—82°.

Example 18

Tetrapropylene → 2 - ethyl - 5' - tert.dodecyl - 2' - hydroxy - N,N' - diphenyloxamide, a colourless viscous oil.

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In the following Examples 19 to 22 the reaction is carried out as in Example 1 or 2 using 2-ethyl-2'-ethoxy-N,N'-diphenyloxamide and the stated alcohol or olefin.

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Example 19

Iso-propanol—→2 - ethyl - 2' - ethoxy - 4,3',5' - tri - isopropyl - N,N' - diphenyloxamide, a liquid mixture of isomers.

Example 20

5 Tertiary amyl alcohol—→2 - ethyl - 2' - ethoxy - 5' - tert.amyl - N,N' - diphenyloxamide, m.p. 98—100°. 5

Example 21

Heptene—→2 - ethyl - 2' - ethoxy - 5' - tert.heptyl - N,N' - diphenyloxamide, m.p. 75—78°.

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Example 22

Tripropylene—→2 - ethyl - 2' - ethoxy - 5' - isononyl - N,N' - diphenyloxamide, m.p. 84—87°.

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In the following Examples 23 to 29 the procedure of Example 4 is employed with tertiary butanol.

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Example 23

2 - Ethoxy - 4' - tert.butyl - N,N' - diphenyloxamide—→2 - ethoxy - 5,4' - di - (tert . butyl)-N,N'-diphenyloxamide, m.p. 136—137°.

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Example 24

20 2 - Methoxy - 2' - methyl - N,N' - diphenyloxamide—→2 - methoxy - 5 - tert. butyl-2'-methyl-N,N'-diphenyloxamide, m.p. 144—145°. 20

Example 25

2 - Methoxy - 4' - methyl - N,N' - diphenyloxamide—→2 - methoxy - 5 - tert. butyl-4'-methyl-N,N'-diphenyloxamide, m.p. 177—179°.

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Example 26

25 2 - n - Octyloxy - 2' - methyl - N,N' - diphenyloxamide—→2 - n - octyloxy - 5-tert.butyl-2'-methyl-N,N'-diphenyloxamide, m.p. 83—85°. 25

Example 27

2 - n - Octyloxy - 4' - methyl - N,N' - diphenyloxamide—→2 - n - octyloxy - 5 - tert.butyl-4'-methyl-N,N'-diphenyloxamide, m.p. 96—98°.

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Example 28

2 - n - Butoxy - 2' - ethyl - N,N' - diphenyloxamide—→2 - n - butoxy - 5 - tert.butyl-2'-ethyl-N,N'-diphenyloxamide, m.p. 69—71°.

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Example 29

35 2 - Methoxy - 4' - n - octylthio - N,N' - diphenyloxamide—→2 - methoxy - 5 - tert.butyl-4'-n-octylthio-N,N'-diphenyloxamide, m.p. 75—80°. 35

Examples of Application

Example A

40 Three samples of polypropylene, the first without a protective additive, the second containing 0.5% of the compound 2-ethyl-2'-ethoxy-N,N'-diphenyloxamide and the third 0.5% of 2-ethyl-5'-tert . butyl-2'-ethoxy-N,N'-diphenyloxamide, are exposed to light in the "Xenotest 450" apparatus. The time is determined at which the samples turn brittle, which is 300, 1500 and 2500 hours respectively. These findings show that although the oxamide used as starting compound in Example 1 is quite a good protective agent against light and ultra-violet radiation, alkylation in the benzene nucleus in accordance with the present invention transforms it into a far more effective compound. 45

Example B

Comparative tests with rigid polyvinyl chloride in place of polypropylene are carried out as in Example A. The samples show embrittlement after 800, 2000 and 4000 hours respectively.

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Example C

Polypropylene containing homogeneously distributed 0.5% of the compound produced as in Example 7 is tested as given in Example A. It withstands exposure to xenon light for 3000 hours without becoming brittle.

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Example D

The mixture of monobutylated and dibutylated oxamide produced as in Example 1 is incorporated in polyamide 6 in an amount of 0.3%. In exposure tests in the "Xenotest 450" apparatus a control sample of the material without the additive turns yellow and brittle after 3000 hours, whereas the sample containing the oxamide mixture withstands 8000 hours exposure without change.

Example E

0.5% of the compound named in Example 16 is incorporated in unstabilized polypropylene. Exposure tests alongside polypropylene without the additive show that it is much more resistant to the action of light and ultra-violet radiation. In tests for heat stability at 140° the first sample does not become brittle until after 14 days, whereas the unprotected sample is brittle after only one day's exposure.

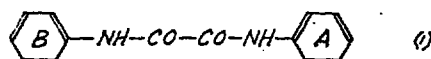
Example F

In a high pressure polyethylene ("Lupolen 1810 H", registered trade mark) 0.5% of the final product of Example 21 is incorporated by the normal method. Sheets of 0.3 mm thickness are moulded with this material, with the same polyethylene containing 0.5% of the starting compound 2-ethyl-2'-ethoxy-N,N'-diphenyloxamide, and with polyethylene containing no additive. The sheets are exposed in the "Xenotest 450" apparatus till brittleness appears. The times that elapse before this effect appears are about 800 hours for the sample without additive, about 1500 hours for the one containing 0.5% of the starting compound, and about 3500 hours for the sample protected with 0.5% of the product of Example 21.

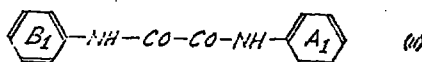
Moreover, migration to the surface ("blooming") of the starting compound is observable in the second sample, whereas this effect is absent in the one containing the product of Example 21.

WHAT WE CLAIM IS:—

1. A process for the production of an alkylated N,N'-diphenyloxamide of formula



in which one or both of the nuclei A and B is or are substituted by 1 to 4 secondary or tertiary alkyl radicals having 3 to 20 carbon atoms, and is or are otherwise unsubstituted or is or are additionally substituted by hydroxyl groups and/or hydrocarbon radicals with 1 to 20 carbon atoms which are bound directly or through an oxygen or sulphur atom to the nucleus, which process includes alkylating in the presence of sulphuric acid of 1 mol of a compound of formula



where one or both of the nuclei A₁ and B₁ is or are unsubstituted or substituted by hydroxyl groups and/or hydrocarbon radicals with 1 to 20 carbon atoms which are bound directly or through an oxygen or sulphur atom to the nucleus, with 1 to 4 mols of an olefin containing 3 to 20 carbon atoms, or a secondary or a tertiary alcohol.

2. A process according to Claim 1 wherein the compound of formula (II) contains no more than 1 hydroxyl group on each benzene nucleus.

3. A process according to Claim 1 wherein the or both of the nuclei A₁ and B₁ are substituted by the substituent(s) being a hydroxy group, alkyl group of 1 to 4 carbon atoms, alkoxy group of 1 to 8 carbon atoms, or alkylmercapto group of 1 to 8 carbon atoms.

4. A process according to Claim 1, Claim 2 or Claim 3 wherein the alkylating agent contains 3 to 9 carbon atoms.

5. A process according to any one of the preceding claims carried out in the presence of concentrated sulfuric acid and a reaction dampening agent.

6. A process according to Claim 5 wherein the dampening agent is formamide, dimethyl formamide, ammonium sulfate, a sulfate of an alkylamine, or a sulfate of a primary alcohol.

Example D

The mixture of monobutylated and dibutylated oxamide produced as in Example 1 is incorporated in polyamide 6 in an amount of 0.3%. In exposure tests in the "Xenotest 450" apparatus a control sample of the material without the additive turns yellow and brittle after 3000 hours, whereas the sample containing the oxamide mixture withstands 8000 hours exposure without change.

Example E

0.5% of the compound named in Example 16 is incorporated in unstabilized polypropylene. Exposure tests alongside polypropylene without the additive show that it is much more resistant to the action of light and ultra-violet radiation. In tests for heat stability at 140° the first sample does not become brittle until after 14 days, whereas the unprotected sample is brittle after only one day's exposure.

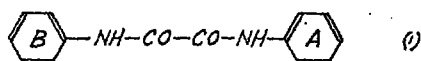
Example F

In a high pressure polyethylene ("Lupolen 1810 H", registered trade mark) 0.5% of the final product of Example 21 is incorporated by the normal method. Sheets of 0.3 mm thickness are moulded with this material, with the same polyethylene containing 0.5% of the starting compound 2-ethyl-2'-ethoxy-N,N'-diphenyloxamide, and with polyethylene containing no additive. The sheets are exposed in the "Xenotest 450" apparatus till brittleness appears. The times that elapse before this effect appears are about 800 hours for the sample without additive, about 1500 hours for the one containing 0.5% of the starting compound, and about 3500 hours for the sample protected with 0.5% of the product of Example 21.

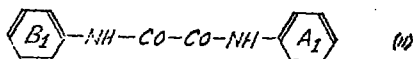
Moreover, migration to the surface ("blooming") of the starting compound is observable in the second sample, whereas this effect is absent in the one containing the product of Example 21.

WHAT WE CLAIM IS:—

1. A process for the production of an alkylated N,N'-diphenyloxamide of formula



in which one or both of the nuclei A and B is or are substituted by 1 to 4 secondary or tertiary alkyl radicals having 3 to 20 carbon atoms, and is or are otherwise unsubstituted or is or are additionally substituted by hydroxyl groups and/or hydrocarbon radicals with 1 to 20 carbon atoms which are bound directly or through an oxygen or sulphur atom to the nucleus, which process includes alkylating in the presence of sulphuric acid of 1 mol of a compound of formula



where one or both of the nuclei A₁ and B₁ is or are unsubstituted or substituted by hydroxyl groups and/or hydrocarbon radicals with 1 to 20 carbon atoms which are bound directly or through an oxygen or sulphur atom to the nucleus, with 1 to 4 mols of an olefin containing 3 to 20 carbon atoms, or a secondary or a tertiary alcohol.

2. A process according to Claim 1 wherein the compound of formula (II) contains no more than 1 hydroxyl group on each benzene nucleus.

3. A process according to Claim 1 wherein the or both of the nuclei A₁ and B₁ are substituted by the substituent(s) being a hydroxy group, alkyl group of 1 to 4 carbon atoms, alkoxy group of 1 to 8 carbon atoms, or alkylmercapto group of 1 to 8 carbon atoms.

4. A process according to Claim 1, Claim 2 or Claim 3 wherein the alkylating agent contains 3 to 9 carbon atoms.

5. A process according to any one of the preceding claims carried out in the presence of concentrated sulfuric acid and a reaction dampening agent.

6. A process according to Claim 5 wherein the dampening agent is formamide, dimethyl formamide, ammonium sulfate, a sulfate of an alkylamine, or a sulfate of a primary alcohol.



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