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## POLYAMIDES CONTAINING A COMBINATION OF (1) A PHENOL, (2) A PHOSPHORUS ACID SALT OR ESTER, (3) A MANGANESE SALT, AND (4) A DICARBOXYLIC ACID AS STABILIZERS

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This invention relates to synthetic polyamide compositions, to processes for their production and to shaped articles, including textile fibres, made from such compositions.

Polyamides, such as polyhexamethylene adipamide and polycaprolactam, are widely used for many purposes because of their remarkable mechanical strength. Their main field of application is the production of synthetic fibres, but they also find increasing use in other branches of manufacture, as, for example, in the production of tools and machine parts. The excellent properties of these polyamides are, however, considerably impaired by their tendency to become yellow under various conditions in the presence of oxygen. The yellowing occurs, for example, when polyamides are subjected to elevated temperatures, when they are repeatedly washed with hot water, and when they are exposed to light and then kept for some time in the dark.

This sensitiveness of polyamides is especially inconvenient for the textile industry, where it is desired to obtain fibres and fabrics of a pure white or of coloured shades unimpaired by any yellowish tinge. It is, therefore very disturbing that discolouration occurs during some stages of manufacture, e.g. when the molten polyamide is discharged from an autoclave, in melt-spinning, and above all, in the dry heat-setting of spun filaments and of knitted or woven fabrics. The troublesome yellowing which appears during these processes may be partially removed by a bleaching treatment, e.g. with sodium chlorite, but such treatment requires an additional working step and may also be harmful to the fibre or fabric. It is, however, known that bleaching with sodium chlorite, while removing the colour present for the time being, considerably increases the tendency of the fibre to future discolouration.

Substances such as phenols and amines, which are antioxidants, have been proposed as stabilizers as it is generally assumed that oxidation is a primary cause of the discolouration of polyamides. Other substances described as stabilizers include manganese salts and phosphorus compounds, and it has also been proposed to use combinations of two or more stabilizing substances. Thus, United States Patent No. 2,887,462 describes the use of salts of manganese with certain reducing acids, and United States Patent No. 2,984,647 mentions manganese phosphates. British specification No. 689,629 proposes manganese or copper salts of salicylic or anthranilic acid, and French Patent No. 1,099,407 suggests a combination of manganese and copper salts. All these combinations are described as being effective against damage by light. As stabilizing agents for polyamides against heat, British specification No. 652,947 proposes copper salts of monocarboxylic acids together with diketones, United States Patent No. 2,705,227 describes a combination of copper, inorganic halogen salts, and phosphorus compounds, and German Auslegeschrift No. 1,111,376 mentions a mixture of cerium (III) and/or titanium (III) salts and hypophosphoric acids. This German specification also points out that the addition of aliphatic carboxylic acids does not stabilize polyamides against the effects of light or heat. None of the above-mentioned combinations of stabilizers have, however, yet led to any final and completely satisfactory solution of the problem of yellowing caused by heat and light.

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The present invention provides synthetic polyamide compositions, especially suitable for making textile fibres, which are substantially free from colour and possess a substantial stability against discolouration caused by heat and light. The expression "free from colour" is used herein to mean absence of any undesired colouration of the polyamide, but does not exclude colour intentionally produced by the addition of dyes or pigments.

The synthetic polyamide compositions of the invention comprise a composite stabilizing agent consisting essentially of (1) a thermally stable phenol, (2) a salt or ester of an inorganic, phosphorus oxy-acid, (3) a manganese salt, and (4) an organic dicarboxylic acid. It will, of course, be understood that all the components of the stabilizing agent must be such that they will not themselves give rise to any colour when incorporated in the polyamide, either because they are coloured per se or because they give rise to coloured substances on irradiation or heating to the temperatures used during manufacture or processing of polyamides. The components of the stabilizing agent must comply with the stated limitations. Thus, for example, simple phenols cannot be used as they are oxidized too quickly, but thermally stabilized phenols containing, e.g. one or more tertiary butyl groups such as 2,5-di-tert-butyl-hydroquinone, 2,2'-methylene-bis-(4-methyl-6-tert-butyl-phenol), 2,2'-methylene-bis-(4-ethyl-6-tert-butyl-phenol), or 4,4'-butylidene bis-(6-tert-butyl-m-cresol), have been found to be very suitable. As the second component, sodium hypophosphite and triphenyl phosphate, which are both reliable, are preferred. For the manganese salt, manganous lactate, manganous oxalate and manganous hypophosphite are very suitable. As the dicarboxylic acid component, adipic acid, sebacic acid, and terephthalic acid are very satisfactory. A further advantage of the invention is that these dicarboxylic acids, in addition to acting as stabilizers, act also as chain terminators for the polycondensation process for making the polyamides. They can, therefore, replace the acetic acid which is usually employed for this purpose. The conventional type of chain terminating mono-carboxylic acid cannot (as shown in the Example III below) be used to replace component (4) in the stabilizing agent of the invention.

The relative quantities of the various components of the stabilizing agent used for optimum results will differ with the specific nature of the components. However, combinations giving especially good protection contain between 0.02 and 0.2% of 2,5-di-tert-butyl-hydroquinone, 2,2'-methylene-bis-(4-methyl-6-tert-butyl-phenol), 2,2'-methylene-bis-(4-ethyl-6-tert-butyl-phenol) or 4,4'-butylidene-bis-(6-tert-butyl-m-cresol), between 0.05 and 0.5% of sodium hypophosphite or triphenyl phosphate, between 20 and 80 parts of manganese per million parts of polyamide in the form of manganous lactate, manganous oxalate, or manganous hypophosphite, and between 0.2 and 1.0% of adipic acid, sebacic acid or terephthalic acid, all the proportions being based on the total weight of the polyamide compositions.

Some of the aforementioned substances have already been proposed as stabilizers for polyamides, but only as isolated substances and not in the specified combination. It has been surprisingly found that the protection against both heat and light afforded by the combination characteristic of this invention is far superior to that afforded by any of the components taken alone. As shown in Example III, combinations containing only three of the components do not give the same satisfactory results.

The stabilizers have the further advantage that they work well in the presence of titanium dioxide, which is usually incorporated in polyamides as a delustering pigment and which is known to increase considerably their sensitivity to light. Dyeing and addition of optical

brightening agents do not impair the effects of the stabilizer combination of this invention and are likewise not disturbed by its presence in the polyamide.

The excellent protection afforded by the new four-component stabilizer against heat is especially important in the textile industry, because polyamides are necessarily heated at several stages in the manufacture of textile fibres. Although poly-condensation is carried out in a nitrogen atmosphere, traces of oxygen are still present, and, in any case, oxidation is possible when the molten mass is discharged from an autoclave or extruded from a spinneret. Unprotected polyamide chips and fibres have, therefore, a distinct ivory colour, while compositions containing the four-component stabilizing agent of the present invention are free from colour or are pure white when delustered. Further discolouration of polyamides usually occurs in the dry heat-setting process, and this operation causes considerable yellowing of unprotected fibres and makes an additional bleaching treatment necessary. It is, therefore, of great value that polyamide fibres and fabrics produced in accordance with the present invention do not need bleaching, that they possess and keep a bright, pure white, and that when dyed, they preserve a clear and distinct colour shade without any yellowish tinge. The same advantages are, of course, shown by other articles made from the polyamide compositions, such as films, foils, tools, and many other goods.

The four components of the stabilizing agent are incorporated in the polyamides during the polycondensation process of manufacture of the polyamides, and the presence of the components has little or no tendency to influence adversely the structural and mechanical properties of the articles obtained. Tests of viscosity, tensile strength, and elongation at break of polyamide fibres have been carried out and showed no appreciable differences between the figures obtained for fibres with and without the addition of the stabilizers.

The reasons for the discolouration of polyamides have not yet been finally ascertained, but the surprisingly good protection afforded by the use of the four-component stabilizing agent of the present invention suggests the following possibility for the reaction mechanism. The chain of reactions leading to discolouration starts with free radicals formed from traces of impurities under the influence of heat or light. These radicals are oxidized in the presence of air to peroxides which, in turn, trigger the formation of polyamide peroxides. The decomposition of the polyamide peroxides then leads to unsaturated compounds which react with free amine end groups with the formation of heterocyclic substances, e.g. pyrroles. The pyrroles finally react by condensation with keto-enol groups in the polyamide, thus producing the actual yellow-coloured materials.

Such a view of the reaction mechanism is substantiated by various observations. When a polyamide is heated for some time in an oxygen-containing atmosphere it shows an increasing oxygen absorption, a fairly constant peroxide concentration, a decrease of the number of amine end groups and a corresponding increase of the pyrrole concentration, as can be seen from the following table:

HEATING OF POLYHEXAMETHYLENE ADIPAMIDE AT 150° C. IN AIR

Time (Hours)	Oxygen absorption (g./kg.)	Peroxide concentration (mg./kg.)	Concentration of amine end groups (mmol/kg.)	Pyrrole contents Specific absorption at 530 m $\mu$ <sup>1</sup>
0.....	-----	24	40.9	0.882
2.....	4.3	18	33.3	1.211
4.....	8.0	18	18.4	1.317
6.....	11.1	18	14.4	1.348
8.....	12.7	16	11.7	1.423
10.....	14.0	16	10.8	1.443
12.....	15.1	17	10.0	1.498
14.....	16.2	16	10.0	1.541

<sup>1</sup> Determined in a 0.4% polyamide solution in 90% formic acid dyed with 1% dimethyl-amino-benzaldehyde.

It seems probable, therefore, that the peroxides decompose as quickly as they are formed and that oxidation, although playing a major role, is only one link in the complex chain of reactions resulting in discolouration. Accordingly, the mere addition of anti-oxidants is insufficient; it is necessary not only to prevent oxidation but to interrupt the course of colour-forming reactions more thoroughly and at several distinct stages. This is accomplished by the four-component stabilizing agent of the present invention, wherein the individual components trap and make harmless any free radicals, reduce peroxides already formed and, finally, block the free amine end groups of the polyamide.

The following examples illustrate the invention. Polycondensation is carried out in the conventional manner, except that in all cases where a dicarboxylic acid is employed as a component of the stabilizer, no acetic acid is added as chain terminator.

The polyhexamethylene adipamide compositions are prepared as follows. A 50% aqueous solution of hexamethylene diamine adipate is evaporated until a concentration of 75 to 80% is achieved and is then heated in an autoclave until the pressure reaches 18 atmospheres. The pressure is maintained until all the water has evaporated and is then gradually released during 90 minutes. Polycondensation is continued under atmospheric pressure for 30 minutes at a temperature of about 277° C.

The addition of the stabilizers, of titanium dioxide, and of any optical brightening agents can take place at various stages during manufacture. In the examples the manganese salt is mixed with the 50% hexamethylene diamine adipate solution, the titanium dioxide dispersion is added 30 minutes after the pressure of 18 atmospheres is reached and the phenolic compound, the phosphorus compound and the dicarboxylic acid, dissolved in a little ethanol, are added after the water has been evaporated.

From the polyamide compositions obtained, fibres are melt-spun in the usual manner, and compared with fibres containing no stabilizer and with fibres containing different combinations of only three of the four stabilizers used in the present invention. The relative viscosity is determined at 25° C. on an 11% solution of the polyamide composition in 90% formic acid. The heating test is carried out with a "Thermotest Rhodiaceta" developed by Rhodiaceta S.A., Paris, and made by Societe Pour la Diffusion d'Appareils, de Mesure et de Controle, S.A., Tassin-la-Demi-Lune, Rhone, France. In this test small hanks of yarn are brought into contact during 60 seconds with heated metal plates having a temperature between 210° and 240° C., after which the colour of the yarn is judged visually.

When carrying out the irradiation test, fibres not containing an optical brightening agent are used, because these agents are decomposed by light and may become yellow themselves. The fibres are exposed to sunlight of an intensity equal to rating 7 of the blue standard, according to test 95810 of the Swiss Standards Institution (SNV), and subsequently kept in the dark for three months, after which the colours of the light-exposed and the unexposed fibres are compared.

All percentages of quantities of materials mentioned in the following examples are by weight of the total weight of the polyamide composition.

#### Example I

Fibres are melt-spun from a polyamide composition made from 5.5 kg. of hexamethylene diamine adipate containing 1.9% of titanium dioxide and, as stabilizers, 0.05% of 2,2' - methylene - bis - (4 - methyl - 6 - tert - butylphenol), 0.3% of triphenyl phosphate, 0.01% of manganese oxalate equal to 38 parts of manganese per million parts of polyamide, and 0.4% of adipic acid. The relative viscosity of the fibres is 37, their tensile strength 6.6 g./denier, and their elongation at break 26%. The colour of the fibres both before and after heating to 225°

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C. and when subjected to the irradiation test is a pure white.

### Example II

Fibres are melt-spun from a polyamide composition made from 5 kg. of hexamethylene diamine adipate containing 1.9% of titanium dioxide and, as stabilizers, 0.05% of 2,2'-methylene-bis-(4-ethyl-6-tert-butyl-phenol), 0.2% of triphenyl phosphate, 0.01% of manganous oxalate, equal to 38 parts of manganese per million parts of polyamide, and 0.48% of terephthalic acid. The relative viscosity of the fibres is 43, and their colour both before and after heating to 220° C. and when subjected to the irradiation test is a pure white.

### Example III

Fibres are melt-spun from a polyamide composition made from 5.5 kg. of hexamethylene diamine adipate containing 1.9% of titanium dioxide and, as stabilizers, 0.05% of 2,2'-methylene-bis-(4-methyl-6-tert-butyl-phenol), 0.2% of triphenyl phosphate, 0.1% of manganous oxalate, equal to 38 parts of manganese per million parts of polyamide, and 0.81% of sebacic acid. The relative viscosity of the fibres is 46, and their colour both before and after heating to 220° C. or when subjected to the irradiation test, is a pure white. From the same polyamide composition, yarns are spun having a titre of 40 denier and composed of 13 filaments. Five samples of fabrics are warp-knitted from the yarns, one of which is left untreated, and the others are washed for 30 minutes in an aqueous solution having a temperature of 70° C. and containing 5 grams of soap and 2 grams of soda per litre, and then dried at 40° C. The washing and drying is repeated ten times, whereupon the washed fabrics show the same white colour as the untreated sample.

Fibres made for comparison in the same manner, but containing, instead of sebacic acid, 0.46% of caproic acid, have a relative viscosity of 37. The colour of the fibres is originally ivory-white and becomes distinctly yellow when they are heated to 220° C. or subjected to the irradiation test.

#### I claim:

1. Synthetic polyamide compositions which are substantially free from colour and of good stability against discolouration by heat and light, in which have been incorporated during polycondensation (1) between 0.02 and 0.2% of a compound selected from the class consisting of 2,5-di-tert-butyl-hydroquinone, 2,2'-methylene-bis-(4-

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methyl-6-tert-butyl-phenol), 2,2'-methylene-bis-(4-ethyl-6-tert-butyl-phenol), and 4,4'-butylidene-bis-(6-tert-butyl-m-cresol), (2) between 0.05 and 0.5% of triphenyl phosphate, (3) between 20 and 80 parts of manganese per million parts of said polyamide composition in the form of a compound selected from the class consisting of manganous lactate, manganous oxalate, and manganous hypophosphite, and (4) between 0.2 and 1.0% of a member of the class consisting of adipic acid, sebacic acid, and terephthalic acid, the proportions being based on the total weight of the composition.

2. The composition of claim 1 wherein said polyamide compositions are polyhexamethylene adipamide textile fibres.

3. The composition of claim 1 wherein said polyamide compositions are polycaprolactam textile fibres.

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