TITLE: THERMALLY STABLE POLYOXYMETHYLENE BLENDS

Abstract

Incorporation of 0.05 to 3.0 weight percent of a non-meltable polymer stabilizer having a number average particle size of 10 microns or less and containing formaldehyde reactive nitrogen groups into polyoxymethylene/thermoplastic polyurethane/amorphous thermoplastic polymer blends results in improved melt processing stability for said blends, provided that the non-meltable polymer stabilizer has a number average particle size in the blend of 10 microns or less. Further improvement in the melt processing stability of said blends is achieved by incorporation therein of 0.1 to 1.00 weight percent of a co-stabilizer component such as a polyamide, a hydroxy-containing polymer or oligomer, or microcrystalline cellulose, in addition to the non-meltable polymer stabilizer.
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TITLE
THERMALLY STABLE
POLYOXYMETHYLENE BLENDS

BACKGROUND

Technical Field

This invention relates to certain polyoxymethylene blends comprised of a polyoxymethylene component, a thermoplastic elastomer component, and an amorphous thermoplastic polymer component that are stabilized with a certain polymer stabilizer that is non-melttable and that contains formaldehyde reactive nitrogen groups. The blends stabilized with the polymer stabilizer described herein are characterized as having excellent melt processing stability and a good overall balance of physical properties.

Polyoxymethylene compositions (also referred to in the art as "polyacetal" compositions) are generally understood to include compositions based on homopolymers of formaldehyde or of cyclic oligomers of formaldehyde, for example trioxane, the terminal groups of which are end-capped by esterification or etherification, as well as copolymers of formaldehyde or of cyclic oligomers of formaldehyde, with oxyalkylene groups with at least two adjacent carbon atoms in the main chain, the terminal groups of which copolymers can be hydroxyl terminated or can be end-capped by esterification or etherification. The proportion of the comonomers can be up to 20 weight percent. Compositions based on POM of relatively high molecular weight, i.e., 20,000 to 100,000 are useful in preparing semi-finished and finished articles by any of the techniques commonly used with thermoplastic materials, e.g., compression molding, injection molding, extrusion, blow molding, melt spinning,
stamping and thermoforming. Finished products made from such polyoxymethylene compositions possess extremely desirable physical properties, including high stiffness, strength, and solvent resistance.

Polyoxymethylene compositions containing thermoplastic polyurethanes have been recently developed and said compositions possess extraordinary toughness and/or impact resistance, along with also possessing a good overall balance of physical properties, such as stiffness and elongation. It was also recently discovered that the degree of mold shrinkage experienced by these polyoxymethylene/thermoplastic polyurethane compositions could be significantly reduced by blending the polyoxymethylene/thermoplastic polyurethane composition with at least one amorphous thermoplastic polymer.

With the development of new polyoxymethylene/thermoplastic polyurethane/amorphous thermoplastic polymer blends, there became a need to find a stabilizer to protect the blends against degradation during melt processing. For the stabilizer to be effective, it would have to act as a stabilizer for not only the polyoxymethylene component of the blend but also for the other components of the blend. It thus was not known if conventional polyoxymethylene thermal stabilizers, such as, for example, nylon, would stabilize the blends against degradation during melt processing.

It was surprisingly found that a polymer stabilizer that is non-meltable, has a number average particle size in the blend of 10 microns or less, and that contains formaldehyde reactive nitrogen groups, as described in further detail below, not only was effective as a melt processing stabilizer for the
blends but also that it imparted superior melt processing stability, on average, to the polyoxymethylene/thermoplastic polyurethane/amorphous thermoplastic polymer blends. This result was surprising in part because experimental data, as disclosed herein, showed no significant difference in melt processing stability between polyoxymethylene/thermoplastic polyurethane compositions containing the polymer stabilizer described herein and polyoxymethylene/thermoplastic polyurethane compositions containing the more conventional polyoxymethylene stabilizers, such as nylon and ethylene vinyl alcohol. Thus, the fact that the polymer stabilizer described herein improved the melt processing stability of the polyoxymethylene/thermoplastic polyurethane/amorphous thermoplastic polymer blends to a significantly greater degree than did the more conventional polyoxymethylene stabilizers was not only unexpected but was also quite surprising.

It was further surprisingly found that even better melt processing stability could be attained if the stabilizer incorporated into the polyoxymethylene/thermoplastic polyurethane/amorphous thermoplastic polymer blend was a mixture of the polymer stabilizer, as described below, and a co-stabilizer selected from conventional meltable nylon (or polyamide) based stabilizers, meltable hydroxy containing oligomers or polymers, such as ethylene vinyl alcohol, or microcrystalline cellulose. The melt processing stability of the blends containing such a mixed stabilizer system was better than the melt processing stability of the same blend containing only the polymer stabilizer, described below, or the co-stabilizer.
The polyoxymethylene blends of the present invention are useful as injection molding resins in applications where the properties of a polyoxymethylene or polyoxymethylene/thermoplastic polyurethane composition are desired and where enhanced melt processing stability is required.

**Background Art**

Polyoxymethylene/thermoplastic polyurethane compositions are described in commonly assigned European Patent No. 0117664 and U.S. Patent 4,804,716.

Polyoxymethylene compositions stabilized with examples of nylon-type stabilizers are disclosed in U.S. patent 4,640,949; U.S. patent 3,960,984; and U.S. patent 4,098,843. In U.S. patent 4,640,949, polyoxymethylene compositions are stabilized with a blend comprised of a thermoplastic polyurethane with a polyamide dispersed therein as a separate phase. In U.S. patent 3,960,984, polyoxymethylene compositions are stabilized with dicapped amide oligomers having a molecular weight of 800 to 10,000. In U.S. patent 4,098,843, polyoxymethylene compositions are stabilized with a dispersion of a polyamide in a carrier resin. In each of these patents, control examples are provided wherein other types of polyamide stabilizers are incorporated into polyoxymethylene. Conventional polyamide stabilizers for polyoxymethylene are also described in Alsup et al., U.S. patent 2,993,025.

Hydroxy-containing polymers and oligomers useful as stabilizers in polyoxymethylene are disclosed in U.S. patent 4,766,168.

**SUMMARY OF THE INVENTION**

In the present invention, it was found that the melt processing stability of a
polyoxymethylene/thermoplastic polyurethane/amorphous thermoplastic polymer blend could be significantly improved by the incorporation therein of 0.05 to 3.0 weight percent, based upon the weight of the blend, of a polymer stabilizer that is non-meltable, has a number average particle size in the blend of less than ten microns, and contains formaldehyde reactive nitrogen groups wherein the amount of formaldehyde reactive nitrogen groups present as or part of the side chains of the backbone of the polymer stabilizer is at least three times greater than the amount of formaldehyde reactive nitrogen groups, if any, present in the backbone of the polymer stabilizer. The melt processing stability of said blends is improved even further by the incorporation therein of a 0.01 to 1.00 weight percent, based upon the weight of the blend, of a co-stabilizer, said co-stabilizer being selected from meltable polyamide-based stabilizers, meltable hydroxy-containing polymer or oligomer stabilizers, and microcrystalline cellulose. The stabilized blends are useful as injection molding resins where the properties of a polyoxymethylene are desired and where enhanced thermal stability is required.

**DETAILED DESCRIPTION OF THE INVENTION**

This invention relates to certain polyoxymethylene blends characterized by improved melt processing stability. Specifically, the polyoxymethylene blends consist essentially of (a) a polyoxymethylene component, (b) a thermoplastic polyurethane component, (c) an amorphous thermoplastic polymer component, and (d) a polymer stabilizer component. The melt processing stability of said blends is even further improved by the inclusion therein of a specific co-stabilizer component (e). The co-stabilizer component (e) is selected from
conventional meltable nylon-based stabilizers, meltable hydroxy-containing polymer and oligomer stabilizers, and microcrystalline cellulose stabilizers. Each component of the blends of the present invention is described below.

BLEND COMPONENTS

Component (a) Polyoxymethylene

The component (a) "polyoxymethylene" includes homopolymers of formaldehyde or of cyclic oligomers of formaldehyde, the terminal groups of which are end-capped by esterification or etherification, and copolymers of formaldehyde or of cyclic oligomers of formaldehyde and other monomers that yield oxyalkylene groups with at least two adjacent carbon atoms in the main chain, the terminal groups of which copolymers can be hydroxyl terminated or can be end-capped by esterification or etherification.

The polyoxymethylene used in the blends of the present invention can be branched or linear and will generally have a number average molecular weight in the range of 10,000 to 100,000, preferably 20,000 to 90,000, and more preferably 25,000 to 70,000. The molecular weight can be conveniently measured by gel permeation chromatography in m-cresol at 160°C using a Du Pont PSM bimodal column kit with nominal pore size of 60 and 1000 A. Although polyoxymethylene having higher or lower molecular weight averages can be used, depending on the physical and processing properties desired, the polyoxymethylene molecular weight averages mentioned above are preferred to provide optimum balance of good mixing of the various ingredients to be melt blended into the polyoxymethylene blend with the most desired

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combination of physical properties in the molded articles made from such blends.

As an alternative to characterizing the polyoxymethylene by its number average molecular weight, it can be characterized by its melt flow rate. Polyoxymethylenes which are suitable for use in the blends of the present invention will have a melt flow rate (measured according to ASTM-D-1238, Procedure A, Condition G with a 1.0 mm (0.0413 inch) diameter orifice of 0.1-40 grams/10 minutes. Preferably, the melt flow rate of the polyoxymethylene used in the blends of the present invention will be from 0.5-35 grams/10 minutes. The most preferred polyoxymethylenes are linear polyoxymethylenes with a melt flow rate of about 1-20 gram/10 minutes.

As indicated above, the polyoxymethylene can be either a homopolymer, a copolymer, or a mixture thereof. Copolymers can contain one or more comonomers, such as those generally used in preparing polyoxymethylene compositions. Comonomers more commonly used include alkylene oxides of 2-12 carbon atoms and their cyclic addition products with formaldehyde. The quantity of comonomer will not be more than 20 weight percent, preferably not more than 15 weight percent, and most preferably about 2 weight percent. The most preferred comonomer is ethylene oxide. Generally polyoxymethylene homopolymer is preferred over copolymer because of its greater stiffness and strength. Preferred polyoxymethylene homopolymers include those whose terminal hydroxyl groups have been end-capped by a chemical reaction to form ester or ether groups, preferably acetate or methoxy groups, respectively.

It is understood that the polyoxymethylene may also contain those additives, ingredients, and

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modifiers that are known to be added to polyoxymethylene.

Component (b) Thermoplastic Polyurethane

The component (b) "thermoplastic polyurethanes" suited for use in the blends of the present invention can be selected from those commercially available or can be made by processes known in the art. (See, for example, Rubber Technology, 2nd edition, edited by Maurice Morton (1973), Chapter 17, Urethane Elastomers, D. A. Meyer, especially pp. 453-6). Thermoplastic polyurethanes are derived from the reaction of polyester or polyether polyols with diisocyanates and optionally also from the further reaction of such components with chain-extending agents such as low molecular weight polyols, preferably diols, or with diamines to form urea linkages. Thermoplastic polyurethanes are generally composed of soft segments, for example polyether or polyester polyols, and hard segments, usually derived from the reaction of the low molecular weight diols and diisocyanates. While a thermoplastic polyurethane with no hard segments can be used, those most useful will contain both soft and hard segments.

In the preparation of the thermoplastic polyurethanes useful in the blends of the present invention, a polymeric soft segment material having at least about 500 and preferably from about 550 to about 5,000 and most preferably from about 1,000 to about 3,000, such as a dihydric polyester or a polyalkylene ether diol, is reacted with an organic diisocyanate in a ratio such that a substantially linear polyurethane polymer results, although some branching can be present. A diol chain extender having a molecular weight less than about 250 may also be incorporated. The mole ratio of isocyanate to hydroxyl in the
polymer is preferably from about 0.95 to 1.08 more preferably 0.95 to 1.05, and most preferably, 0.95 to 1.00. In addition, monofunctional isocyanates or alcohols can be used to control molecular weight of the polyurethane.

Suitable polyester polyols include the polyesterification products of one or more dihydric alcohols with one or more dicarboxylic acids. Suitable polyester polyols also include polycarbonate polyols. Suitable dicarboxylic acids include adipic acid, succinic acid, sebacic acid, suberic acid, methyldipropionic acid, glutaric acid, pimelic acid, azelaic acid, thiodipropionic acid and citraconic acid and mixtures thereof, including small amounts of aromatic dicarboxylic acids. Suitable dihydric alcohols include ethylene glycol, 1,3- or 1,2-propylene glycol, 1,4-butanediol, 1,3-butanediol, 2-methylpentanediol-1,5, diethylene glycol, 1,5-pentanediol, 1,5-hexanediol, 1,2-dodecanediol, and mixtures thereof.

Further, hydroxycarboxylic acids, lactones, and cyclic carbonates, such as $\varepsilon$-caprolactone and 3-hydroxybutyric acid can be used in the preparation of the polyester.

Preferred polyesters include poly(ethylene adipate), poly(1,4-butylene adipate), mixtures of these adipates, and poly$\varepsilon$ caprolactone.

Suitable polyether polyols include the condensation products of one or more alkylene oxides with a small amount of one or more compounds having active hydrogen containing groups, such as water, ethylene glycol, 1,2- or 1,3-propylene glycol, 1,4-butanediol and 1,5-pentanediol and mixtures thereof. Suitable alkylene oxide condensates include those of ethylene oxide, propylene oxide and butylene
oxide and mixtures thereof. Suitable polyalkylene ether glycols may also be prepared from tetrahydrofuran. In addition, suitable polyether polyols can contain comonomers, especially as random or block comonomers, ether glycols derived from ethylene oxide, 1,2-propylene oxide and/or tetrahydrofuran (THF). Alternatively, a THF polyether copolymer with minor amounts of 3-methyl THF can also be used.

Preferred polyethers include poly(tetramethylene ether) glycol (PTMEG), poly(propylene oxide) glycol, and copolymers of propylene oxide and ethylene oxide, and copolymers of tetrahydrofuran and ethylene oxide. Other suitable polymeric diols include those which are primarily hydrocarbon in nature, e.g., polybutadiene diol.

Suitable organic diisocyanates include 1,4-butylene diisocyanate, 1,6-hexamethylene diisocyanate, cyclopentylene-1,3-diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, isophorone diisocyanate, cyclohexylene-1,4-diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, isomeric mixtures of 2,4- and 2,6-toluene diisocyanate, 4,4'-methylene bis(phenylisocyanate), 2,2-diphenylpropane-4,4'-diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, xylene diisocyanate, 1,4-naphthylene diisocyanate, 1,5-naphthylene diisocyanate, 4,4'-diphenyl diisocyanate, azobenzene-4,4'-diisocyanate, m- or p-tetramethylexylene diisocyanate, and 1-chlorobenzene-2,4-diisocyanate. 4,4'-Methylene bis(phenylisocyanate), 1,6-hexamethylene diisocyanate, 4,4'-dicyclohexylmethane diisocyanate and 2,4-toluene diisocyanate are preferred.
Secondary amide linkages including those derived from adipyl chloride and piperazine, and secondary urethane linkages, including those derived from the bis-chloroformates of PTMEG and/or butanediol, can also be present in the polyurethanes.

Dihydricalcohols suitable for use as chain extending agents in the preparation of the thermoplastic polyurethanes include those containing carbon chains which are either uninterrupted or which are interrupted by oxygen or sulfur linkages, including 1,2-ethanediol, 1,2-propanediol, isopropyl-α-glyceryl ether, 1,3-propanediol, 1,3-butanediol, 2,2-dimethyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, 2-methyl-2,4-pentanediol, 2,2,4-trimethyl-1,3-pentanediol, 2-ethyl-1,3-hexanediol, 1,4-butanediol, 2,5-hexanediol, 1,5-pentanediol, dihydroxycyclopentane, 1,6-hexanediol, 1,4-cyclohexanediol, 4,4'-cyclohexanediisocyanate, thiodiglycerol, diethylene glycol, dipropylene glycol, 2-methyl-1,3-propanediol, 2-methyl-2-ethyl-1,3-propanediol, dihydroxyethyl ether of hydroquinone, hydrogenated bisphenol A, dihydroxyethyl terephthalate and dihydroxymethyl benzene and mixtures thereof. Hydroxyl terminated oligomers of 1,4-butanediol terephthalate can also be used, giving a polyester-urethane-polyester repeating structure. Diamines can also be used as chain extending agents giving urea linkages. 1,4-Butanediol, 1,2-ethanediol and 1,6-hexanediol are preferred.

In the preparation of the thermoplastic polyurethanes, the ratio of isocyanate to hydroxyl
should be close to unity, and the reaction can be a one step or a two step reaction. Catalyst can be used, and the reaction can be run neat or in a solvent.

The moisture content of the blend, in particular of the thermoplastic polyurethane, can influence the results achieved. Water is known to react with polyurethanes, causing the polyurethane to degrade, thereby lowering the effective molecular weight of the polyurethane and lowering the inherent and melt viscosity of the polyurethane. Accordingly, the drier the better. In any event, the moisture content of the blend, and of the individual components of the blend, should contain less than 0.2 percent by weight of water, preferably less than 0.1 percent, especially when there is no opportunity for the water to escape, for example during an injection molding process and other techniques of melt processing.

The thermoplastic polyurethane can also contain those additives, ingredients, and modifiers known to be added to thermoplastic polyurethane.

Component (c) Amorphous Thermoplastic Polymer

Component (c) is at least one amorphous thermoplastic polymer. These amorphous thermoplastic polymers are thermoplastic polymers that are generally used by themselves in extrusion and injection molding processes. These polymers are known to those skilled in the art as extrusion and injection molding grade resins, as opposed to those resins that are known for use as minor components (i.e., processing aids, impact modifiers, stabilizers) in polymer compositions.

By the term "amorphous", it is meant that the polymer has no distinct crystalline melting point, nor does it have a measurable heat of fusion (although with very slow cooling from the melt, or with of
sufficient annealing, some crystallinity may develop). The heat of fusion is conveniently determined on a differential scanning calorimeter (DSC). A suitable calorimeter is the Du Pont Company's 990 thermal analyzer, Part Number 990000 with cell base II, Part Number 990315 and DSC cell, Part Number 900600. With this instrument, heat of fusion can be measured at a heating rate of 20°C per minute. The sample is alternately heated to a temperature above the anticipated melting point and cooled rapidly by cooling the sample jacket with liquid nitrogen. The heat of fusion is determined on any heating cycle after the first and should be a constant value within experimental error. Amorphous polymers are defined herein as having a heat of fusion, by this method, of less than 1 cal/gram. For reference, semicrystalline 66 nylon polyamide with a molecular weight of about 17,000 has a heat of fusion of about 16 cal/gm.

By the term "thermoplastic" it is meant that the polymer softens, when heated, to a flowable state in which under pressure it can be forced or transferred from a heated cavity into a cool mold and upon cooling in the mold, it hardens and takes the shape of the mold. Thermoplastic polymers are defined in this manner in the Handbook of Plastics and Elastomers (published by McGraw-Hill).

The amorphous thermoplastic polymers useful in the present blends must be "melt processible" at the temperature at which the polyoxymethylene blend is melt processed. Polyoxymethylene, and blends thereof, is normally melt processed at melt-temperatures of about 170-260°C, preferably 185-240°C, and most preferably 200-230°C. By "melt processible", it is meant that the amorphous thermoplastic polymer must soften or have a sufficient flow such that it can be
melt compounded at the particular melt processing temperature for the polyoxymethylene blend.

The minimum molecular weight of the amorphous thermoplastic polymer is not considered to be significant for the present blends, provided that the polymer has a degree of polymerization of at least twenty and further provided that the polymer is melt processible (i.e., it flows under pressure) at the temperature at which the polyoxymethylene is melt processed. The maximum molecular weight of the amorphous thermoplastic polymer should not be so high that the amorphous thermoplastic polymer by itself would not be injection moldable by standard present techniques. The maximum molecular weight for a polymer to be used for injection molding processes will vary with each individual, particular amorphous thermoplastic polymer. However, said maximum molecular weight for use in injection molding processes is readily discernible by those skilled in the art.

To realize optimum physical properties for the ternary blend, it is recommended that the polyoxymethylene polymer and the amorphous thermoplastic polymer have matching melt viscosity values under the same conditions of temperature and pressure.

The amorphous thermoplastic polymer can be incorporated into the blend as one amorphous thermoplastic polymer or as a blend of more than one amorphous thermoplastic polymer. Preferably, component (c) consists of one amorphous thermoplastic polymer. Whether it is incorporated as one amorphous thermoplastic polymer or as a blend of more than one, the weight percent of all amorphous thermoplastic polymers in the composition shall not exceed the weight percent ranges given above.
Amorphous thermoplastic polymers, which are injection molding and extrusion grade, suited for use in the blends of the present invention are well known in the art and can be selected from those commercially available or can be made by processes known in the art. Examples of suitable amorphous thermoplastic polymers can be selected from the group consisting of styrene acrylonitrile copolymers (SAN), SAN copolymers toughened with a mostly unsaturated rubber, such as acrylonitrile-butadiene-styrene (ABS) resins, or toughened with a mostly saturated rubber, such as acrylonitrile-ethylene-propylene-styrene resins (AES), polycarbonates, polyamides, polyarylates, polyphenylenepoxyides, polyphenylene ethers, high impact styrene resins (HIPS), acrylic polymers, imidized acrylic resins, styrene maleic anhydride copolymers, polysulfones, styrene acrylonitrile maleic anhydride resins, and styrene acrylic copolymers, and derivatives thereof.

The preferred amorphous thermoplastic polymers are selected from the group consisting of styrene acrylonitrile copolymers (SAN), SAN copolymers toughened with a mostly unsaturated rubber, such as acrylonitrile-butadiene-styrene (ABS) resins, or toughened with a mostly saturated rubber, such as acrylonitrile-ethylene-propylene-styrene resins (AES), polycarbonates, and derivatives thereof. Most preferred amorphous thermoplastic polymers are SAN copolymers, ABS resins, AES resins, and polycarbonates.

The amorphous thermoplastic polymers disclosed above are all known in the art and can be prepared by techniques readily available to those skilled in the art. Further description of said polymers is provided below.
Amorphous thermoplastic SAN copolymers that are useful herein are well known in the art. SAN copolymer is generally a random, amorphous, linear copolymer produced by copolymerizing styrene and acrylonitrile. The preferred SAN copolymer has a minimum molecular weight of 10,000 and consists of 20-40% acrylonitrile, 60-80% styrene. The more preferred SAN copolymer consists of 25-35% acrylonitrile, 65-75% styrene. SAN copolymer is commercially available or it can be readily prepared by techniques well known to those skilled in the art. Amorphous thermoplastic SAN copolymers are further described on pages 214-216 in Engineering Plastics, volume 2, published by ASM INTERNATIONAL, Metals Park, Ohio (1988).

Amorphous thermoplastic ABS and AES resins, which are injection molding and extrusion grade resins, that are useful herein are well known in the art. ABS resin is produced by polymerizing acrylonitrile and styrene in the presence of butadiene, or a mostly butadiene, rubber. Preferably, the ABS resin is comprised of 50-95% of a matrix of SAN, with said matrix being comprised of 20-40% acrylonitrile and 60-80% styrene, and 5-50% of a butadiene rubber or a mostly butadiene rubber, such as styrene butadiene rubber (SBR). More preferably, it is comprised of 60-90% of a matrix of SAN, with said matrix more preferably being comprised of 25-35% acrylonitrile and 65-75% styrene, and 10-40% of a butadiene rubber. AES resin is produced by polymerizing acrylonitrile and styrene in the presence of a mostly saturated rubber. The preferred and more preferred AES resin is the same as the preferred and more preferred ABS resin except that the rubber component is comprised of mostly ethylene-propylene.
copolymer, as opposed to butadiene, or mostly butadiene, rubber. Other alpha-olefins and unsaturated moieties may be present in the ethylene-propylene copolymer rubber. Both ABS and AES copolymers are commercially available or can be readily prepared by techniques well known to those skilled in the art. Amorphous thermoplastic ABS resin is further described on pages 109-114 in Engineering Plastics, referenced above.

Amorphous thermoplastic polycarbonates that are useful herein are well known in the art and can be most basically defined as possessing the repetitive carbonate group

\[ \text{O} \]

\[ \text{||} \]

\[ \text{-O-C-O-} \]

and in addition will always have the

\[ \text{phenylene moiety attached to the carbonate group (cf. U.S. Pat. No. 3,070,563).} \]

Preferably, the polycarbonate can be characterized as possessing recurring structural units of the formula

\[ \text{wherein Z is a single bond, an alkylene or alkylidene moiety with 1-7 carbon atoms, a cycloalkylene or} \]

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cycloalkylidene moiety with 5-12 carbon atoms, -O-, -S-, -CO-, -SO- or -SO_2-, preferably methylene or isopropylidene; R_1 and R_2 are a hydrogen, a halogen, or an alkylene or alkylidene moiety having 1-7 carbon atoms, and n equals 0 to 4.

Amorphous thermoplastic polycarbonates are commercially available or can be readily prepared by techniques well known to those skilled in the art. The most preferred aromatic polycarbonate on the basis of commercial availability and available technical information is the polycarbonate of bis(4-hydroxyphenyl)-2,2-propane, known as bisphenol-A polycarbonate. Amorphous thermoplastic polycarbonate is further described on pages 149-150 of Engineering Plastics, referenced above.

The amorphous thermoplastic polyamide polymers useful herein are described in U.S. patent 4,410,661, incorporated herein by reference.

The amorphous thermoplastic polyarylate polymers useful herein are described in U.S. patent 4,861,828, incorporated herein by reference.

The amorphous thermoplastic polyphenylene ethers (PPE) and polyphenylene oxides (PPO) useful herein are known in the art. PPE homopolymer is frequently referred to as PPO. The chemical composition of the homopolymer is poly(2,6-dimethyl-4,4-phenylene ether) or poly(oxy-(2-6-dimethyl-4,4-phenylene)):

\[
\begin{array}{c}
\text{CH}_3 \\
-o- \\
\text{CH}_3 \\
\end{array}
\]

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
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\text{O} \\
\text{O} \\
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_3 \\
n \\
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The chemical composition of PPE, which is a copolymer, is as follows:

![Chemical structure of PPE]

Both PPE and PPO are described on pages 183-185 in Engineering Plastics, referenced above.

The amorphous thermoplastic high impact styrene (HIPS) resins that are useful herein are produced by dissolving usually less than 20 percent polybutadiene rubber, or other rubber, in styrene monomer before initiating the polymerization reaction. Polystyrene forms the continuous phase of the polymer and the rubber phase exists as discrete particles having occlusions of polystyrene. HIPS resin is further described on pages 194-199 in Engineering Plastics, referenced above.

The amorphous thermoplastic acrylics useful herein are those polymers in which the major monomeric constituents belong to two families of ester-acrylates and methacrylates. Amorphous thermoplastic acrylic polymers are described on pages 103-108 in Engineering Plastics, referenced above. The molecular weight of the amorphous thermoplastic acrylic polymer, in order for it to be injection moldable by standard techniques, should not be greater than 200,000. The preferred amorphous thermoplastic acrylic resin is polymethyl methacrylate.

The amorphous thermoplastic imidized acrylics useful herein are disclosed in U.S. patent
4,246,374, incorporated herein by reference, and also in U.S. patent application ser. no. 06/476,092, which was allowed on May 26, 1989.

The amorphous styrene maleic anhydride copolymers that are useful herein are produced by the reaction of styrene monomer with smaller amounts of maleic anhydride. The structure of styrene maleic anhydride is as follows:

\[ \text{[-C-C-C-C-C-C-C-C-\text{]}_n} \]

Amorphous thermoplastic styrene maleic anhydride copolymers are further described on pages 217-221 in *Engineering Plastics*, referenced above.

The amorphous thermoplastic polysulfones that are useful herein have the following structure:

\[ \text{[SO}_2\text{-CH}_3\text{-O-CH}_3\text{-CH}_3\text{-O-\text{]}_n} \]

It is produced from bisphenol A and 4,4'-dichlorodiphenylsulfone by nucleophilic displacement chemistry. It is further described on pages 200-202 in *Engineering Plastics*, referenced above.

The amorphous thermoplastic polymers may also contain those additional ingredients, modifiers, stabilizers, and additives commonly included in such polymers.
Component (d) Polymer Stabilizer

The "polymer stabilizer" used in the blends of the present invention is a homopolymer or copolymer containing "formaldehyde reactive" nitrogen groups, is "non-meltable" at the temperature at which the polyoxymethylene blend is melt processed, and has a number average particle size, before melt processing and thereafter, of less than ten microns.

By "formaldehyde reactive" it is meant that the nitrogen group contains a nitrogen with one or two hydrogen atoms bonded to it. Formaldehyde will react with the -NH bonds of the polymer stabilizer. These reactive sites are referred to herein as formaldehyde reactive sites. It is preferred that the polymer stabilizer contain formaldehyde reactive nitrogen groups having the maximum number of formaldehyde reactive sites. For example, a polymer stabilizer containing formaldehyde reactive nitrogen groups wherein there are two hydrogen atoms attached directly to the nitrogen atom (i.e., two formaldehyde reactive sites in the group) is preferred over one containing formaldehyde reactive nitrogen groups wherein there is only one hydrogen atom attached directly to the nitrogen atom (i.e., one formaldehyde reactive site in the group).

The polymer stabilizer further has at least ten repeat units. It preferably has a weight average molecular weight of greater than 5,000, most preferably greater than 10,000. Higher weight average molecular weights are most preferred and further, such higher weight average molecular weights may be advantageous for reducing mold deposit formation.

The polymer stabilizer is "non-meltable" at the temperature at which the polyoxymethylene blend is melt processed. More specifically, by the term
"non-meltable", it is meant that the polymer stabilizer has its "major melting point" above the temperature at which the polyoxymethylene blend is melt processed and thus remains essentially a solid during melt processing of the polyoxymethylene blend. Alternatively, the polymer stabilizer is "non-meltable" if the stabilizer has its "major melting point" below the temperature at which the polyoxymethylene blend is melt processed but it does not undergo significant melt flow at that temperature. The melt flow rate of the polymer stabilizer may not be significant because the polymer stabilizer has a high viscosity, attributed to, for example, high molecular weight or crosslinking. In the case where the polymer stabilizer has its "major melting point" below the temperature at which the polyoxymethylene blend is melt processed, the melt flow rate of the polymer stabilizer, as measured in accordance with ASTM-D 1238 (at 200°C under a load of 2.16 kg), is preferably less than one-tenth that of the polyoxymethylene in the blend. It is recommended that for most accurate results, the polymer stabilizer be dried for 12 hours at 90°C prior to measuring its melt flow rate.

The "major melting point" of the polymer stabilizer can be determined on a differential scanning calorimeter, preferably on a DU PONT Model 9900 DIFFERENTIAL SCANNING CALORIMETER. A nitrogen atmosphere should be used. To eliminate the possible effect of small amounts of moisture or solvent, it is recommended that the polymer stabilizer be first heated to 140°C and held there for 10 minutes. The polymer stabilizer sample should then be cooled to about 25°C and then heated at a rate of 20°C/minute up to 350°C. The temperature at which endotherms occurred
will be reported. Also reported will be the amount of heat absorbed, in Joules/gram, at each respective endotherm. "Major melting point" is the temperature at which the amount of heat absorbed, by the polymer stabilizer, is greatest (in Joules/gram); i.e., it is the temperature at which the polymer stabilizer shows the greatest endotherm.

The polyoxymethylene blends described herein are usually melt processed at melt temperatures of about 170-260°C; preferably 185-240°C, most preferably 200-230°C.

The polymer stabilizer must also have a number average particle size of less than 10 microns after melt processing in the blend. It further should have a number average particle size of less than 10 microns before melt processing with the polyoxymethylene blend. It should be understood that a high degree of loose agglomeration of particles in the polymer stabilizer may occur during the preparation and isolation of the polymer stabilizer, such as, for example, during the drying of the polymer stabilizer. In order for one to obtain a true and accurate measurement of the number average particle size, prior to melt processing, for a polymer stabilizer containing a high degree of loose agglomerates, the loose agglomerates should be broken up prior to measuring the number average particle size of the polymer stabilizer or, alternatively, they should be discounted in making said measurement. Whether or not a polymer stabilizer contains a high degree of loose agglomerates can be determined by standard techniques of transmission electron microscopy. The details of determining the number average particle size, both before and after melt processing, are disclosed below.
The formaldehyde reactive nitrogen groups can be incorporated into the polymer stabilizer by using an appropriate nitrogen containing monomer, such as, for example, acrylamide and methacrylamide. Preferred nitrogen containing monomers are those that result in the polymer stabilizer containing formaldehyde reactive nitrogen groups, wherein there are two hydrogen atoms attached to the nitrogen. The particularly preferred monomer is acrylamide which, when polymerized, results in a polymer stabilizer having substantially all of the formaldehyde reactive nitrogen groups attached directly as a side chain of the polymer backbone or indirectly as a side chain of the polymer backbone. Alternatively, the formaldehyde reactive nitrogen groups can be generated on the polymer stabilizer by modification of the polymer or copolymer. The formaldehyde reactive nitrogen groups may be incorporated by either method as long as the resultant polymer prepared therefrom is non-meltable, or is capable of being made non-meltable, at the temperature at which the polyoxymethylene blend is melt processed.

The quantity of the formaldehyde reactive nitrogen groups in the polymer stabilizer must be such that the atoms in the backbone to which the formaldehyde reactive nitrogen groups are attached, either directly or indirectly, are separated from each other (i.e., connected to each other) by not more than twenty chain atoms. Preferably, the polymer stabilizer will contain at least one formaldehyde reactive nitrogen group per each twenty carbon atoms in the backbone of the polymer. More preferably, the ratio of formaldehyde reactive nitrogen groups to carbon atoms in the backbone will be 1:2-1:10, most preferably 1:2-1:5.
The formaldehyde reactive nitrogen groups should be present in the polymer stabilizer such that the amount of the formaldehyde reactive nitrogen groups as, or part of, the side chains of the polymer stabilizer backbone is at least 3 times, preferably at least ten times, the amount of the formaldehyde reactive nitrogen groups, if any, present in the backbone of the polymer stabilizer. In other words, the formaldehyde reactive nitrogen groups, attached directly or indirectly to the atoms in the backbone of the stabilizer polymer, should be at least three times as great, preferably at least ten times as great, as those in the backbone of the polymer stabilizer, if such are present. The formaldehyde reactive nitrogen groups attached directly or indirectly to the side of the polymer backbone are preferably present in a substantially greater quantity than the formaldehyde reactive nitrogen groups, if any, present in the the polymer backbone. Most preferably, nearly one hundred percent of the formaldehyde reactive nitrogen groups are attached to the sides of the polymer backbone.

The polymer stabilizer can be a homopolymer or a copolymer, provided it is non-meltable. It is preferred that the polymer stabilizer be polymerized from acrylamide or methacrylamide monomer by free radical polymerization and that the polymer stabilizer prepared therefrom consist of at least 75 mole percent
of a unit of the form

\[
\begin{align*}
R \quad | \\
-(\text{CH}_2-\text{C})- \quad | \\
\text{CNH}_2 \quad || \\
\text{O}
\end{align*}
\]

where R=hydrogen or methyl. More preferably, it consists of at least 90 mole percent of the above units, even more preferably, it consists of at least 95 mole percent of the above units, and most preferably, it consists of at least 99 mole percent of the above unit.

The polymer stabilizer may be a copolymer in that it is polymerized from more than one monomer. The comonomer may or may not contain formaldehyde reactive nitrogen and/or formaldehyde reactive hydroxyl groups. Examples of other monomers that may be thus incorporated include styrene, ethylene, alkyl acrylates, alkyl methacrylates, N-vinylpyrrolidone, acrylonitrile, and ethylene vinyl alcohol. The polymer stabilizer that is a copolymer must still be non-meltable. It further must possess the required quantity of formaldehyde reactive nitrogen groups, in the required ratio, and it must have the required number average particle size. The comonomer preferably should be added such that it does not unduly minimize the number of moles of formaldehyde reactive groups per gram of polymer stabilizer. Further, it should not unduly minimize the number of formaldehyde reactive sites per gram of polymer stabilizer.
Specific preferred stabilizers that are copolymeric include copolymers of hydroxypropyl methacrylate with acrylamide, methacrylamide, or dimethylaminoethyl methacrylate. The polymer stabilizer must have a number average particle size of less than 10 microns, preferably less than 5 microns, and most preferably less than 2 microns, as measured before processing in polyoxymethylene blend. Along with the polymer stabilizer being non-meltable, the number average particle size of the polymer stabilizer is important in achieving the improved stability for polyoxymethylene blend demonstrated herein. Stability is related to the interaction that occurs between the polyoxymethylene blend components and the polymer stabilizer and as such, it is desirable to have good interaction between the polyoxymethylene and the polymer stabilizer. Maximizing the surface area/gram of polymer stabilizer increases interaction between the polymer stabilizer and the blend components. The surface area/gram of polymer stabilizer increases as the particle size of the polymer stabilizer decreases. Thus, a stabilizer with small particle size is highly desired.

If the polymer stabilizer particle size is, on average, on the order of 10-100 microns, then the polymer stabilizer may impart stability to the polyoxymethylene blend but the physical properties of the articles manufactured from the polyoxymethylene blend may be reduced. Relatively large particles may also cause uneven surface in the articles manufactured from polyoxymethylene containing stabilizer with large particles. In some cases, it may however be desirable to produce articles with surfaces having reduced surface gloss. In that case, a polymer stabilizer of
large particle size, more near the upper limit of the number average particle size, may actually be preferred.

The small number average particle size of the polymer stabilizer may be obtained directly during the polymerization of the monomer or comonomers. To obtain the small average particle size, the stabilizer polymerization is carried out by conventional dispersion polymerization methods in an organic media or by conventional emulsion polymerization methods in water, the techniques of each of which are well known in the art. Whether the polymerization technique is dispersion polymerization or emulsion polymerization, the polymer stabilizer prepared therefrom should be insoluble in the polymerization media. Thus, the particular media selected for polymerization is dependent upon the particular monomer or comonomers chosen and the polymer that will result therefrom. For example, where acrylamide or methacrylamide is a monomer for polymerization, the preferred media is a lower alkyl alcohol. The polymerization may be by addition or condensation polymerization or free radical polymerization. The most preferred method is one that will result in the number of formaldehyde reactive sites in the formaldehyde reactive group being maximized. Generally, free radical polymerization is the preferred method of polymerization. Polymer stabilizer prepared from acrylamide is most preferably prepared by free radical polymerization. In any event, the polymerization method must be such that it results in a polymer stabilizer having formaldehyde reactive nitrogen groups in the quantities and amounts previously defined.
In some cases, the polymer stabilizer produced by the polymerization to small particle size will have a sufficient major melting point or have a sufficiently low melt flow rate such that it is non-meltable as polymerized. In other cases, the polymer stabilizer may not be non-meltable as polymerized but, prior to or during the melt processing in polyoxymethylene blend, it will crosslink, due to, for example, application of heat, to a sufficiently high molecular weight such that it has a low melt flow rate and is non-meltable at the temperature at which the polyoxymethylene blend is melt processed. Whether the polymer stabilizer will be non-meltable as polymerized or will become non-meltable after polymerization depends upon the nature of the particular monomer or comonomers being polymerized.

In some cases, the polymer stabilizer produced by the polymerization of the monomer or comonomers will not be non-meltable as polymerized and it will not become non-meltable subsequent to polymerization. This can be easily determined by measuring the melting point or melt flow rate of the stabilizer after it has been compounded with polyoxymethylene. In such cases, it is desirable to include at least one monomer that crosslinks the polymer stabilizer either during polymerization or at a later time. Monomers that will cause crosslinking during polymerization include polyfunctional, unsaturated monomers, such as, for example, acrylates, methacrylates, acrylamides, and methacrylamides, and derivatives thereof. Specifically preferred monomers are ethylene glycol dimethacrylate and N,N'-methylenebisacrylamide. Monomers that may cause crosslinking after polymerization of the stabilizer
polymer is complete include, for example, glycidyl methacrylate, acrylic acid, methacrylic acid, and derivatives thereof. The crosslinking monomer should be added in an amount that is sufficient to yield a polymer stabilizer that is non-meltable at the temperature at which the polyoxyethylene is melt processed.

During the polymerization to small particle size in an organic media, with or without a crosslinking monomer, it can be advantageous to have a dispersing aid present. During the polymerization to small particle size in an emulsion, it can be advantageous to have an emulsifier present. Dispersing aids and the methods of preparing them are well known in the art. A description of the methods of making and choosing dispersing aids is included in Dispersion Polymerization in Organic Media (by K. E. J. Barrett, New York: John Wiley & Sons, 1975). Particularly preferred dispersing aids include polyethylene glycol and its derivatives, methyl methacrylate copolymers, and poly(oxypropylene)-poly(oxyethylene) glycol block copolymers. Emulsifiers and the method of preparing them are well known in the art. Emulsion polymerizations are discussed in Emulsion Polymerization Theory and Practice (by D. C. Blackley, New York: John Wiley & Sons, 1975).

The dispersant or dispersant solution or the emulsifier is added to the polymerization reaction vessel simultaneously with the monomer and polymerization medium, and, where applicable, comonomer and crosslinking monomer. When a dispersant or dispersant solution or emulsifier is added to the stabilizer, it is advantageous remove the dispersant or dispersant solution or emulsifier from the stabilizer polymer by washing the stabilizer polymer,
after it is prepared, with a solvent in which the dispersant solution or dispersant or emulsifier is soluble but in which the polymer stabilizer is insoluble. This is particularly true if the dispersant or dispersant solution or emulsifier is known to destabilize polyoxymethylene. If the dispersant or dispersant solution or emulsifier is not known to destabilize polyoxymethylene in particular, it may be advantageous to leave it in the polymer stabilizer as it can act to reduce any agglomeration of particles that may occur during the drying of the polymer stabilizer.

The small number average particle size of the polymer stabilizer may alternatively be obtained subsequent to the polymerization of the monomer or comonomers, while the polymer stabilizer is still in the polymerization medium or is in solution. In such cases, the small number average particle size of the stabilizer may be obtained by adding a crosslinking monomer to the polymer stabilizer in the polymerization medium, after which the stabilizer polymer becomes insoluble in the medium. Alternatively, the small number average particle size of the stabilizer may be obtained by adding a solvent in which the stabilizer polymer is insoluble to the polymer stabilizer in the polymerization medium. Similarly, the polymer stabilizer in the polymerization medium may be added to a solvent in which the polymer stabilizer is insoluble. Small number average particle size can be obtained by other known means of separating the polymer from the polymerization medium. It can be advantageous to use dispersing aids or emulsifiers such as those previously described to separate the stabilizer polymer from the polymerization medium.
Any method may be used to prepare the polymer stabilizer provided that such method will yield a polymer stabilizer having small particles, with a number average size less than 10 microns, prior to melt processing with the polyoxymethylene blend. Further, the small particles should be non-meltable at the temperature at which the polyoxymethylene blend is melt processed and should not coalesce or agglomerate to such an extent that they are not readily dispersible in the polyoxymethylene melt.

The number average particle size of the polymer stabilizer before it is melt processed with the polyoxymethylene blend components can be measured by any means capable of determining number average particle size.

The preferred means is the MICROTRAC II SMALL PARTICLE ANALYZER (ANALYZER), manufactured by Leeds & Northrup. A preferred model is 158705/158708. By this method, the polymer stabilizer is added to a liquid, such as, for example, 2-propanol (usually about 0.1 grams of polymer stabilizer in 15 ml. of liquid), and shaken by hand to disperse the polymer stabilizer in the liquid. From this dispersion, the number average particle size for the polymer stabilizer is determined by the ANALYZER. Specifically, the ANALYZER is equipped with a seventeen channel detector system that covers a particle size range of 0.17 to 60 microns. The ANALYZER prints the percent of particle volume that has a diameter of less than the given detector channel. From the diameter and particle volume, the number average particle size of the polymer stabilizer can be calculated. In this calculation, the particle diameter for a given detector channel is approximated.
by the channel diameter. The number of particles in each channel is calculated by the following formula:

\[ N = \frac{(10000\%)}{(0.5236d^3/6)} \]

where \( N \) = number of particles in a given channel
\( V\% \) = volume of particles in that channel
\( d \) = channel diameter

By summing the number of particles in all 17 channels, the total number of particles can be calculated. By multiplying the number of particles in a channel by 100, and dividing the result by the total number of particles, the percent of particles in each channel can be calculated. To calculate the total number percent having a diameter of less than that channel, a cumulative number percent is calculated by adding the number percent in all channels that have a diameter less than or equal to that particular channel. From this cumulative sum of number percents, the median number average particle size of the polymer stabilizer can be calculated. The median number average particle size of the polymer stabilizer will be 10 microns or less for purposes of this invention.

With respect to the measuring of the number average particle size of the polymer stabilizer, it is noted that in some cases, a high concentration of loose agglomerates may have occurred during the preparation of the polymer stabilizer. In such cases, more intensive mixing may be desired in order to break up the loose agglomerates. An example of a device capable of providing such intensive mixing is a "POLYTRON" (sold by Brinckman Instruments).

The number average particle size of the polymer stabilizer after it has been melt processed with the components of the polyoxymethylene blend should be less than 10 microns, preferably less than 5 microns, and most preferably less than 2 microns. It
can be measured by any technique capable of measuring number average particle size for particles in a polymer. The preferred method of measuring the number average particle size of the polymer stabilizer in the polyoxymethylene blend is by transmission electron microscopy.

It is important that the polymer stabilizer used in the blends of the present invention be substantially free of compounds which destabilize polyoxymethylene resins.

In stabilizing blends based upon ester-capped or partially ester-capped polyoxymethylene homopolymer, the polymer stabilizer should be substantially free of basic materials which can destabilize the polyoxymethylene. Basic impurities should preferably be removed to levels of not more than 50 ppm and most preferably to not more than 10 ppm. In stabilizing blends based upon polyoxymethylene copolymer or homopolymer that is substantially all ether-capped, higher concentrations of basic materials can be tolerated. In addition, it should be understood that if the impurity is only weakly basic relatively higher amounts can be tolerated.

In stabilizing blends based upon either homopolymer and copolymer polyoxymethylene, acidic impurities in the polymer stabilizer should be minimized. Acidic impurities should preferably be removed to levels of not more than 50 ppm and most preferably to not more than 10 ppm. As with basic impurities, it should be understood that if the impurity is only weakly acidic, relatively higher amounts can be tolerated.

When acidic and/or basic impurities are present in the polymer stabilizer in amounts large enough to cause destabilization of the
polyoxymethylene blends, the polymer stabilizer should be purified before it is introduced into the blends of the present invention. Polymer stabilizers used in the blends of the present invention can be purified by washing with an appropriate liquid, such as methanol and/or water. Polymer stabilizers prepared with dispersants or emulsifiers that have destabilizing effects because, for example, they are highly acidic or highly basic, can be purified by washing the stabilizer with a solvent in which the dispersants or emulsifiers are soluble and in which the polymer stabilizer is insoluble.

Component (e) Co-stabilizer Component

The component (e) co-stabilizer component is selected from the group consisting of conventional "meltably" polyamide stabilizers for polyoxymethylene, certain "meltably" hydroxy containing polymers or oligomers, and microcrystalline cellulose. The term "meltably" means the inverse of the term "non-meltably", as described above. More specifically, it means that the co-stabilizer component has its "major melting point", as described above, below the temperature at which the polyoxymethylene blend is melt processed.

The conventional meltably polyamide co-stabilizers useful herein are described in U.S. patents 2,993,025; 4,640,949; 3,960,984; and 4,098,843, each of which is incorporated herein by reference and described briefly above. The preferred conventional meltably nylon stabilizer is a terpolymer of polycaprolactam/polyhexamethylene adipamide/polyhexamethylene sebacamide terpolymer, most preferably in the ratio of 43/34/23. Alternatively, it is referred to as a terpolymer of nylon 6/nylon 66/nylon 610.
The certain meltably hydroxy containing polymer or oligomer co-stabilizers are disclosed in U.S. 4,766,168, incorporated herein by reference. More specifically, these co-stabilizers are polymers/oligomers containing hydroxy groups wherein the atoms in the backbone of the polymer or oligomer to which the hydroxy groups are attached, directly or indirectly, are separated from each other, on average, by not more than twenty chain atoms and provided further that the polymer or oligomer is substantially free of acidic materials. The preferred hydroxy containing co-stabilizer is a polymer or oligomer of ethylene vinyl alcohol.

The microcrystalline cellulose co-stabilizer useful herein is described in U.S. patent 3,023,104, incorporated herein by reference. Microcrystalline cellulose is referred to therein as "cellulose crystallite aggregates". Microcrystalline cellulose is also described in "Hydrolysis and Crystallization of Cellulose", Industrial and Engineering Chemistry, vol. 42, 502-507 (1950).

The microcrystalline cellulose useful herein will have an average particle size no greater than 300 microns. The average particle size is the point at which 50% of the particles are greater than average and 50% of the particles are less than average. Average particle size can be determined by standard techniques, such as microscopic inspection, gravitational sedimentation, sieve analysis, and electron microscopy. The preferred method is gravitational sedimentation.

It is preferred that the average particle size of the microcrystalline cellulose used herein be 100 microns or less, more preferably, 50 microns or
less, even more preferably, 25 microns or less, and most preferably, 10 microns or less.

Other Components

It should be understood that the compositions of the present invention can include, in addition to the components of the polyoxymethylene blend, other ingredients, modifiers, and additives as are generally used in polyoxymethylene molding resins, including co-stabilizers other than those described above, anti-oxidants, especially amide-containing phenolic antioxidants such as N,N'-hexamethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamide and mixtures thereof, pigments, colorants, UV stabilizers, hindered amine light stabilizers, toughening agents, nucleating agents, lubricants, glass, talc, and fillers. It should also be understood that some pigments and colorants can, themselves, adversely affect the stability of polyoxymethylene compositions.

Blend Composition

To achieve the improvements in thermal stability, the polymer stabilizer should be present in the blends of the present invention in the amount of 0.05-3 weight percent, based on the weight of components (a), (b), and (c), preferably 0.15-1.5 weight percent and most preferably 0.2-1.0 weight percent. Higher amounts of the polymer stabilizer can be used and the thermal stability of the polyoxymethylene blend may be improved; however, with increased loading of the polymer stabilizer, the physical properties of the polyoxymethylene blend may decrease.

When the co-stabilizer component is present, it should be incorporated into the blend at the following weight percent ranges, with said weight percent ranges being based upon the total of
components (a), (b), and (c) only: 0.01 to 1.00 weight percent, preferably 0.01 to 0.50 weight percent, and more preferably, 0.05 to 0.30 weight percent.

The weight percent range of components (a), (b), and (c) should be as follows, with said weight percent ranges being based upon the total weight of components (a), (b), and (c) only: 40 to 98 weight percent component (a) polyoxymethylene, 1 to 40 weight percent component (b) thermoplastic polyurethane, and 1 to 59 weight percent component (c) amorphous thermoplastic polymer. Preferably, the weight percent range of components (a), (b), and (c) is as follows: 45-90 weight percent component (a) polyoxymethylene, 5-30 weight percent component (b) thermoplastic polyurethane, and 5-50 weight percent component (c) amorphous thermoplastic polymer. Preferably, the weight percent range of components (a), (b), and (c) is as follows: 50-90 weight percent component (a) polyoxymethylene, 5-20 weight percent component (b) thermoplastic polyurethane, and 5-45 weight percent component (c) amorphous thermoplastic polymer.

METHOD OF PREPARATION

The compositions of the present invention can be prepared by mixing the polymer stabilizer, which has a number average particle size of less than 10 microns and which is non-meltable, or can be made non-meltable during processing, with the polyoxymethylene polymer at a temperature above the melting point of the polyoxymethylene polymer using any intensive mixing device conventionally used in preparing thermoplastic polyoxymethylene compositions, such as rubber mills, internal mixers such as "Banbury" and "Brabender" mixers, single or multiblade internal mixers with a cavity heated externally or by friction, "Ko-kneaders", multibarrel mixers such as
"Farrel Continuous Mixers", injection molding machines, and extruders, both single screw and twin screw, both co-rotating and counter rotating, both intermeshing and non-intermeshing. These devices can be used alone or in combination with static mixers, mixing torpedoes and/or various devices to increase internal pressure and/or the intensity of mixing, such as valves, gate or screws designed for this purpose. Extruders are preferred. Of course, such mixing should be conducted at a temperature below which significant degradation of the polyoxymethylene will occur. The polymer stabilizer in the composition after melt processing will have a number average particle size less than 10 microns.

Shaped articles can be made from the compositions of the present invention using any of several common methods, including compression molding, injection molding, extrusion molding, blow molding, rotational molding, melt spinning, and thermoforming. Injection molding is preferred. Examples of shaped articles include sheet, profiles, rod stock, film, filaments, fibers, strapping, tape tubing, and pipe. Such shaped articles can be post treated by orientation, stretching, coating, annealing, painting, laminating, and plating. Such shaped articles and scrap therefrom can be ground and remolded.

Processing conditions used in the preparation of the compositions of the present invention and shaped articles made therefrom include melt temperatures of about 170-260°C, preferably 185-240°C, most preferably 200-230°C. When injection molding the compositions of the present invention, the mold temperature will generally be 10-120°C, preferably 10-100°C, and most preferably about 50-90°C.
EXAMPLES

In the following examples, there are shown specific embodiments of the present invention, along with comparative examples. It is shown that the blends stabilized with the polymer stabilizer described herein are characterized as having better thermal stability than do the same blends stabilized with conventional polyoxymethylene stabilizers. It is further shown that blends stabilized with a mixed stabilizer system containing the polymer stabilizer described herein and either a polyamide stabilizer or a hydroxy containing stabilizer have better melt processing stability than blends stabilizer with one component of the stabilizer system. The blends stabilized with the polymer stabilizer described herein are also shown to have at least an acceptable balance of physical properties.

COMPONENTS OF THE EXAMPLES

The components used in the blends of the following examples were as follows:

Polyoxymethylene (POM) Polymer

"POM-A" was an acetate end-capped homopolymer having a number average molecular weight of about 35,000.

"POM-B" was a commercially available polyoxymethylene copolymer having a melt flow index of about 9.0 at 190°C under a load of 2160 g. It was prepared from the cationic polymerization of trioxane and ethylene oxide using bor trifluoride as a catalyst.

SUBSTITUTE SHEET
Stabilizers

Stabilizer "A" was the non-meltable polymer stabilizer, containing formaldehyde reactive nitrogen groups, of the present invention. It was prepared by adding a solution of 14.3 kg of acrylamide and 145.15 grams of 1,4-butanediol diacrylate to a refluxing solution of 1.44 kg of polyethylene glycol having a molecular weight of about 8000 in 48.06 kg of methanol (approximately 64°C) over a period of about two hours. Throughout this addition, a total of 195.04 grams of tert-butylperoxypivalate polymerization initiator was portionwise added. The resulting reaction suspension was cooled and filtered. The resulting white solid was washed with methanol and dried in a vacuum oven (6.75x10^4 Pa) at 70°C for 1 day and at 100°C for 1 day.

Co-Stabilizer "B" was a 43/34/23 polycaprolactum/polyhexamethylene adipamide/polyhexamethylene sebacamide terpolymer.

This is also known as a 43/34/23 terpolymer of nylon 6, nylon 66, and nylon 610, respectively. It had a melting point, measured in accordance with ASTM D796, between 148-160°C.

Co-Stabilizer "C" was a 29/79 copolymer of ethylene and vinyl alcohol prepared in accordance with U.S. 4,766,168. It had a melting point, measured in accordance with ASTM D796, of about 191°C.

Co-Stabilizer "D" was nylon 66 dispersed in an ethylene/methacrylate copolymer, prepared as described in U.S. 4,098,843. Specifically, it was nylon 66 (33.5%) in an 85/15 ethylene/methacrylate copolymer (66.5%) partially crosslinked by zinc salts. The percent of neutralization with the zinc salts is about 58%. It had a melt flow rate of 0.7 g/10min, as measured by ASTM D-1238, and a melting point of 88°C.
as measured by Differential Thermal Analysis (ASTM D3418, heating rate of 10°C/minute.

**Thermoplastic Polyurethane (TPU)**

The thermoplastic polyurethane used in the blends of the examples below had an inherent viscosity of 1.33, a soft segment glass transition temperature (Tg) of -35°C, and was comprised of 37% adipic acid, 39% butanediol, and 24% 4,4'-methylene bisphenyl isocyanate. Inherent viscosity was measured by ASTM D-2857 with a "Schott" automatic viscometer at 0.1% polyurethane in dimethyl formamide at 30°C. The Tg was determined using a Du Pont Model 981 Dynamic Mechanical Analysis Cell attached to a Model 990 DTA instrument. The cell was modified to use liquid nitrogen as the coolant and to allow the use of a 3.2 cm (1.25 inch) gap holding the specimen. The oscillation amplitude was set at 0.2 mm. A heating rate of 2.5°C/min was used from -170°C to 0°C to 40°C depending on the signal amplitude. Readings were taken every 1°C increment. The storage and loss moduli were plotted and the major loss modulus peak was defined as the soft segment glass transition temperature.

**Amorphous Thermoplastic Polymer**

Unless otherwise specified, the melt viscosity data, in Pascal seconds, on the amorphous thermoplastic polymer component used in the blends of the examples below was obtained at 220°C, at shear rates of 100 1/sec and 1000 1/sec. The viscosity data for the individual amorphous thermoplastic polymers used in the examples is reported firstly for a shear rate of 100 1/sec and secondly for a shear rate of 1000 1/sec. The individual amorphous thermoplastic polymeric components used in the examples are described as follows:
SAN-A was a styrene acrylonitrile copolymer having a melt viscosity of 934 and 241, respectively, and consisting of 30% acrylonitrile, 70% styrene.

SAN-B was a styrene acrylonitrile copolymer having a melt viscosity of 1713 and 329, respectively, and consisting of 24% acrylonitrile, 76% styrene.

AES was an acrylonitrile-ethylene-propylene-styrene resin having a melt viscosity of 1841 and 363, respectively, and consisting of 51% styrene, 21% acrylonitrile, and 28% ethylene propylene rubber.

ABS was an acrylonitrile-butadiene-styrene resin having a melt viscosity of 1081 and 223, respectively, and consisting of 77% styrene, 18% acrylonitrile, and 5% butadiene.

PC-A was a polycarbonate of bisphenol A having a melt viscosity of 218 Pascal seconds, measured at a shear rate of 250 sec⁻¹ at 280°C and 187 Pascal seconds, measured at a shear rate of 1000 sec⁻¹ at 280°C.

**Antioxidants**

Antioxidant "A" was 2,2-methylene-bis-(4-methyl-6-tert-butyl-phenol).

Antioxidant "B" was N,N’-hexamethylene-bis-3-(3,5-di-tert-butyl-4-hydroxyphenol) propionate.

Antioxidant "C" was a triethyleneglycol-bis-3(tert-butyl-4-hydroxy-5-methylphenyl) propionate.

**PREPARATION OF THE BLENDS**

**Method A**

The components of the blends were melt compounded on a 28 mm Werner & Pfleiderer bilobal extruder, using a screw design containing two working sections with five kneading elements (70 mm total), and two reverse elements (24 mm total). All components were supplied from the main feeder at the rear of the extruder. The extruder was operated at
about 150 rpm with 15-25 pounds per hour throughput. The temperature of the melt coming out of the die ranged from 210°C to 230°C.

**Method B**

The components of the blend were melt compounded in two steps. In the first step, the polyoxyethylene component, the thermal stabilizer component(s), and the antioxidant(s) were compounded on a 2 1/2" sterling screw extruder with a screw speed of 60 rpm. The temperature of the melt exiting the extruder was between 225-240°C. The resultant polyoxyethylene product was pelletized. In the second step, the pelletized product was melt compounded with the thermoplastic polyurethane component and the amorphous thermoplastic polymer components of the blend under the same conditions as described in Method A, above.

**Method C**

The components of the blend were melt compounded on a 2" sterling single screw extruder, using a single stage screw design with a metering ratio of 2.5/1.0 and a barrier section 8" long and 6" from the front of the screw. All components were supplied from the rear side of the screw. The temperature of the melt coming out of the valve die ranged from 225°C to 240°C. The extruder was operated at 60-80 rpm with 25-45 pounds per hour throughput.

**Method D**

The components of the blend were melt compounded on a 30 mm Werner & Pfleiderer bilobal extruder with/without a seed feeder. The screw contained two kneading sections (84 mm total) and two reverse sections (20 mm total). The temperature of the melt exiting the die ranged from 200°C to 210°C and the throughput was 15-25 pounds per hour.
extruder was operated at 140-160 rpm. The components of the blend were added to the extruder via the rear side of the screw and side feeder as described in TABLE I below.

<table>
<thead>
<tr>
<th>Method No.</th>
<th>Rear Feed Components</th>
<th>Side Feed Components</th>
<th>Feed Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>D.1</td>
<td>POM, stabilizer(s), antioxidant(s)</td>
<td>TPU, amorphous resin</td>
<td>1:1</td>
</tr>
<tr>
<td>D.2</td>
<td>POM, stabilizer(s), TPU, antioxidant(s)</td>
<td>amorphous resin</td>
<td>6:4</td>
</tr>
<tr>
<td>D.3</td>
<td>All</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In TABLE I, the feed ratio is the ratio of rear feed:side feed.

Method E

The components of the blend were melt compounded on a 57 mm Werner and Pfleiderer bilobal extruder. The polyoxymethylene polymer and stabilizer components were supplied from the rear of the extruder while the thermoplastic polyurethane and amorphous thermoplastic polymer components were added via a side feeder. The ratio of rear feed:side feed was 45:55. The screw had four kneading blocks and four reverse sections. The temperature of the melt coming out of the die was about 244°C. The extruder was operated at 100 rpm.

TESTING OF THE BLENDS

The thermal stability of the polyoxymethylene blends of the examples was determined using a thermally evolved formaldehyde (TEF) test procedure. A weighed sample of polyoxymethylene blend was placed in a tube and the tube was fitted with a cap for introduction of nitrogen to the test sample for removal of any evolved gases from the apparatus while maintaining the sample in an oxygen-free
environment. The tube that contained the sample was heated at either 250°C or 259°C in a silicon oil bath. The nitrogen and any evolved gases transported thereby were bubbled through 75 ml of a 40 g/liter sodium sulfite in water solution. Any evolved formaldehyde reacts with the sodium sulfite to liberate sodium hydroxide. The sodium hydroxide was continuously neutralized with standard 0.1 N HCl. The results were obtained as a chart of ml of titer versus test time.

The percent evolved formaldehyde was calculated by the formula

\[
\frac{0.03 \times 100}{SW} \left(\frac{V}{N}\right)
\]

where \( V \) = the volume of titer in milliliters

\( N \) = the normality of the titer, and

\( SW \) = the sample weight in grams.

The factor “0.03” is the milliequivalent weight of formaldehyde in g/milliequivalent. Thermally evolved formaldehyde results are reported after 15 minutes and 30 minutes for the blend.

Also, in some instances, the percent thermally evolved formaldehyde resulting only from the polyoxymethylene component of the blend is reported after 30 minutes. This was calculated as follows:

\[
\frac{0.03 \times 10000}{SW \times WP} \left(\frac{V}{N}\right)
\]

where \( V \) = the volume of titer in milliliters

\( N \) = the normality of the titer

\( SW \) = the sample weight in grams

\( WP \) = the weight percent of polyoxymethylene in the sample.

The total percent weight loss of the blend after 30 minutes of testing by the TEF procedure was also determined in some instances. Total percent
weight loss was determined by the following equation:

\[
\frac{(W_2 - W_3)}{W_1} \times 100
\]

where \( W_1 \) = original sample weight (in grams)

\( W_2 \) = original sample weight (in grams) + glass tube weight (in grams)

\( W_3 \) = weight of sample (in grams) + glass tube weight after 30 minutes of testing (in grams)

In some cases, the physical properties of the stabilized blends were tested. Specifically, the physical properties that were tested were as follows: mold shrinkage, strength (i.e., tensile), elongation, and toughness (i.e., notched Izod).

Mold shrinkage was determined on bars molded from the melt-compounded stabilized blends. Unless otherwise specified, the pellets of the melt compounded stabilized blend were loaded into a 6 ounce C Molding Machine using cylinder temperature settings of about 200°C, a mold temperature set to 60°C, a back pressure of 50 psi, a screw speed of 60 rpm, a cycle of 15 seconds injection/15 seconds hold, mold pressure about 6 kpsi, and a general purpose screw. The melted blend was injection molded into standard 12.7 cm X 1.27 cm X 0.32 cm (5 in X 1/2 in X 1/8) test bars that are used in measuring "Izod" toughness (according to ASTM-0256, Method A). The length of the mold was measured. The sample blend was allowed to stand in the test bar mold at least 2 days in an air conditioned room, after which time the molded sample bar was removed and its length was measured. Mold shrinkage was determined by the following formula:

\[
\text{Mold Shrinkage} = \left(\frac{\text{mold length} - \text{molded sample bar length}}{\text{mold length}}\right) \times 100
\]

The value reported is the average value obtained for three test bars.
Strength (i.e., tensile) was determined in accordance with ASTM D638 on three molded sample bars and the average value is reported. Samples were allowed to stand at least two days in an air conditioned room after molding and prior to testing. Testing was done at 23°C (50% RH).

Elongation was measured in accordance with ASTM-D638 at 2"/min. Samples were allowed to stand at least two days in an air conditioned room after molding and prior to testing. Testing was done at 23°C (50% RH). The value reported is the average of the value obtained on three test bars.

Toughness, reported as "Izod", was measured according to ASTM D-256, Method A. Samples were notched using a single toothed cutting wheel on a TMI Notching Cutter Model 43-15 with a cutter speed setting of 10.0 and a feed speed setting of 6.0. The samples were allowed to stand at least two days in an air conditioned room after molding prior to testing. Testing was done at 23°C (50% RH). Sample bars were prepared as for the mold shrinkage test, i.e., from a 12.7 cm X 1.27 cm X 0.32 cm (5 in X 1/2 X 1.8 in) injection molded bar. The sample bar was cut in half with a notch in each half cut approximately 3.1 cm (1 1/4 in) from each end. Six samples of each composition were tested and the average value was reported.

Average particle size of the polymer stabilizer in the blend was determined by transmission electron microscopy (TEM). TEM samples were prepared by cross-sectional microtoming of molded flexural bars (1/8 inch) of the melt processed blend, said bars being prepared as described for the mold shrinkage tests. The TEM samples were microtomed so that cross sectional views perpendicular to the direction of flow
of the blend would be cut from the flexural bar. Using standard
-90°C cryo-ultramicrotomy techniques, 90-120
nanometer sections of each sample were microtomed. The
sections were mounted on copper TEM grids and exposed
to ruthenium tetroxide vapors for staining. The
stained sections were examined using a Zeiss EM10CR
transmission electron microscope. Images were recorded
at nominal magnifications of 1000x, 2520x, and 5000x.
Magnification calibrations performed on an annual
basis using a commercially available grating replica
were combined to give the final image magnification,
which included 4640x, 11800x, and 23600x. To determine
the average particle size of the polymer stabilizer in
the blend, minimum and maximum size particles were
selected in the TEM photograph (X4640 AND X11800) and
the diameter of the particle was measured with a
ruler. Any agglomerated particles were treated as one
particle. The number average particle size of the
polymer stabilizer in the blend was determined by
averaging the values obtained for measurement of at
least 15 particles. Reported in the Examples below is
the range of particle sizes of the polymer stabilizer
A observed in a TEM photograph of a melt compounded
blend.

In all cases in the Examples below where the
particle size of the polymer stabilizer in the blend
was determined, the polymer stabilizer was observed as
white round particles, indicating that said stabilizer
did not melt during the extrusion and molding
processes.

**EXAMPLES 1-5**

The blend components and method of
preparation of Examples 1-5, along with control
examples C1-C13 are detailed in TABLE IIIA, below.

Thermal stability data for each blend is reported in
TABLE IIA, below, and physical property data for each blend, where available, is reported in TABLE IIB, below. The polyoxymethylene used in the blends of TABLES IIA and IIB was polyoxymethylene A.

Examples C1-C4 and Example 1.1 show the effect of various stabilizers on the thermal stability of a POM/TPU blend. Stabilizers A-D worked equally well in stabilizing the POM/TPU blend. Example 1.1 showed, however, that a stabilizer system consisting of the polymer stabilizer A and the nylon stabilizer B acted to improve the stability of the POM/TPU blend to a greater extent than did polymer stabilizer A alone or nylon stabilizer B alone. Samples of the C4 blend were taken for TEM analysis, as described above. The particle size of the polymer stabilizer A in the C4 blend ranged from 0.6-1.4 microns.

Examples C5-C7 and 2.1-2.2 show the effect of the polymer stabilizer A and conventional stabilizers on the thermal stability of POM/TPU/PC blends. Samples of the Example 2.1 blend were taken for TEM analysis, as described above. The particle size of the polymer stabilizer A in Example blend 2.1 ranged from 0.6-1.8 microns. The polymer stabilizer A provided significantly better thermal stability at 15 minutes of testing to the POM/TPU/PC blend than did the other conventional thermal stabilizers. Also, a mixed stabilizer system consisting of polymer stabilizer A and nylon stabilizer B imparted better thermal stability to the POM/TPU/PC blend than did either stabilizer by itself.

In Examples C8-C9 and 3.1-3.2, stabilized POM/TPU/ABS blends were tested. In Examples C10-C12 and 4.1-4.3, POM/TPU/AES blends were tested. In both cases, the polymer stabilizer A imparted significantly better thermal stability to the blends than did the
other conventional stabilizers. Further, in both cases, a mixed stabilizer system consisting of polymer stabilizer A and nylon stabilizer B imparted better thermal stability to the blend than did either stabilizer alone. Samples were taken from the blends of Example 3.2, Example 4.1, and Example 4.3 for TEM analysis, as described above. The particle size of the polymer stabilizer A in Example 3.2 ranged from 0.6-1.3 microns. The particle size of the polymer stabilizer A in Example 4.1 ranged from 0.8-1.2 and in Example 4.3 it ranged from 0.8-1.6.

In Examples C13 and 5.1-5.2, stabilized POM/TPU/SAN blends were tested. Results showed the weight loss experienced by the blend during testing was less when polymer stabilizer A was used then when the stabilizer of choice was conventional nylon stabilizer B.

The physical property data presented in TABLE IIIB, below, shows that the blends stabilized with polymer stabilizer A have a useful balance of physical properties.
<table>
<thead>
<tr>
<th>Eg. No.</th>
<th>Blend Type</th>
<th>% Ratios</th>
<th>Method</th>
<th>Stabilizer</th>
<th>Wt.% AO</th>
<th>15 min</th>
<th>30 min (blend)</th>
<th>30 min (POM)</th>
<th>Wt. % Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>POM/TPU</td>
<td>90/10</td>
<td>A</td>
<td>0.71B</td>
<td>0.18B</td>
<td>0.40</td>
<td>1.02</td>
<td>1.13</td>
<td>nm</td>
</tr>
<tr>
<td>C2</td>
<td>POM/TPU</td>
<td>90/10</td>
<td>A</td>
<td>0.67C</td>
<td>0.18B</td>
<td>0.43</td>
<td>1.20</td>
<td>1.33</td>
<td>nm</td>
</tr>
<tr>
<td>C3</td>
<td>POM/TPU</td>
<td>90/10</td>
<td>A</td>
<td>0.71D</td>
<td>0.18B</td>
<td>0.23</td>
<td>0.96</td>
<td>1.07</td>
<td>nm</td>
</tr>
<tr>
<td>C4</td>
<td>POM/TPU</td>
<td>90/10</td>
<td>A</td>
<td>0.45A</td>
<td>0.18B</td>
<td>0.30</td>
<td>1.08</td>
<td>1.20</td>
<td>nm</td>
</tr>
<tr>
<td>1.1</td>
<td>POM/TPU</td>
<td>90/10</td>
<td>A</td>
<td>0.27B/0.45A</td>
<td>0.18B</td>
<td>0.18</td>
<td>0.79</td>
<td>0.88</td>
<td>nm</td>
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<td>C5</td>
<td>POM/TPU/PC</td>
<td>50/10/40</td>
<td>A</td>
<td>0.40B</td>
<td>0.10B</td>
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<td>C6</td>
<td>POM/TPU/PC</td>
<td>50/10/40</td>
<td>A</td>
<td>0.37C</td>
<td>0.10B</td>
<td>0.21</td>
<td>0.86</td>
<td>1.72</td>
<td>nm</td>
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<tr>
<td>C7</td>
<td>POM/TPU/PC</td>
<td>50/10/40</td>
<td>A</td>
<td>0.40D</td>
<td>0.10B</td>
<td>0.08</td>
<td>0.35</td>
<td>0.70</td>
<td>nm</td>
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<tr>
<td>2.1</td>
<td>POM/TPU/PC</td>
<td>50/10/40</td>
<td>A</td>
<td>0.45A</td>
<td>0.10B</td>
<td>0.03</td>
<td>0.40</td>
<td>0.80</td>
<td>nm</td>
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<td>2.2</td>
<td>POM/TPU/PC</td>
<td>50/10/40</td>
<td>A</td>
<td>0.45A/0.27B</td>
<td>0.10B</td>
<td>1.03</td>
<td>0.20</td>
<td>0.40</td>
<td>nm</td>
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<tr>
<td>C8</td>
<td>POM/TPU/ABS</td>
<td>50/10/40</td>
<td>B</td>
<td>0.40B</td>
<td>0.06A</td>
<td>0.59</td>
<td>1.69</td>
<td>3.38</td>
<td>nm</td>
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<tr>
<td>C9</td>
<td>POM/TPU/ABS</td>
<td>50/10/40</td>
<td>B</td>
<td>0.37C</td>
<td>0.04B</td>
<td>1.33</td>
<td>3.06</td>
<td>6.12</td>
<td>nm</td>
</tr>
<tr>
<td>3.1</td>
<td>POM/TPU/ABS</td>
<td>50/10/40</td>
<td>B</td>
<td>0.25A</td>
<td>0.11C</td>
<td>0.17</td>
<td>0.54</td>
<td>1.08</td>
<td>nm</td>
</tr>
<tr>
<td>3.2</td>
<td>POM/TPU/ABS</td>
<td>50/10/40</td>
<td>B</td>
<td>0.25A/0.13C</td>
<td>0.06C/ 0.05B</td>
<td>0.08</td>
<td>0.33</td>
<td>0.66</td>
<td>nm</td>
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<tr>
<td>C10</td>
<td>POM/TPU/AES</td>
<td>50/10/40</td>
<td>A</td>
<td>0.40B</td>
<td>0.10B</td>
<td>0.85</td>
<td>2.45</td>
<td>4.90</td>
<td>8.54</td>
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<tr>
<td>C11</td>
<td>POM/TPU/AES</td>
<td>50/10/40</td>
<td>A</td>
<td>0.37C</td>
<td>0.10B</td>
<td>2.94</td>
<td>6.20</td>
<td>12.40</td>
<td>9.71</td>
</tr>
<tr>
<td>C12</td>
<td>POM/TPU/AES</td>
<td>50/10/40</td>
<td>A</td>
<td>0.40D</td>
<td>0.10B</td>
<td>1.91</td>
<td>5.54</td>
<td>11.08</td>
<td>8.75</td>
</tr>
<tr>
<td>4.1</td>
<td>POM/TPU/AES</td>
<td>50/10/40</td>
<td>A</td>
<td>0.45A</td>
<td>0.10B</td>
<td>0.57</td>
<td>1.87</td>
<td>3.74</td>
<td>3.20</td>
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<td>4.2</td>
<td>POM/TPU/AES</td>
<td>50/10/40</td>
<td>A</td>
<td>0.45A/0.27C</td>
<td>0.10B</td>
<td>0.45</td>
<td>1.31</td>
<td>2.62</td>
<td>5.40</td>
</tr>
<tr>
<td>4.3</td>
<td>POM/TPU/AES</td>
<td>50/10/40</td>
<td>A</td>
<td>0.45A/0.40B</td>
<td>0.10B</td>
<td>0.47</td>
<td>1.62</td>
<td>3.24</td>
<td>4.25</td>
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<tr>
<td>C13</td>
<td>POM/TPU/SAN-A</td>
<td>40/10/50</td>
<td>A</td>
<td>0.40B</td>
<td>0.10A</td>
<td>0.08</td>
<td>0.28</td>
<td>0.58</td>
<td>1.86</td>
</tr>
<tr>
<td>5.1</td>
<td>POM/TPU/SAN-A</td>
<td>40/10/50</td>
<td>A</td>
<td>0.45A</td>
<td>0.11C</td>
<td>0.08</td>
<td>0.29</td>
<td>0.58</td>
<td>1.13</td>
</tr>
<tr>
<td>5.2</td>
<td>POM/TPU/SAN-A</td>
<td>40/10/50</td>
<td>A</td>
<td>0.25A/0.13C</td>
<td>0.06C/ 0.05B</td>
<td>0.07</td>
<td>0.27</td>
<td>0.54</td>
<td>1.36</td>
</tr>
</tbody>
</table>

nm = not measured
<table>
<thead>
<tr>
<th>Eg. No.</th>
<th>Blend type</th>
<th>Stabilizer</th>
<th>Tensile (kpsi)</th>
<th>Elongation (%)</th>
<th>Izod (ft-lb/in)</th>
<th>Shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>POM-A/TPU</td>
<td>B</td>
<td>8.82</td>
<td>52.5</td>
<td>1.95</td>
<td>2.55</td>
</tr>
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<td>C2</td>
<td>POM-A/TPU</td>
<td>C</td>
<td>8.65</td>
<td>19.0</td>
<td>1.93</td>
<td>2.44</td>
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<td>C3</td>
<td>POM-A/TPU</td>
<td>D</td>
<td>8.80</td>
<td>39.0</td>
<td>1.60</td>
<td>2.53</td>
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<td>C4</td>
<td>POM-A/TPU</td>
<td>A</td>
<td>8.75</td>
<td>39.0</td>
<td>1.66</td>
<td>2.58</td>
</tr>
<tr>
<td>1.1</td>
<td>POM-A/TPU</td>
<td>A/B</td>
<td>8.70</td>
<td>38.0</td>
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<td>POM-A/TPU/PC</td>
<td>B</td>
<td>7.38</td>
<td>17.0</td>
<td>1.87</td>
<td>1.31</td>
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<tr>
<td>C6</td>
<td>POM-A/TPU/PC</td>
<td>C</td>
<td>7.62</td>
<td>17.0</td>
<td>2.05</td>
<td>1.91</td>
</tr>
<tr>
<td>C7</td>
<td>POM-A/TPU/PC</td>
<td>D</td>
<td>7.58</td>
<td>15.0</td>
<td>1.71</td>
<td>1.36</td>
</tr>
<tr>
<td>2.1</td>
<td>POM-A/TPU/PC</td>
<td>A</td>
<td>7.58</td>
<td>15.0</td>
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<td>A/B</td>
<td>7.31</td>
<td>13.0</td>
<td>1.80</td>
<td>1.29</td>
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<td>C8</td>
<td>POM-A/TPU/ABS</td>
<td>B</td>
<td>6.19</td>
<td>25.5</td>
<td>1.74</td>
<td>1.05</td>
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<tr>
<td>C9</td>
<td>POM-A/TPU/ABS</td>
<td>C</td>
<td>6.28</td>
<td>27.7</td>
<td>1.68</td>
<td>1.04</td>
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<td>3.1</td>
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<td>30.4</td>
<td>1.65</td>
<td>0.89</td>
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<tr>
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<td>POM-A/TPU/ABS</td>
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<td>6.00</td>
<td>30.0</td>
<td>1.74</td>
<td>0.98</td>
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<tr>
<td>C10</td>
<td>POM-A/TPU/AES</td>
<td>B</td>
<td>5.76</td>
<td>31.0</td>
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<td>1.42</td>
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<tr>
<td>C11</td>
<td>POM-A/TPU/AES</td>
<td>C</td>
<td>5.65</td>
<td>37.0</td>
<td>1.36</td>
<td>1.30</td>
</tr>
<tr>
<td>C12</td>
<td>POM-A/TPU/AES</td>
<td>D</td>
<td>5.67</td>
<td>29.0</td>
<td>1.19</td>
<td>1.40</td>
</tr>
<tr>
<td>4.1</td>
<td>POM-A/TPU/AES</td>
<td>A</td>
<td>5.77</td>
<td>23.0</td>
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<td>4.2</td>
<td>POM-A/TPU/AES</td>
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<td>nm</td>
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<tr>
<td>4.3</td>
<td>POM-A/TPU/AES</td>
<td>A/B</td>
<td>5.62</td>
<td>29.0</td>
<td>1.07</td>
<td>1.35</td>
</tr>
<tr>
<td>C13</td>
<td>POM-A/TPU/SAN</td>
<td>B</td>
<td>nm</td>
<td>nm</td>
<td>nm</td>
<td>nm</td>
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<td>POM-A/TPU/SAN</td>
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<td>9.50</td>
<td>9.0</td>
<td>0.79</td>
<td>0.91</td>
</tr>
</tbody>
</table>

**nm** = not measured
EXAMPLES 6-9

The components and the method used in preparing the blends of examples 6-9, along with examples C14-C17, are described in TABLE III, below. Thermal stability results for these blends are also reported in TABLE III. In each case, the polyoxymethylene used was polyoxymethylene A.

In each case, the thermal stability of a blend containing the polymer stabilizer A was significantly improved over that of the same blend containing conventional nylon stabilizer B in place of the polymer stabilizer A.
<table>
<thead>
<tr>
<th>Eg. No.</th>
<th>Blend Type</th>
<th>% Ratios</th>
<th>Method</th>
<th>Wt. % Stabilizer</th>
<th>Wt. % Antioxidant</th>
<th>15 min (blend)</th>
<th>30 min (blend)</th>
<th>Wt loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C14</td>
<td>POM/TPU/SAN-A</td>
<td>40/50/10</td>
<td>C</td>
<td>0.32B</td>
<td>0.05A</td>
<td>0.49</td>
<td>1.84</td>
<td>2.23</td>
</tr>
<tr>
<td>6.1</td>
<td>POM/TPU/SAN-A</td>
<td>40/50/10</td>
<td>C</td>
<td>0.20A</td>
<td>0.08C</td>
<td>0.05</td>
<td>0.31</td>
<td>0.84</td>
</tr>
<tr>
<td>C15</td>
<td>POM/TPU/ABS</td>
<td>50/40/10</td>
<td>C</td>
<td>0.40A</td>
<td>0.06A</td>
<td>0.82</td>
<td>2.20</td>
<td>4.34</td>
</tr>
<tr>
<td>7.1</td>
<td>POM/TPU/ABS</td>
<td>50/40/10</td>
<td>C</td>
<td>0.25A</td>
<td>0.11C</td>
<td>0.07</td>
<td>0.17</td>
<td>0.57</td>
</tr>
<tr>
<td>C16</td>
<td>POM/TPU/PC</td>
<td>50/40/10</td>
<td>C</td>
<td>0.40B</td>
<td>0.06A</td>
<td>0.18</td>
<td>1.34</td>
<td>2.12</td>
</tr>
<tr>
<td>8.1</td>
<td>POM/TPU/PC</td>
<td>50/40/10</td>
<td>C</td>
<td>0.25A</td>
<td>0.11C</td>
<td>0.08</td>
<td>0.23</td>
<td>0.80</td>
</tr>
<tr>
<td>C17</td>
<td>POM/TPU/AES</td>
<td>50/40/10</td>
<td>C</td>
<td>0.40B</td>
<td>0.16A</td>
<td>1.73</td>
<td>4.77</td>
<td>nm</td>
</tr>
<tr>
<td>9.1</td>
<td>POM/TPU/AES</td>
<td>50/40/10</td>
<td>C</td>
<td>0.25A</td>
<td>0.11C</td>
<td>0.82</td>
<td>3.68</td>
<td>nm</td>
</tr>
</tbody>
</table>

nm = not measured
EXAMPLE 10

Example 10 relates to blends of POM, TPU, and AES. The blends, along with the method by which each was prepared, are described in TABLE IV, below.

In each case, the polyoxymethylene used was polyoxymethylene A.

In each case, the blend containing a stabilizer system consisting of polymer stabilizer A and conventional nylon stabilizer B had significantly better thermal stability than did blends containing as a stabilizer only the conventional nylon stabilizer B.
<table>
<thead>
<tr>
<th>Eg. No.</th>
<th>Blend Type</th>
<th>% Ratios</th>
<th>Method</th>
<th>Wt. % Stabilizer</th>
<th>Wt. % Antioxidant</th>
<th>Thermally Evolved CH₂O (%) at 250°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>15 min</td>
</tr>
<tr>
<td>C18</td>
<td>POM/TPU/AES</td>
<td>50/40/10</td>
<td>D.1</td>
<td>0.40B</td>
<td>0.06A</td>
<td>1.92</td>
</tr>
<tr>
<td>10.1</td>
<td>POM/TPU/AES</td>
<td>50/40/10</td>
<td>D.1</td>
<td>0.20A/0.15B</td>
<td>0.10B</td>
<td>0.67</td>
</tr>
<tr>
<td>C19</td>
<td>POM/TPU/AES</td>
<td>50/40/10</td>
<td>D.2</td>
<td>0.40B</td>
<td>0.06A</td>
<td>1.77</td>
</tr>
<tr>
<td>10.2</td>
<td>POM/TPU/AES</td>
<td>50/40/10</td>
<td>D.2</td>
<td>0.20A/0.15B</td>
<td>0.10B</td>
<td>0.56</td>
</tr>
<tr>
<td>10.3</td>
<td>POM/TPU/AES</td>
<td>50/40/10</td>
<td>D.3</td>
<td>0.20A/0.15B</td>
<td>0.10B</td>
<td>0.68</td>
</tr>
</tbody>
</table>
EXAMPLE 11

In this example, a 45/15/40 POM-A/TPU/SAN-B blend was prepared by Method E. The blend contained as a stabilizer system 0.27 weight percent polymer stabilizer A and 0.14 weight percent conventional nylon stabilizer B. No antioxidant was added to the blend. The TEF results (at 250°C) on the blend were as follows: 0.11 after 15 minutes of testing and 0.29 after 30 minutes of testing. The weight loss of the blend after 30 minutes of testing by the TEF procedure was 1.81. These results show that the blend containing the stabilizer system consisting of polymer stabilizer A and the conventional nylon stabilizer was thermally stable in the absence of an antioxidant.

EXAMPLE 12

Example 12 and C20 relate to blends of POM-B (a polyoxymethylene copolymer), TPU, and ABS. The blends, and the method by which they were prepared, are described in TABLE V, below.

The thermal stability of the blend was improved when polymer stabilizer A was incorporated into the blend and the weight loss experienced by the blend was significantly reduced when polymer stabilizer A was added to the blend.
<table>
<thead>
<tr>
<th>Blend Type</th>
<th>% Ratios</th>
<th>Method</th>
<th>Stabilizer</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOM/TPU/ABS 50/40/10</td>
<td>A</td>
<td>A</td>
<td>0.80A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Wt. Loss</th>
<th>C20</th>
<th>11.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 min</td>
<td>0.15</td>
<td>0.08</td>
</tr>
<tr>
<td>30 min</td>
<td>0.10</td>
<td>0.06</td>
</tr>
<tr>
<td>60 min</td>
<td>0.10</td>
<td>0.06</td>
</tr>
</tbody>
</table>

| Wt. Loss (g) | 1.310 | 0.750 |

**TABLE V**
CLAIMS

1. A blend consisting essentially of
   (a) 40-98 weight percent of a
       polyoxymethylene polymer,
   (b) 1-40 weight percent of a thermoplastic
       polyurethane,
   (c) 1-59 weight percent of an amorphous
       thermoplastic polymer selected from the
       group consisting of styrene
       acrylonitrile copolymers,
       acrylonitrile-butadiene-styrene
       resins,
       acrylonitrile-ethylene-propylene-styrene
       resins, polycarbonates, polyamides,
       polyarylates, polyphenylenoxides,
       polyphenylene ethers, high impact
       styrene resins, acrylic polymers,
       imidized acrylic resins, styrene maleic
       anhydride copolymers, polysulfones,
       styrene acrylonitrile maleic
       anhydride resins, styrene acrylic
       copolymers, and
   (d) 0.05-3.0 weight percent of a
       non-meltable polymer stabilizer
       containing formaldehyde reactive
       nitrogen groups having a number
       average particle size in the blend of
       ten microns or less,

   wherein all weight percents are based upon the weight
   of (a), (b), and (c) only and provided that the atoms
   in the backbone of the polymer stabilizer (d) to which
   the formaldehyde reactive nitrogen groups are attached
   directly or indirectly are separated from each other,
on average, by not more than twenty chain atoms and further provided that the amount of formaldehyde reactive nitrogen groups attached directly or indirectly to the atoms which are in the backbone of the polymer stabilizer (d) is, on average, at least three times as great as the amount of formaldehyde reactive nitrogen groups present in the backbone of the polymer stabilizer (d).

2. The blend of Claim 1 further comprised of 0.01-1.00 weight percent, of a co-stabilizer compound that is substantially free of acidic materials and that is selected from the group consisting of microcrystalline cellulose having an average particle size of 100 microns or less, meltale nylon-based stabilizers, meltale hydroxy containing polymer or oligomer stabilizers wherein the atoms in the backbone of said polymer or oligomer to which the hydroxy groups are attached directly or indirectly are separated, on average, by not more than twenty chain atoms.

3. The blend of Claims 1 or 2 wherein the polymer stabilizer of component (d) is substantially free of acidic materials.

4. The blend of Claims 1 or 2 wherein the polyoxymethylene polymer is homopolymer and the polymer stabilizer of component (d) is substantially free of acidic and basic materials.

5. The blend of Claims 1 or 2 wherein the polyoxymethylene polymer is a copolymer.

6. The blend of Claims 1 or 2 wherein the thermoplastic polyurethane is derived from the reaction of 1,4-butylene adipate, 4,4'-methylene bis(phenylisocyanate), and 1,4-butanediol.

7. The blend of Claims 1 or 2 wherein the amorphous thermoplastic polymer component is selected.
from the group consisting of styrene acrylonitrile copolymers, acrylonitrile-butadiene-styrene resins, acrylonitrile-ethylene-propylene-styrene resins, and polycarbonate.

8. The blend of Claims 1 or 2 wherein the amorphous thermoplastic polymer component is a styrene acrylonitrile copolymer.

9. The blend of Claims 1 or 2 wherein the amorphous thermoplastic polymer component is an acrylonitrile-butadiene-styrene resin.

10. The blend of Claims 1 or 2 wherein the amorphous thermoplastic polymer component is an acrylonitrile-ethylene-propylene-styrene resin.

11. The blend of Claims 1 or 2 wherein the amorphous thermoplastic polymer component is a polycarbonate.

12. The blend of Claims 1 or 2 wherein the non-meltable polymer stabilizer component (d) is polyacrylamide or polymethacrylamide.

13. The blend of Claims 1 or 2 wherein the non-meltable polymer stabilizer component (d) is a copolymer of a hydroxy-containing compound and a comonomer selected from the group consisting of acrylamide and methacrylamide.

14. The blend of Claim 13 wherein the hydroxy-containing compound is hydroxypropylmethacrylate or ethylene vinyl alcohol.

15. The blend of Claim 13 wherein the hydroxy-containing compound is hydroxypropylmethacrylate and the comonomer is acrylamide.

16. The blend of Claims 1 or 2 wherein the number average particle size of the non-meltable polymer stabilizer component (d) in the blend is less than 5 microns.
17. The blend of Claims 1 or 2 wherein the number average particle size of the non-meltable polymer stabilizer component (d) in the blend is less than 2 microns.

18. The blend of Claim 2 wherein the co-stabilizer compound is substantially free of basic materials and the polyoxymethylene polymer is a homopolymer.

19. The blend of Claim 2 wherein the co-stabilizer compound is a non-meltable polyamide.

20. The blend of Claim 19 wherein the non-meltable polyamide is a 43/34/23 terpolymer of nylon 6, nylon 66, and nylon 610, respectively.

21. The blend of Claim 2 wherein the co-stabilizer compound is a meltable hydroxy containing polymer or oligomer.

22. The blend of Claim 2 wherein the co-stabilizer compound is microcrystalline cellulose.

23. The blend of Claim 22 wherein the microcrystalline cellulose has an average particle size of ten microns or less.

24. The blend of Claims 1 or 2 further comprising at least one of antioxidants, pigments, colorants, UV stabilizers, hindered amine light stabilizers, toughening agents, nucleating agents, lubricants, glass, talc, and fillers.

25. Shaped articles made from the blends of Claims 1 or 2.
# INTERNATIONAL SEARCH REPORT

## I. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both National Classification and IPC

<table>
<thead>
<tr>
<th>IPC (5)</th>
<th>U.S. CLASS (CL)</th>
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<tr>
<td>CO8L 61/02, 75/04</td>
<td>525/125, 155, 399</td>
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</tbody>
</table>

## II. FIELDS SEARCHED

<table>
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<tr>
<th>Classification System</th>
<th>Classification Symbols</th>
</tr>
</thead>
<tbody>
<tr>
<td>U.S.</td>
<td>525/125, 155, 399</td>
</tr>
</tbody>
</table>

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

## III. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of Document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to Claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y,P</td>
<td>US, A, 4,972,014 (HAYES) 20 NOVEMBER 1990 See entire document.</td>
<td>1,3-5,12-18, 24,25</td>
</tr>
<tr>
<td>Y</td>
<td>US, A, 4,814,397 (NOVAK) 21 MARCH 1989 See entire document.</td>
<td>1,3-5,13-18, 24,25</td>
</tr>
<tr>
<td>A</td>
<td>US, A, 4,080,356 (GERGEN) 21 MARCH 1978</td>
<td>1</td>
</tr>
<tr>
<td>A</td>
<td>US, A, 4,640,949 (WAGMAN) 03 FEBRUARY 1987</td>
<td>1</td>
</tr>
<tr>
<td>A</td>
<td>US, A, 4,179,479 (CARTER, JR) 18 DECEMBER 1979</td>
<td>1</td>
</tr>
</tbody>
</table>

* Special categories of cited documents:
  - "Y" document member of the same patent family
  - "A" document defining the general state of the art which is not considered to be of particular relevance
  - "E" earlier document but published on or after the international filing date
  - "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  - "O" document referring to an oral disclosure, use, exhibition or other means
  - "P" document published prior to the international filing date but later than the priority date claimed
  - "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  - "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
  - "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. Claim numbers _______ because they relate to subject matter 1/2 not required to be searched by this Authority, namely:

2. Claim numbers _______ because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out 1/2, specifically:

3. Claim numbers _______ because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This International Searching Authority found multiple inventions in this international application as follows:

I. Claims 1, 3-17, 24, 25 drawn to a polyoxymethylene blend; classified in Class 525 Subclass 125.

II. Claims 2-25 drawn to the blend of Group I with an additional co-stabilizer, classified in Class 525 Subclass 131.

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

   1, 3-10, 12, 16, 17, 24, 25

4. As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest:

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.
Claim 1 is directed to the following patentably distinct species of the claimed invention: amorphous thermoplastic polymers (component c)

1) styrene acrylonitrile copolymers, acrylonitrile-butadiene-styrene resins and acrylonitrile-ethylene-propylene-styrene resins
2) polycarbonates
3) polyamides
4) polyarylates
5) polyphenylene oxides and polyphenylene ethers
6) high impact styrene resins
7) acrylic polymers
8) imidized acrylic resins
9) styrene maleic anhydride copolymers
10) polysulfones
11) styrene acrylonitrile maleic anhydride resins
12) styrene acrylic copolymers

Claims 1, 12-15 are directed to the following patentably distinct species of the claimed invention: non-meltable stabilizers (component D)

1) polyacrylamide or polymethacrylamide
2) a copolymer of a hydroxypropylmethacrylate and a comonomer of acrylamide or methacrylamide
3) a copolymer of ethylene vinyl alcohol and a comonomer of acrylamide or methacrylamide

If the invention of Group II, claims 2-25 is elected the following patentably distinct species of the claimed invention are present: co-stabilizers

1) microcrystalline cellulose
2) meltable nylon based stabilizers
3) meltable hydroxy containing polymer or oligomer