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- (54) COMPOSITIONS A BASE DE RESINE POLYOXYMETHYLENIQUE AYANT DES PROPRIETES DE MOULAGE AMELIOREES
- (54) POLYOXYMETHYLENE RESIN COMPOSITIONS HAVING IMPROVED MOLDING CHARACTERISTICS

(57) Compositions comprising polyoxymethylene; polyalkylene/unsaturated carboxylic acid lower alkyl ester polymeric nucleating material; waxy material; and nucleant. Included are compositions comprising polyoxymethylene; ethylene/methyl acrylate copolymer; aliphatic amide wax; and branched or cross-linked acetal copolymer or terpolymer or tale. Shaped articles having advantageous properties may be molded therefrom.

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# POLYOXYMETHYLENE RESIN COMPOSITIONS HAVING IMPROVED MOLDING CHARACTERISTICS

## ABSTRACT OF THE DISCLOSURE

Compositions comprising polyoxymethylene; polyalkylene/unsaturated carboxylic acid lower alkyl ester polymeric nucleating material; waxy material; and nucleant. Included are compositions comprising polyoxymethylene; ethylene/methyl acrylate copolymer; aliphatic amide wax; and branched or cross-linked acetal copolymer or terpolymer or talc. Shaped articles having advantageous properties may be molded therefrom.

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## POLYOXYMETHYLENE RESIN COMPOSITIONS HAVING IMPROVED MOLDING CHARACTERISTICS

## Background of the Invention

The present invention relates to polyoxymethylene (also referred to herein as polyacetal) resin compositions having improved moldability and improved physical properties of the molded article.

Polyacetal resin is manufactured by polymerizing a mostly formaldehyde monomer or a formaldehyde trimer (trioxane). Acetal homopolymer is a homopolymer of formaldehyde (for example, Delrin® acetal resin, manufactured by E.I. du Pont de Nemours and Company). Acetal copolymer is obtained, for example, by copolymerizing alkylene oxide with for example, trioxane.

Polyoxymethylene resin, because of its high mechanical strength, excellent abrasion resistance, fatigue resistance, moldability, and the like, is extensively used, for example, in electrical and electronic applications, automotive applications, and precision machine applications.

Polyoxymethylene resins are the most crystalline of the engineering polymers and as a consequence, freeze quickly in a mold. However, these resins also exhibit high shrinkage, which often leads to dimensional imbalance problems for precise part molding. Recently, nucleated polyoxymethylene resins have been introduced to improve set-up time and reduce shrinkage. But, it is still desirable to provide a polyoxymethylene resin having reduced post mold shrinkage character, a lower thermal expansion coefficient, and improved gear preciseness if the application is a gear application.

## Summary of the Invention

Our invention includes a composition comprising polyoxymethylene; polyalkylene/unsaturated carboxylic acid lower alkyl ester polymeric nucleating material, in an amount between about 0.1 and about 20 weight percent of the composition; waxy material, in an amount between about 0.05 and 5 weight percent of the composition; and nucleant, in an amount between about 0.001 and about 6 weight percent of the composition. In one aspect, the polymeric nucleating material comprises ethylene/methyl acrylate copolymer, the waxy material comprises aliphatic amide wax, and the nucleant comprises branched or cross-linked acetal copolymer or terpolymer in an amount between about 0.1 and

about 5 weight percent of the composition. In another aspect, the nucleant comprises talc, silane coated talc or boron nitride, in an amount between about 0.001 and about 1 weight percent of the composition. The aliphatic amide wax may comprise ethylene bis stearamide.

Our invention also includes articles molded from our compositions. In one aspect, the molded article is a gear. In another aspect, the molded article is a printer gear.

## Detailed Description of the Preferred Embodiments

Preferred compositions in accordance with this invention comprise polyoxymethylene, polymeric nucleating material, waxy material, and nucleant. These compositions may also include other ingredients, modifiers, and additives.

Our compositions exhibit advantageous properties, such as reduced post mold shrinkage character, lower thermal expansion coefficients, and improved preciseness in molding applications.

## 15 Polyoxymethylene

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The polyoxymethylene component preferably comprises the balance of the composition after all other components and additives are accounted for. The polyoxymethylene component may also comprise preferably between about 70 and about 99 weight percent of the composition, more preferably between about 75 and about 99 weight percent of the composition, and even more preferably between about 90 and about 98 weight percent of the composition. These ranges, however, are not meant to be limiting in any way.

The polyoxymethylene preferably includes a wide variety of homopolymers and copolymers which are known in the art. These polymers are generally polymers of formaldehyde in which the polymer chain, exclusive of the terminal portions of the chain, is a series of methylene to oxygen linkages. The polymer chain can also include moieties of the general formula:

wherein m is an integer of 1 to 5 and  $R_1$  and  $R_2$  are inert substituents which will not cause undesirable reactions in the polymer. Such additional components of the polymer chain are present as a minor proportion of the repeating units.

More specifically, the polyoxymethylene resin component as used herein includes homopolymers of formaldehyde or a cyclic oligomer of formaldehyde, the terminal groups of which are end capped by esterification or etherification, and copolymers of formaldehyde or of a cyclic oligomer 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 resin used in this invention can be linear or substantially linear with only minor amounts of branching and will generally have a weight average molecular weight in the range of 5,000 to 200,000, preferably 30,000 to 85,000, more preferably 30,000 to 75,000. The molecular weight can conveniently be measured by gel permeation chromatography in m-cresol at 160°C or alternatively, hexafluoroisopropanol at room temperature. Although polyoxymethylene resins of higher or lower weight average molecular weights can be used, depending on the physical and processing properties desired, the polyoxymethylene resins with the above mentioned weight average molecular weight are preferred to provide optimum balance of good mixing of various ingredients to be melt blended into the composition with the desired combination of physical properties in the components made from such compositions.

As indicated above, the polyoxymethylene resin can be either homopolymer with different weight average molecular weights, copolymers of different weight average molecular weights or mixtures 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 preferably not be more than 20 weight percent, more preferably not more than 15 percent, and most preferably about 2 weight percent. The commonly used comonomers include ethylene oxide, dioxalane, and butylene oxide. Generally, polyoxymethylene homopolymer is preferred over copolymer, because homopolymer has greater tensile strength and stiffness as well as a lower thermal expansion coefficient than copolymer. 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.

## Polymeric Nucleating Material

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The polymeric nucleating material comprises preferably between about

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0.1 and about 20 weight percent of the composition, more preferably between about 0.2 and about 10 weight percent of the composition, and even more preferably between about 0.5 and about 5 weight percent of the composition. More than one of the below described compounds may comprise the polymeric nucleating material component of our compositions.

Preferred polymeric nucleating materials include polyalkylene/unsaturated carboxylic acid lower alkyl ester polymeric nucleating materials. Polyalkylene/unsaturated carboxylic acid lower alkyl ester polymeric nucleating materials in general are copolymers or terpolymers of a lower alkene ( $C_2$ - $C_4$ ) and a lower alkyl ester of an unsaturated acid. An example of polymeric nucleating materials useful in this invention are ethylene-based polymers of the formula E/X/Y, preferably E/X, where E is ethylene and X, Y is an unsaturated carboxylic acid ester.

The unsaturated carboxylic acid esters include alkyl (C<sub>1</sub> to C<sub>8</sub>, preferably C<sub>1</sub> to C<sub>4</sub>) esters of unsaturated carboxylic acids having 3 to 8 carbon atoms. Illustrative unsaturated acids include acrylic and methacrylic acids. Particular examples of esters are methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, among which ethyl acrylate and methyl methacrylate are preferred.

Ethylene methyl acrylate copolymer ("EMA") component is particularly preferred as the polymeric nucleating material and is, in general, a commercially available material and can be prepared by known means. The amount of methyl acrylate in the EMA is generally about 3-40 weight percent, preferably about 15-25 weight percent, of the EMA.

The polyalkylene/unsaturated carboxylic lower alkyl ester nucleating additive can also be an ethylene-based random polymer of the formula E/X/Y wherein E is ethylene, X is selected from methylmethacrylate, ethyl acrylate, and butyl acrylate, and Y is selected from glycidyl methacrylate and glycidyl acrylate, and glycidyl methacrylate is preferred for Y. E/X/Y consists essentially of about 5-99% E, about 0-35% X, and about 0.5-10% Y.

An example of the ethylene-based random polymer consists essentially of about 90%-99% by weight ethylene and about 1%-10% by weight glycidylmethacrylate. Preferably, this ethylene/glycidyl methacrylate ("EGMA") random polymer consists essentially of about 90%-97% by weight ethylene and

about 3%-10% by weight glycidyl methacrylate ("GMA").

Another preferred ethylene-based random polymer consists essentially of about 55%-98.5% by weight ethylene, about 0.5-35% by weight butyl acrylate ("BA"), and about 1%-10% by weight glycidyl methacrylate ("GMA"). Preferably, this ethylene/butyl acrylate/glycidyl methacrylate ("EBAGMA") random polymer consists essentially of about 55%-84% by weight ethylene, about 15%-35% by weight BA, and about 1%-10% by weight GMA. Most preferably, this EBAGMA random polymer consists essentially of about 57.5%-74% by weight ethylene, about 25%-35% by weight BA, and about 1%-7.5% GMA.

The ethylene-based random polymer component can be prepared by techniques readily available to those in the art. An example of the EBAGMA random polymer is provided in U.S. Pat. No. 4,753,980.

### Waxy Material

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The waxy material component comprises preferably between about 0.05 and about 5 weight percent of the composition, more preferably between about 0.1 and about 2 weight percent of the composition, and even more preferably between about 0.3 and about 1 weight percent of the composition. More than one of the below described compounds may comprise the waxy material component of our compositions.

The waxy material is preferably a material that is capable of being dispersed in the polyacetal resin and may be a liquid at normal room temperatures. Alternatively, if this material is a solid at normal room temperatures, it must become fluidized at a temperature lower than the temperature at which the polyacetal is being processed or molded.

A highly preferred waxy material is an aliphatic amide wax. Aliphatic amide wax is a chemical compound that is obtained preferably by the dehydration of aliphatic carboxylic acid and aliphatic amine, and it has at least one (preferably two) amide bond segment(s) in a molecule. The melting point of the above compounds is preferably greater than about 60 deg C, more preferably greater than about 80 deg C, and most preferably greater than about 100 deg C. A preferred aliphatic amide wax is ethylene bis stearamide wax, such as Kaowax EB-FF (available from Kao Corporation, Tokyo, Japan) or Acrawax C (available from Lonza, Fairlawn, NJ, U.S.A.). Other aliphatic amide waxes include without limitation stearamide; 12-hydroxystearamide; N, N'-Ethylene bis lauramide; N, N'-Ethylene behenamide; and N, N'-Distearyl adipic amide.

Other examples of useful wax materials are natural or synthetic waxes, for example hydrocarbon and polymeric waxes. Hydrocarbon waxes include mineral, petroleum, paraffin or microcrystalline waxes and synthetic waxes, such as, for example ethylenic polymers. The polymeric waxes include polyethylenes, polypropylenes and ethylene/propylene copolymers. Good blending is obtained if the components are mixed together in a twin-screw extruder, which is the preferred mixing device.

## Nucleant

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The nucleant component comprises any finely divided solid and preferably includes at least one of boron nitride, talc, silane coated talc, silica, polyimides, branched or cross-linked acetal copolymer or terpolymer, a melamine-formaldehyde resin, calcium carbonate, diatomite, dolomite, or other commonly known nucleants for polyoxymethylene. The nucleant component comprises preferably between about 0.001 and about 6 weight percent of the composition, and more preferably between about 0.01 and about 4 weight percent of the composition.

If present in the nucleant component, branched or cross-linked acetal copolymer or terpolymer comprises preferably between about 0.1 and about 5 weight percent of the composition, and more preferably between about 0.5 and about 2 weight percent of the composition. All other nucleants, if present in the nucleant component, each comprises preferably between about 0.001 and about 1 weight percent of the composition, more preferably between about 0.01 and about 0.5 weight percent of the composition, and even more preferably between about 0.02 and about 0.2 weight percent of the composition.

Branched or cross-linked polyoxymethylene copolymers, talc or silane coated talc and boron nitride are particularly preferred. Preferred branched or cross-linked polyoxymethylene copolymers include Duracon U-10 (available from Polyplastics K.K., Osaka, Japan) and Celcon CFX 0288 (available from Ticona, Summit, NJ, U.S.A.). Preferred talc sources include Mistron CB talc (available from Luzenac America, Engelwood, CO, U.S.A.) and Ultratalc 609 (available from Barretts Minerals, Inc., Dillon, MT, U.S.A.).

In a preferred embodiment, the nucleant component comprises branched or cross-linked acetal copolymer or terpolymer in an amount preferably between about 0.1 and about 5 weight percent of the composition, and more preferably between about 0.5 and about 2 weight percent of the composition.

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In a another preferred embodiment, the nucleant component comprises talc, silane coated talc or boron nitride in an amount preferably between about 0.001 and about 1 weight percent of the composition, more preferably between about 0.01 and about 0.5 weight percent of the composition, and even more preferably between about 0.02 and about 0.2 weight percent of the composition.

Also, especially preferred is the use of branched or cross-linked polyoxymethylene copolymers, talc or silane coated talc, when the waxy material component is an aliphatic amide wax, such as ethylene bis stearamide. The nucleant can optionally be surface treated by standard processes.

The branched or cross-linked polyoxymethylenes useful as nucleants in the invention may be obtained:

- a. by copolymerization of trioxane with at least one compound reacting multifunctionally and being copolymerizable with trioxane and, optionally, with at least one compound monofunctionally reacting and copolymerizable with trioxane, or
- b. by branching or cross-linking reactions performed subsequently with a linear poly(oxymethylene) having lateral or chainlinked functional groups, or
- c. by copolymerization of trioxane with at least one compound reacting monofunctionally and being copolymerizable with trioxane and a branched or cross-linked polyether or by reaction of a linear poly(oxymethylene) with a branched or cross-linked polyether.

Small average particle size is preferred for the nucleant. The average particle size of the nucleant should be less than 20 microns, preferably less than 10 microns, and more preferably less than 5 microns.

- The nucleant may be an encapsulated nucleant. As used herein, "encapsulated nucleant" consists essentially of an encapsulant polymer and a nucleant, and includes within its meaning a "predispersed nucleant," that is, a nucleant that is predispersed in, rather than encapsulated by, the encapsulant polymer.
- The encapsulant polymer can be any moderate melting polymer, i.e., any polymer which melts at the processing temperatures of the polyoxymethylene resin of the encapsulated nucleant. Illustrative encapsulant polymers include linear low density polyethylene ("LLDPE"), high density polyethylene ("HDPE"), and polypropylene, each of which have a solid density of less than or equal to 1 gram per cubic centimeter, as measured by ASTM D1505. Preferably, the

encapsulant polymer is either LLDPE or HDPE. The encapsulant polymer either lacks long chain polymer branching in its molecular structure or it is predominantly linear. The lack of long chain branching is due to the method by which the encapsulant polymer is produced.

The encapsulant polymer is selected from a group of polymers well known in the art. The encapsulant polymers are commercially available or, alternatively, can be prepared by techniques readily available to those skilled in the art. Generally, the encapsulant polymers are prepared by polymerizing ethylene or ethylene and alpha-olefin comonomers in solution phase or gas phase reactors using coordination catalysts, particularly Zieglar or Phillips type catalysts.

It is preferred that the LLDPE encapsulant polymer have a melt index, as measured by ASTM D1238 method, condition E, in the range of 5 to 55 grams per 10 min. It is preferred that the HDPE encapsulant polymer have a melt index, as measured by ASTM D1238 method, condition E, of about 0.5-7 grams per 10 min. Compositions containing LLDPE or HDPE having melt indices outside the range given above may yield stock shapes with good porosity values, but can give rise to compounded resin and extruded stock shapes having other undesirable characteristics, such as decreased stability or separation of the polyoxymethylene and LLDPE or HDPE (i.e., de-lamination).

## Other optional components

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Compositions in accordance with our invention may optionally include, in addition to the components described above, other ingredients, modifiers, and additives, including without limitation lubricants, thermal stabilizers and costabilizers, antioxidants, colorants (including pigments), toughening agents (such as thermoplastic polyurethanes), reinforcing agents, ultraviolet stabilizers (such as benzotriazoles or benzophenones), including hindered amine light stabilizers (especially those wherein the hindered nitrogen is of tertiary amine functionality or wherein the hindered amine light stabilizer contains both a piperidine, or piperazinone ring, and a triazine ring), polytetrafluoroethylene powder or fiber, glass, and fillers. Suitable thermal stabilizers include polyamides (including a nylon terpolymer of nylon 66, nylon 6/10, and nylon 6 and the polyamide stabilizer of U.S. Pat. No. 3,960,984); meltable hydroxy-containing polymers and copolymers, including ethylene vinyl alcohol copolymer and the stabilizers described in U.S. Pat. No. 4,814,397 and U.S. Pat. No. 4,766,168; non-meltable hydroxy-containing or nitrogen-containing polymers as described in U.S. Pat. No. 5,011,890 and in particular, polyacrylamide; and microcrystalline cellulose;

polybeta-alanine (as described in German published application 3715117); polyacrylamide; or stabilizers disclosed in U.S. Pat. Nos. 4,814,397, 4,766,168, 4,640,949, and 4,098,984; and mixtures of any of the above. Typical antioxidants include hindered phenols such as triethyleneglycolbis(3-(3'-tertbutyl-4'hydroxy-5'methylphenyl)proprionate, N,N'-hexamethylenebis(3,5-di-tert-butyl-4-hydroxy-hydrocinnamide), and mixtures thereof as well as antioxidants, including those described in U.S. Pat. No. 4,972,014.

Additives or ingredients that can have an adverse effect on the oxidative or thermal stability of polyoxymethylene should be avoided.

The compositions described herein may be prepared by mixing all 10 components with the acetal polymer at a temperature above the melting point of the acetal polymer by methods known in the art. It is known to use intensive mixing devices, 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 15 Continuous Mixers", injection molding machines, and extruders, both single screw and twin screw, both co-rotating and counter rotating, in preparing thermoplastic polyacetal compositions. These devices may 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, gates, or screw designed for this purpose. Extruders are preferred, with twin screw extruders being most preferred. Of course, such mixing should be conducted at a temperature below which significant degradation of the polyacetal component will occur. Generally, polyacetal compositions are melt processed at between 170 °C and 290 °C, preferably between 185 °C and 240 °C and most preferably 195 °C and 225 °C.

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Shaped articles may be made from the compositions of the present invention using methods known in the art, including compression molding, injection molding, extrusion, blow molding, rotational molding, melt spinning, and thermoforming. Injection molding is preferred.

Examples of shaped articles include gears, sheet, profiles, rod stock, film, filaments, fibers, strapping, tape, tubing, conveyor links or chains and pipe. In particular, gears can be molded with high preciseness and low post mold reduced shrinkage. To make a relatively precise gear, it is desirable to control dimensional changes (e.g. shrinkage, post mold shrinkage, and thermal expansion) caused by environmental changes. With our resin composition, it is

possible to mold a gear having reduced thermal expansion as well as high preciseness and low post mold reduced shrinkage. Particularly preferred are printer gears molded from our compositions. Also, conveyor links or chains can be formed by injection molding. 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.

## Examples

The following examples illustrate embodiments of our invention. Our invention, however, is not limited to these examples.

The following abbreviations used in the examples are explained as follows:

POM: polyoxymethylene

EMA: ethylene/methyl acrylate copolymer

EBSA: ethylene bis stearamide

## 15 Example 1

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Sample Nos. 1-7 are embodiments of our invention. The compositions of Sample Nos. 1-3 are displayed below in Table 1A, and the compositions of Sample Nos. 4-7 are displayed below in Table 1B.

In Samples 1 and 3, the POM is a capped POM with a flow grade of 900, whereas in Sample 2, the POM is a capped POM with a flow grade of 1700.

In Sample 6, the branched POM copolymer is Duracon U-10, whereas in Sample 7, the branched POM copolymer is Celcon CFX 0288.

TABLE 1A

Sample No.	1	2	3
POM	95.475	96.45	96.45
EMA	2.000	2.00	2.00
EBSA	0.800	0.80	0.80
Branched POM Copolymer	1.000		-
Talc	**	0.15	0.15
Polyacrylamide (thermal stabilizer)	0.625	0.50	0.50
Irganox 245 (antioxidant)	0.100	0.10	0.10
TOTAL	100.00	100.00	100.00

TABLE 1B

Sample No.	4	5	6	7
POM	96.375	96.375	95.475	95.475
EMA	2	2	2	23.473
EBSA	0.8	0.8	0.8	0.8
Branched POM Copolymer		-	1.0	1.0
Fine Talc	0.1		**	
Silane Coated Talc		0.1	-	
Polyacrylamide (thermal stabilizer)	0.625	0.625	0.625	0.625
Irganox 245 (antioxidant)	0.1	0.1	0.1	0.1
TOTAL	100.00	100.00	100.00	100.00

### Example 2

Sample Nos. 1-3 were evaluated for shrinkage, post mold shrinkage, roundness, gate seal time, and crystallization half time.

All dimensional measurements were conducted on a molded pulley having a 100 mm outer diameter, a 10 mm inner diameter, and a 10 mm height.

Shrinkage and post mold shrinkage for evaluated resins were measured by the calculation of the following formulae.

$$S = \frac{\left(D_m - D_p\right)}{D_m} \times 100 \quad \text{(I)}$$

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where S is Shrinkage, Dm is Dimension of Mold tool, and Dp is Dimension of Parts; and

$$PMS = S_{initial} - S_{annealed}$$
 (II)

where PMS is Post Mold Shrinkage, S  $_{initial}$  is Shrinkage as mold, and S  $_{annealed}$  is Shrinkage after annealed for 4 hours in 70 deg C air oven.

With respect to roundness, we measured roundness of the pulley using a roundness tester. We employed a Mitutoyo Roundtest RA-2A (available from Mitutoyo Corporation, Kanagawa, Japan).

Regarding gate sealing time, we defined gate sealing time as the time the weight of the pulley remained unchanged as the hold pressure time increased gradually.

We measured crystallization half time using isothermal DSC. The test conditions were as follows.

Starting temperature: 200 deg C

End temperature: 150 deg C

5 Cooling rate: 200 deg C / min.

The results are displayed below in Table 2.

TABLE 2

Property	Sample No. 1 Sample No. 2		Sample No. 3	
Shrinkage (%)	2.13	1.90	1.97	
Post mold shrinkage (%)	0.062	0.065	0.075	
Roundness (µm)	29	21		
Gate seal time (secs)	12	15	16	
Crystallization half time (min.)	0.31	0.39	0.39	

### Example 3

Sample Nos. 1-3 were evaluated for warpage. Warpage evaluations were conducted using a three dimensional coordinate measurement machine on a round molded article having a 100 mm diameter and 1.6 mm thickness. We used a Mitutoyo Coordinate Measuring Machine LJ704 (available from Mitutoyo Corporation). Before measurement, the molded article remained in the temperature/humidity-controlled room for three days after being molded.

Warpage value should be as low as possible for precise part application. The results are set forth in Table 3 below.

TABLE 3

Sample No.	1	2	3
Warpage (mm)	0.135	0.072	0.055

#### 20 Example 4

Sample Nos. 1-3 were evaluated for tensile strength, elongation, flexural modulus, and N Izod impact. Each test was conducted in accordance with ASTM methods widely used for the evaluation of engineering plastics.

The results are set forth in Table 4 below.

TABLE 4

Property	Sample No. 1	Sample No. 2	Sample No. 3
Tensile strength (MPa)	63.5	64.2	66.4
Elongation (%)	50.3	20.4	32.3
Flexural modulus (MPa)	3077	3106	3200
N Izod impact (J/m)	62.1	48	61.1

## Example 5

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Sample Nos. 4-7 were evaluated for post mold shrinkage, roundness, and gate seal time in accordance with the same procedures employed in Example 2.

The results are set forth in Table 5 below.

TABLE 5

Property	Sample No. 4	Sample No. 5	Sample No. 6	Sample No. 7
Post mold shrinkage (%)	0.06	0.04	0.04	0.05
Roundness (µm)	30	32	34	30
Gate seal time (secs)	11	11	11	11

While this invention has been described with respect to what is at

present considered to be the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments. To the contrary, the invention is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims. The scope of the following claims is to be accorded the broadest interpretation so as to encompass all such modifications and equivalent formulations and functions.

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#### WHAT IS CLAIMED IS:

1. A composition comprising:

polyoxymethylene;

polyalkylene/unsaturated carboxylic acid lower alkyl ester polymeric nucleating material, in an amount between about 0.1 and about 20 weight percent of said composition;

waxy material, in an amount between about 0.05 and about 5 weight percent of said composition; and

nucleant, in an amount between about 0.001 and about 6 weight percent of said composition.

- 2. The composition of Claim 1, wherein said polymeric nucleating material comprises ethylene/methyl acrylate copolymer and said waxy material comprises aliphatic amide wax.
- 3. The composition of Claim 2, wherein said nucleant comprises branched or cross-linked acetal copolymer or terpolymer in an amount between about 0.1 and about 5 weight percent of the composition.
  - 4. The composition of Claim 3, wherein said aliphatic amide wax comprises ethylene bis stearamide.
- 5. The composition of Claim 2, wherein said nucleant comprises talc, silane coated talc or boron nitride, in an amount between about 0.001 and about 1 weight percent of the composition.
  - 6. The composition of Claim 5, wherein said aliphatic amide wax comprises ethylene bis stearamide.
- 7. The composition of Claim 1, wherein said polyoxymethylene comprises between about 70 and about 99 weight percent of the composition.
  - 8. The composition of Claim 1, wherein said polyoxymethylene is a homopolymer of formaldehyde or a cyclic oligomer of formaldehyde, the terminal groups of which are end capped by esterification or etherification, or a copolymer of formaldehyde or of a cyclic oligomer of formaldehyde and other monomers that yield oxyalkylene groups with at least two adjacent carbon atoms in the main

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chain, the terminal groups of which copolymers can be hydroxyl terminated or can be end capped by esterification or etherification.

- 9. The composition of Claim 1, further comprising polytetrafluoroethylene powder or fiber.
- 10. A molded gear produced from the composition of Claim 1.
  - 11. A molded printer gear produced from the composition of Claim 1.