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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Oxymethylene Polymer Compositions

We, CELANESE CORPORATION OF AMERICA, of 522 Fifth Avenue, New York 36, State of New York, United States of America, a company incorporated in accordance with the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to compositions of matter and, more particularly, compositions mouldable under heat and pressure and having a basis of an oxymethylene polymer.

In the moulding under heat and pressure of normally solid thermoplastics it is common to use an organic lubricant to reduce friction losses, and thereby increase the production rate, especially when using plunger type moulding devices such as some injection moulding devices. The lubricant is applied as a surface layer to large particles, e.g. pellets $\frac{1}{8}$ inch long and $\frac{1}{8}$ inch diameter, of the thermoplastics. The use of such lubricants in this way can be employed to increase the production rate when moulding normally solid oxymethylene polymers but the moulded articles then obtained commonly exhibit undesirable features, e.g. blistering and discoloration.

According to the present invention, an oxymethylene polymer moulding composition comprises a normally solid oxymethylene polymer in the form of particles smaller than 20 mesh size United States Sieve Standard and having uniformly dispersed therein from 0.001 to 0.25 per cent of its weight of a solid organic lubricant. With such compositions it has been found possible to obtain satisfactory moulded products free from undesirable features such as blistering and discoloration. To this end, however, it is essential that the amount of organic lubricant should not exceed 0.25 per cent of the polymer weight and that it should be uniformly dispersed throughout

[Price 4s. 6d.]

the finely divided polymer the particle size of which is preferably less than 30 mesh; particles only slightly larger, e.g. 8 to 11 mesh, lead to such imperfections as surface blistering during moulding. The initially blended mixture can be improved as regards uniformity of distribution of the lubricant by mixing under conditions of high shear. For instance, a better product is obtained by passing the mixture through a commercial extruder than is obtained using a small screw type injection moulding apparatus; the mixture leaving the extruder may be passed through an orifice of suitable size to form threads which can be cut or broken into conventional moulding pellets.

The invention may be applied in general to normally solid thermoplastic oxymethylene polymers including homopolymers such as may be obtained by polymerising formaldehyde or trioxane and polymers the molecules of which consist of chains of oxymethylene groups with other groups having adjacent carbon atoms forming links in the chains distributed along them. The latter type of polymer may be such as can be obtained by copolymerising trioxane with one or more comonomers; e.g. ethylene oxide.

The polymers may be used as particles of 20 to 250 mesh, or smaller. The particle form may be of any desired configuration including, for example, spherical or oval, or of indeterminate shape. As already stated, the particle size employed in the incorporation process has been found to be a critical factor in effecting the improved results achieved with the aid of the invention and generally the particle size is lower than 30 mesh, e.g. 35 to 40 mesh, and preferably a major proportion of the polymer charge falls in a range of 35 to 55 mesh. The polymer charge is generally substantially anhydrous but small amounts of moisture, such as may be adsorbed on the polymer surface, do not impair the results.

Colouring agents, fillers, including glass, carbon black, titanium dioxide, finely divided

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copper or other additives may also be incorporated with the polymer.

Chemical stabilisers which it is desired to use may be incorporated in the polymer simultaneously with the lubricant and may be any of the well known stabilisers for oxymethylene polymers.

Suitable organic lubricants include the water-insoluble soaps of high melting point and the preferred substances are water-insoluble metal salts of aliphatic carboxylic acids having at least twelve carbon atoms melting at a temperature above 110°C., long-chain aliphatic amides and especially those containing more than ten carbon atoms, fatty acids and waxes. For example, there may be used zinc stearate, aluminium palmitate, magnesium stearate, lithium stearate, calcium stearate, stearic acid, ceresin, stearamide, oleamide, palmitamide, lauramide, ethylene bis-stearamide, erucamide, linolamide, linolenamide, N-palmityl oleamide, N-stearyl oleamide or vinyl acetic acid amide or mixtures of any of these substances.

The preferred lubricants as a class are the amide waxes, and especially aliphatic amides wherein the aliphatic moiety is derived from long-chain saturated or unsaturated (non-benzenoid) hydrocarbons and their substituted derivatives having an open chain or cyclic structure which may include a minor proportion of heteratoms selected from the group consisting of oxygen, sulphur and nitrogen in the skeletal structure. The preferred aliphatic moieties have an open chain (linear or branched) carbon skeleton of up to 33 carbon atoms.

Examples of such amide lubricants include, in addition to those set forth above, propionamide, butyramide, valeramide, capramide, margaramide, carnaubamide, cerotamide, melissamide, linolinamide, sorbamide, methylacrylamide, cyclohexanoamide, N-bromo stearamide, N-methyl lauramide, N-ethoxyoleamide, N-phenyl palmitamide, N-propionamidostearamide, N-butyramidolauramide and N-stearamidopalmitamide.

Additional amide waxes may be found exemplified in the industrial literature, e.g. the Handbook of Chemistry and Physics (Chem. Rubber Pub. Co., Cleveland, 1956-57), in the Table at pages 1404 to 1407.

Preferably the lubricants are dicarboxylic acid amides of aliphatic diamines, having the structure $R_x(NH.CO.R_y)_n$ wherein R_x is an aliphatic moiety derived from a higher fatty carboxylic acid having from 10 to 33 carbon atoms, R_y is the same or another such aliphatic moiety and n is 1 or 2. It is to be understood that the aliphatic moieties may contain additional amide groups of the structure $-NH.CO.R_y$. Suitable such di-fatty acid amides of aliphatic diamines include, for example, ethylene distearamide, propylene distearamide, butylene distearamide, propylidene dioleamide, N-

(ethylideneoleamide) stearamide, methylene-bis-lauramide, N-(ethylene-stearamide) lauramide and N-(methylene palmitamide) capramide.

The lubricants may be provided in any particle form; e.g. as beads, powders or atomised, ranging from 50 to 100 mesh down to as little as 5 microns. While the lubricant may be supplied as a dispersion in a suitable vehicle such as water, the charge is preferably dry powder of small particle diameter.

Preferably the amount of lubricant used is from 0.03 to 0.23 per cent of the polymer weight. From 0.15 up to just below 0.23 per cent is usually employed with the preferred amide waxes, while amounts of from 0.05 up to just below 0.12 per cent are generally utilised with the water-insoluble metal salts of carboxylic acids.

The initial polymer-lubricant admixture may be prepared, for example, by dry blending, roll milling, or drum tumbling, or the substances may be fed for mixing and in apparatus in which they are subjected to high shear. Such apparatus is preferably a commercial extruder, but may also be a Banbury mixer having oppositely rotating blades.

Any commercial extrusion device, ranging from, for example, a $\frac{1}{2}$ inch to a 10 inch size, may be satisfactorily employed. Single or multiple screw devices may be used, having various feed throats, e.g. vertical, slope (such as 45°), or undercut, and any screw construction of full-flighted or torpedo type, e.g. constant pitch with varying channel depth, metering with rapid transition, varying pitch with constant channel depth, constant pitch smooth torpedo or varying pitch full-flighted torpedo. Length to diameter ratios may range from, for instance, 10:1 to 24:1, although the range of 13:1 to 20:1 is generally employed. The screw clearance may range from, for instance, 1 mil to 25 mils and is preferably from 5 to 10 mils. The screw may be driven at rates of, for instance, between 1 and 150 revolutions per minute but is generally driven at 10 to 100 revolutions per minute and preferably between 20 and 75 revolutions per minute. Melt and die temperatures may be between 330° and 550°F. Any suitable orifice, generally having a cross-sectional area of approximately 2 per cent of that of the barrel, may be employed in pelletizing.

A typical extrusion operation employs a $2\frac{1}{2}$ inch extruder with a compression ratio of 3.5/1, four metering flights, a die temperature of 365°F., a stock temperature of 380°F., a barrel temperature of 350°F.-rear, 365°F.-middle and 360°F.-front, and a screw revolutions per minute of 30. Residence times are usually between 0.5 and 10 minutes and are preferably between 2 and 5 minutes.

The extruded and, if desired, pelletized lubricated polymer may be moulded as, for example, by heating the polymer to a substantially plastic state and advancing the

polymer into contact with a shaping surface, to produce particles of excellent surface characteristics and homogeneity, e.g. bearings, wheels, gears, cams, piping, pumps and valves. The lubricated compositions are particularly useful in injection moulding.

Generally any commercial injection moulding device may be employed, ranging in capacity from $\frac{1}{4}$ ounce to 200 ounces, and of a variety of constructions. Pressures may be between 5,000 and 30,000 pounds per square inch, preferably between 15,000 and 20,000 pounds per square inch. Mould temperatures are commonly in the range of 150°F. to 260°F. and are preferably between 180°F. and 220°F. Material temperatures may be between 370°F. and 480°F. for the preferred lubricated compositions, but generally lower temperatures are avoided to prevent surface blistering. For example, melt temperature of between 370°F. and 420°F. are successfully employed with amounts of ethylene distearamide of between 0.16 and 0.18 weight per cent, whereas melt temperatures are generally held above 400°F. for higher concentrations. Total cycle times of 30 to 75 seconds may be employed, but are varied with the size of the moulded part. A typical cycle calls for 25 seconds injection, 15 seconds die close and a 5 second delay, with optionally a 10 second booster during the injection period.

A typical injection moulding operation, e.g. for a sprayer gun body, employs a 12 to 16 ounce device with a 2 cavity mould, a shot weight of 110 grams, injection cylinder temperatures of 400°F.-rear, 350°F.-centre and 350°F.-front, a plunger temperature of 380°F., a mould temperature of 150°F., a clamp pressure of 150 tons, an injection pressure of 20,000 pounds per square inch and a total cycle time of 45 seconds.

The products obtained are of excellent homogeneity and surface appearance and exhibit enhanced lubricity, as measured by the spiral flow test described below, without degradation of other desirable physical properties. The surface commonly exhibits a smoothness of less than 25 microns average height, high gloss and a freedom from surface anomalies such as blisters, as indicated by the blistering test described below, and is free of exudation and of excellent colour. The desirable physical characteristics of the polymers, for instance thermal stability, mouldability and resistance to chemical degradation, are retained.

The lubricity of the polymer compositions may be measured by feeding pelletized lubricated polymer to a 3 ounce Fellows injection moulding machine, and providing a $\frac{1}{4}$ inch cushion by using a constant weight on the cylinder, and moulding at a pressure of 20,000 pounds per square inch and a mould temperature of 200°F. with a cycle time of 45 seconds (25 seconds-injection, 15 seconds-die close, 5

seconds-delay) into a centre-gated spiral mould having a 3 inch radius from the vortex, a semi-circular configuration of $\frac{1}{4}$ inch width and $\frac{1}{4}$ inch radius, and a total length of 35 inches. Constant volume of polymer is maintained by feeding pellets for each succeeding cycle equal to the weight of the preceding moulded spiral. Values are taken at three different melt temperatures, e.g. 360°, 390° and 430°F., and measured in inches of polymer flow in the spiral mould.

The moulded spiral may be directly measured for length, or the spiral mould may be engraved with length measurements which are moulded into the spiral, although values taken on two such moulds will not be directly comparable owing to the increased resistance to flow provided in the engraved mould by the legends.

The preferred copolymers generally exhibit a spiral flow at 360°F. of between 11 and 26 inches, and at 430°F. of between 16 and 38 inches, whereas the preferred acetal terpolymers exhibit spiral flows of 3 to 4 at 360°F. and 6 to 7 at 430°F. Generally, the lubricated compositions exhibit an increased spiral flow of at least 0.5 inch, usually at least 1 inch, at the test temperatures employed. The composition may exhibit an increased spiral flow of up to 2 inches.

A measure of blistering is obtained by directly examining a sample of moulded polymer, e.g. a tensile bar, or immersing the sample in water at room temperature, and observing altered light refraction caused by surface blisters.

The lubricated compositions are measured for colour properties in an Mx moulding discoloration test:—

13 grams of the pelletized copolymer were charged to the bore of an Extrusion Plastometer (described in ASTM D-1238-57T) confined in the barrel for 30 minutes at 230°C., discharged and compression moulded, at 190°C. for one minute without application of pressure, and 4 minutes at 6500 pounds per square inch, into an 11 gram disc having a 2 $\frac{1}{2}$ inch diameter. The compression moulded disc is colour measured with the Hunterlab D-25 Color Meter. The Hunterlab Color Meter test yields a read-out on three scales, L, *a* and *b*. The L scale is a measure of lightness and varies from 100 for perfect white to zero for black. *a* measures redness when plus, gray when zero, greenness when minus, and *b* measures yellowness when plus, gray when zero, blueness when minus. Thus, visually tan to brown discoloration observed after the foregoing test is characterised by increased positive *a* values, increased high positive *b* values and decreased L values.

The polymers were stabilised with 0.40 to 0.65 weight per cent of 2,2'-bis (4-methyl-6-t-butyl phenol) and 0.08 to 0.14 weight per cent of cyanoguanidine, except as otherwise

indicated.

In the following Examples which illustrate the invention the sieve mesh sizes used were United States Standard:—

5 EXAMPLE 1

A copolymer of trioxane with 2 weight per cent of ethylene oxide, having a melt index of 9.0 dg/minute, as a powder of which 70 per cent was in the range of 40 to 50 mesh, was tumbled with 0.18 and 0.25 weight per cent of powdered ethylene distearamide in a drum for 30 minutes at 9 revolutions per minute. The dry dispersed mixture was then extruded in a 2 inch extruder, operated with a screw speed of 90 revolutions per minute, power of 190 watts, 2700 pounds pressure, a

die temperature of 380°F., barrel temperatures of 385 to 390°F., 400°F., 390°F. and 380°F. in rear to forward zones, and a production rate of 40 pounds/hour. Samples of each composition were fed to a 3 ounce Fellows injection moulding machine and moulded at a pressure of 20,000 pounds per square inch ($\frac{1}{4}$ inch cushion with cylinder), a mould temperature of 200°F. and a cycle time of 45 seconds (25 seconds-injection, 15 seconds-die close, 5 seconds-delay) into a centre-gated spiral mould having a 3 inch radius from the gate, a semi-circular configuration of $\frac{1}{4}$ inch width and $\frac{1}{4}$ inch radius and a total length of 35 inches. The spiral flow test gave the following results:—

Lubricant weight %	Melt Temperature		
	400°F.	430°F.	460°F.
0.18	22.7	28.1	34.1
0.25	23.7	29.7	34.6

Samples moulded at melt temperatures of 415°F., 440°F. and 460°F. were visually examined at room temperature for blistering. The only samples exhibiting surface blisters were those obtained at a 0.25 per cent ethylene distearamide concentration and a melt temperature upon moulding of 415°F. Samples containing a lower concentration of lubricant

or obtained with higher melt temperatures exhibited no blisters. Other surface conditions, e.g. gloss and colour, were comparable.

Identical results were obtained with levels of ethylene distearamide of 0.16 and 0.20 weight per cent. Mx colour values taken on samples of the lubricated compositions compared as follows:—

Lubricant weight %	Colour Values		
	L	a	b
0.16	81.6	—1.3	19.8
0.18	81.0	—1.1	20.9
0.20	82.2	—1.7	20.7
0.25	85.2	—2.4	13.9

EXAMPLE 2

0.04 weight per cent of powdered ethylene distearamide, 95 per cent passing through a 100 mesh screen, was tumbled with trioxane—2.0 weight per cent ethylene oxide copolymer flake of which 70 per cent passed through 40 to 50 mesh screens in a drum rotating at 20 revolutions per minute for 30 minutes. The resulting dry, dispersed composition was fed to a $2\frac{1}{2}$ inch extruder with a length:diameter ratio of 24:1 for extrusion and pelletizing, using a die temperature of 370°F., barrel temperatures of 350°F., 370°F., 370°F. and 370°F. from rear to forward zones, a compression ratio of 2/1, a screw speed of 30 revolutions per minute and a

production rate of 90 pounds per hour. Moulded articles made from the pellets were of excellent surface appearance and exhibited no blisters. Identical results were obtained when a lubricant level of 0.10 weight per cent was employed.

Lubricated compositions prepared by dispersing a lubricant at the same concentration level with the copolymer in the form of pellets, nominally $\frac{1}{8}$ inch x $\frac{1}{8}$ inch cylinders, yielded moulded articles exhibiting surface blisters with ethylene distearamide and discoloration with zinc stearate.

EXAMPLE 3

A series of compositions of a trioxane—2.0

- weight per cent ethylene oxide copolymer of melt 2.5 dg/minute in flake form (40 to 50 mesh) and powdered ethylene distearamide were prepared in accordance with the process described in Example 1, at levels of 0.14, 0.16, 0.18 and 0.20 weight per cent lubricant based on the polymer. No blisters or exudation showed on products moulded from the compositions which exhibited excellent surface characteristics.
- 5 Spiral flow measurements, taken as described in Examples 1, were as follows:—

Lubricant weight %	Melt Temperature, °F.	Spiral Flow, Inches
0.16	370	13.6
	400	16.0
0.18	370	14.1
	400	16.5
0.20	370	13.7*
	400	16.9*

* Low value attributed to exposure of moulding machine to air drafts.

The sample containing 0.14 weight per cent of ethylene distearamide exhibited the following representative physical properties:—

Melt Index dg/minute	2.3
10 x/x ratio	18.3
K _D 230°C. (weight per cent/minute)	0.023
Cyanoguanidine (weight per cent)	0.10
2,2'-methylene bis (4-methyl-6-t-butyl phenol) (weight per cent)	0.47
Vicat softening point, (°C.)	161.4
Notched Izod Impact strength (foot pounds/inch of notch)	1.0
Rockwell hardness (M)	76.0
5½ hour weight loss (per cent)	13.65
Tensile impact strength (foot pounds/square inch)	88
Unnotched Izod (foot pounds/inch)	25.66

The compositions exhibited Mx discoloration values, taken as described above, as follows:—

Lubricant weight %	Colour Values		
	L	a	b
0.14	83.9	—1.8	17.9
0.16	81.4	—0.9	19.8
0.18	79.8	—0.1	21.3
0.20	79.1	—0.3	22.1

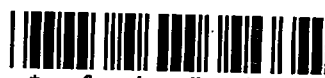
- 20 Nominal colour values for an unlubricated sample of the copolymer described above are L=78.0 minimum, a=0.0 maximum and b=24.0 maximum.

WHAT WE CLAIM IS:—
1. A moulding composition comprising a normally solid oxymethylene polymer in the form of particles smaller than 20 mesh size

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0.16	370	13.6
	400	16.0
0.18	370	14.1
	400	16.5
0.20	370	13.7*
	400	16.9*

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Vicat softening point, (°C.)	161.4
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- 20 Nominal colour values for an unlubricated sample of the copolymer described above are L=78.0 minimum, a=0.0 maximum and b=24.0 maximum.

WHAT WE CLAIM IS:—

1. A moulding composition comprising a normally solid oxymethylene polymer in the form of particles smaller than 20 mesh size



United States Sieve Standard and having uniformly dispersed therein from 0.001 to 0.25 per cent of its weight of a solid organic lubricant.

- 5 2. A moulding composition according to Claim 1, wherein the major parts of the polymer particles are of 35 to 55 mesh.

- 10 3. A moulding composition according to Claim 1 or 2, wherein the lubricant is an amide wax.

4. A moulding composition according to Claim 3, wherein the lubricant is ethylene distearamide.

- 15 5. A moulding composition, substantially as hereinbefore described.

- 20 6. Process for the production of a moulding composition, comprising intimately and uniformly mixing a normally solid oxymethylene polymer in the form of particles of less than 20 mesh size with from 0.001 to 0.25 per cent of its weight of a solid organic lubricant and

then subjecting the mixture to blending at a high shear rate.

7. Process according to Claim 6, wherein the blending is carried out in a commercial extruder. 25

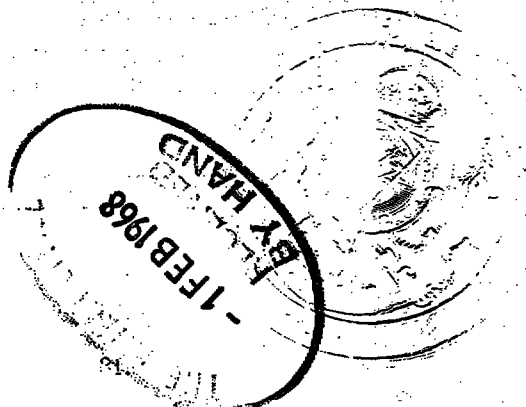
8. Process according to Claim 7, wherein the mixture is forced from the extruder through an orifice and the extrudate formed into pellets. 30

9. Process for the production of a moulding composition, substantially as described in any of the Examples.

10. Moulding compositions whenever produced by any of the processes claimed in Claims 6 to 9. 35

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