



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: PCT/NL85/00047 (22) International Filing Date: 20 November 1985 (20.11.85) (31) Priority Application Number: 244387/1984 (32) Priority Date: 21 November 1984 (21.11.84) (33) Priority Country: JP (71) Applicant (for all designated States except US): STAMI-CARBON B.V. [NL/NL]; P.O. Box 53, NL-6160 AB Geleen (NL). (72) Inventor; and (75) Inventor/Applicant (for US only) : CHIBA, Kazumasa [JP/JP]; Nagoya Plant, Toray Industries, Inc., 9-1, Ohe-cho, Minato-ku, Nagoya (JP). (74) Agent: ROEFFEN, Wilhelmus, Johannes, Maria; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).</p>		<p>(81) Designated States: AT (European patent), BE (European patent), BR, CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), KR, NL (European patent), SE (European patent), SU, US.</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: POLYAMIDE RESIN COMPOSITION</p>		
<p>(57) Abstract</p> <p>Polytetramethylene adipamide resin compositions containing 100 parts by weight of the polyamide and 2 to 20 parts by weight of a silicon oil. Objects produced from the composition possess good surface appearance, excellent sliding properties and high heat resistance and rigidity.</p>		

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-1-

POLYAMIDE RESIN COMPOSITIONDETAILED DESCRIPTION OF THE INVENTION

(Scope of industrial application)

The subject invention relates to polytetramethylene adipamide resin compositions superior in sliding characteristics.

5 (Description of prior art)

Being fundamentally superior in friction and wear characteristics, polyamides are regarded as being suitable for manufacturing gears and bearings and other sliding parts. The wear depends on the pressures applied to the sliding surface, the sliding speeds, the atmospheric conditions, the temperature and so forth.

10 For practical applications resistance to increasingly severe conditions are demanded and polyamide materials have been modified for this. Hitherto polyamide compositions obtained by adding molybdenum disulfide, polyethylene, fluoric polymers and silicon oils to polyamides have generally been used for this purpose.

15 However it has been observed that in the case of the ordinary straight-chain polyamides e.g. polycaprolactam (nylon-6) or polyhexamethylene adipamide (nylon-6.6), the silicon oil is insufficiently accepted by the material and causes considerable bleed-out to the surface of moldings that are obtained from compositions of these polyamides with silicon oils. Because of this bleeding-out effect the moldings become inferior in surface appearance.

20 However for obtaining good sliding properties it is necessary to have the siliconoil present in appreciable amounts. Further the mechanical properties of the polyamide composition should remain high to be useful under severe conditions. One has tried to solve this problem in essentially two manners. In the first solution one uses mixtures of lubricants, in which silicon oil is present in low concentrations. For

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instance a mixture of 2 percent silicon oil and 18 percent by weight polytetra-fluoroethylene in 80 percent by weight polyamide is used in US Patent publication 4428589. Secondly one has tried to incorporate in the polyamide molding an inorganic highly porous material which functions as a carrier for the silicon oil. See for instance JP-A-57174345.

However these compositions have the disadvantage of being difficult to process, or need expensive materials or the physical properties of the polyamide composition have been negatively effected.

The object of the invention is therefore to produce a polyamide/silicon oil composition of superior sliding properties and mechanical strength with good surface appearance.

It has been found that polytetramethylene adipamide (nylon-4.6) shows a supprisingly high affinity for silicon oils, so that even at high concentrations of the silicon-oils no unacceptable level of bleeding is observed. Further the resin composition shows superior properties over present materials to make a highly practicable material for various kinds of gears and bearings. Especially the combination of high heat resistance and rigidity of nylon 4.6 and the vast improvement in sliding performance due to the presence of a relatively high concentration of silicon oil produces these synergistic effects.

Therefore the polyamide resin composition according to the subject invention is obtainable by blending 2 to 20 parts by weight of silicon oil with 100 parts by weight of a polyamide with tetramethylene adipamide as main component.

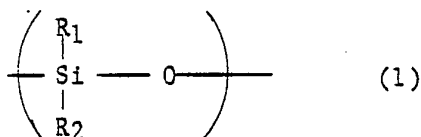
The polyamides according to the subject invention are copolymers and mixtures of polyamides containing polytetramethylene adipamide and tetramethylene adipamide as main components. In principle there exist no limitations concerning the copolymer and mixture components, so that all known amide-forming compounds can be chosen. Representative among the former are 6-aminocaproic, 11-aminoundecanic, 12-aminododecanic, paraminomethylbenzoic and other amino acids; ϵ -caprolactam, ω -lauro lactam and other lactams; hexamethylenediamine, undecamethylenediamine, dodecamethylenediamine, 2.2.4-/2,2,4-tri-

methylnonamethylenediamine, 5-methylnonamethylenediamine, methaxylire-
 nediamine, paraxylirerediamine 1,3- and 1,4-bis (aminomethyl)cyclo-
 hexanes, 1-amino-3-aminomethyl-3,5,5-trimethylcyclohexane,
 bis(4-aminocyclohexyl)methane, bis(3-methyl-4-aminocyclohexyl)methane,
 5 2,2-bis(4-aminocyclohexyl)propane, bis-(aminopropyl)piperazine, amino-
 ethylpiperazine and other diamines and adipic acids; and adipic,
 suberic, azelaic, dodecane-2, terephthalic, isophthalic,
 2-chlorotere-phthalic, 2-methylterephthlatic, 5-methylisophthalic,
 5-sodiumsulfoisophthalic, hexahydroterephthalic, hexahydroisophthalic,
 10 diglycolic and other dicarboxylic acids. The latter include the
 polyamides being composed thereof.

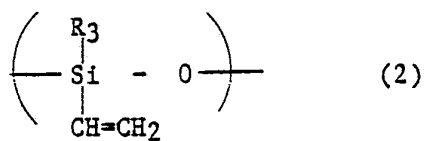
Polyamides containing tetramethylene as main component, for
 instance more than 80 mole percent, can be produced by any known pro-
 cess. However preference should be given to the processes disclosed in
 15 US patent publications 4,460,762, 4,408,036 and 4,463,166 or EP-A
 0039524, 0038094 and 0077106.

High molecular weight polyamides should be produced through solid-
 phase aftercondensation in a water-vapor containing atmosphere of pre-
 polymers having small contents of cyclic endgroups, that are produced
 20 under specific conditions or in 2-pyrrolidone, N-methylpyrrolidone or
 another polar organic solvent. Their degree of polymerization can vary
 in principle over a wide range. The polymers having a relative visco-
 sity between 2.0 and 6.0 g/dl, as measured in a solution of 1 gram in
 100 ml 98 % by weight sulphuric acid, are preferred.

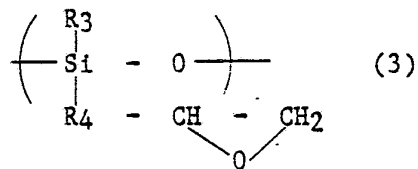
25 The silicon oils according to the subject invention are the
 polymers fundamentally having polysiloxane structures. Representative
 thereamong are for example the modified polysiloxanes containing poly-
 dimethylsiloxane and dimethylsiloxane, the materials with component
 units represented by the following formulae (1) to (7) and materials
 30 possessing endgroups represented by the following formulae (8) to
 (12).



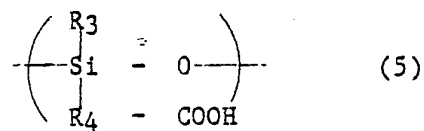
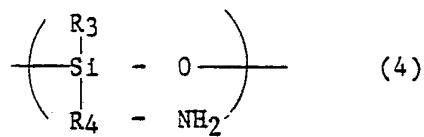
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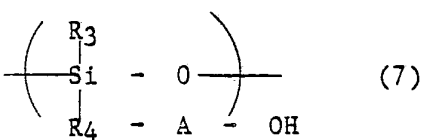
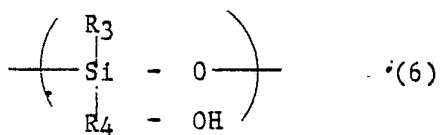
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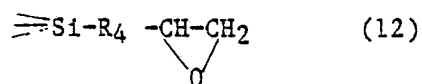
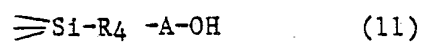
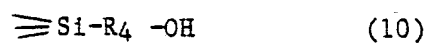
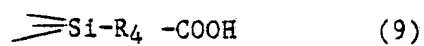
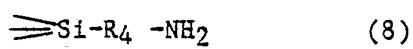
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Wherein R_1 and R_2 denote hydrogen atoms, the alkyl groups having one to four carbon atoms, cyclohexyl groups, phenyl groups and benzyl groups (R_1 and R_2 not being simultaneously hydrogen or a methyl group); R_3 an alkyl group having one to four carbon atoms; R_4 an alkylene group having one to six carbon atoms and A an polyalkylene having a polymerization degree of 1 to 50.

The viscosity fo the silicon oils according to the invention is not limitative and can be selected within the range of 100 to 50,000 centistokes at a temperature of 25 °C. However those having viscosities of 1,000 to 30,000 centistokes are preferably used for the convenience of the handling in blending and mixing with polyamides.

The resin compositions according to the subject invention are produced by adding 2 to 20, preferably 3 to 18, more preferably 5 to 15, parts by weight of silicon oils to 100 parts by weight of polytetramethylene adipamide. Addition ratios less or more than 2 or 20 parts, respectively by weight do not improve them in sliding characteristic or cause decomposition, foaming and other undesirable phenomena.

Other materials e.g. pigments, dyes, reinforcers, fillers, heat stabilizers, anti-oxidants, weather resistants, nucleating agents, mold release agents, plasticizers, flame retardants, antistatics and other polymers may be added to the resin compositions according to the subject invention unless their moldabilities and physical properties are affected. Particularly the addition of reinforcers and fillers is important. The fibrous and powdery reinforcers available therefor include more specifically glass fibers, asbestos fibers, carbon fibers, graphite fibers, wollastonite, talc, calcium carbonate, mica, clay, potassium titanate whisker and glass beads.

The processes for producing resin compositions according to the subject invention are not limited. One of the most common ones is the melting and mixing of both components supplied to a one- or multi-shaft extruder eventually after premixing in solid form. The resin compositions according to the invention can be used for the production

of moldings being superior in physical properties by injection molding, extrusion, blow-molding, compressive and the other molding methods being used for ordinary thermoplastic resins. They are useful for manufacturing various automotive parts, mechanical parts, electric and electronic parts, general miscellaneous goods and so forth.

(Embodiments)

The subject invention will be described in more detail in connection with the examples hereinafter. The following methods were used to evaluate the characteristics of the polymers and their moldings in the examples and comparative examples.

- (1) Relative viscosity: JIS K6810
- (2) Sliding characteristic: the friction coefficient of test pieces with steel (S-45C) and the limit PV product value at which they melt by frictional heat were measured by using a Suzuki type frictional and wear characteristic tester with surface pressure (Pkg/cm²) and running speed (Vm/min.) changed.
- (3) Tensile characteristic: ASTM D638
- (4). Bending characteristic: ASTM D790
- (5) Izod impact strength: ASTM D256
- (6) Thermal deformation temperature: ASTM D648

Example 1

A mixture prepared by mixing 10 parts by weight of polydimethylsiloxane (Toray Silicon K.K.'s SH 200 showing a viscosity of 12,500 cs at a temperature of 25 °C) to 100 parts by weight of nylon-46 powder having a relative viscosity of 3.90 was melted, kneaded and pelletized at a temperature of 305 °C using a 40 mm aperture molder. These pellets were vacuum-dried and used for the molding of various kinds of test pieces for measuring the different physical properties by using an injector molder with its cylinder and mold set at the temperatures of 300 °C and 80 °C respectively. Table 1 shows the results of the evaluation of the sliding characteristics and other physical properties.

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Causing only a little surface bleed-out of silicon oil, the moldign showed to be very superior in sliding characteristics, strength, rigidity and heat resistance. The molding stability of the materials and the physical properties and appearances of the test
5 pieces were measured as shown in the table.

Comparative Example 1:

Test pieces obtained through the injection molding of nylon 4,6 without silicon oil as was used for Example 1 showed the following unsatisfactory values of the sliding characteristics.

10 Wear coefficient: 0.65

Limit PV product value: 600 kg/cm².m/min.

Comparative Example 2:

Experiment 1 was repeated, however 30 parts of polydi-
methylsiloxane had been added. Considerable foam formation happened,
15 indicating a very low operational stability.

Comparative Example 3:

The test pieces obtained through the same extruder kneading and injection molding as being mentioned in connection with Experiment 1 except that nylon 4,6 is replaced with nylon 6,6 showed an inferior
20 appearance caused by considerable surface bleed-out of silicon oil.

Experiments 2 to 14:

Table 1 shows the physical properties of the test pieces obtained through the same operation as described in Experiment 1 with the different kinds and addition ratios of nylon 4,6 and silicon oil.
25 In all cases shown in the table 1, polyamide resin compositions superior in sliding characteristic, strength, ridigity and heat resistance were obtained.

Embodiment 15:

A mixture obtained by adding 12 parts by weight of the poly-
30 dimethylsiloxane from Example 1 and 45 parts by weight of a chopped

strand glass fiber (Nippon Denki Glass ECS03) to 100 parts by weight of nylon 4,6 pellets having a relative viscosity of 3.70 was melted, kneaded and pelletized at a temperature of 310 °C using a 65 mm aperture molder. The following were the physical properties obtained after vacuum-drying and injection-molding of these pellets.

5	Tensile strength:	1,830 kg/cm ²
	Bending strength:	2,750 kg/cm ²
	Bending:	96,000 kg/cm ²
	Izod impact strength:	9 kg.cm/cm-notch
10	Thermal deformation temperature:	285 °C
	Limit PV product:	3,500 kg/cm ² .m/min.

Table 1

Embodiment	1	2	3	4	5	6	7
Polyamide a) (Relative viscosity)	N-46 (3.90)	N-46 (3.60)	N-46 (3.90)	N-46 (3.80)	N-46 (3.90)	N-46 (3.50)	N-46 (3.80)
Silicone oil b) (Amount) (parts by wt.)	SH200 (10)	SH710 (12)	SH1107 (7)	SH410 (5)	SF8417 (10)	SF8418 (10)	SF8427 (10)
Friction coefficient	0.08	0.06	0.11	0.12	0.08	0.07	0.06
Limit PV (kg/cm ² .m/min.)	2,000	2,200	1,800	1,700	2,100	2,200	2,500
Tensile strength at yield (kg/cm ²)	920	900	950	900	940	980	920
Elongation at break (%)	16	20	22	20	18	25	20
Flexural strength (kg/cm ²)	1,010	1,000	1,050	1,010	1,020	1,100	1,100
Flexural modulus (kg/cm ²)	29,200	29,000	29,300	29,000	29,200	29,300	29,000
Izod impact strength (kg.cm/cm notch)	7	7	7	7	6	6	7
Heat distortion temperature (°C) (Load 18.6 kg/cm ²)	170	172	170	170	171	171	170

Surface appearance of molded articles Excellent Excellent Excellent Excellent Excellent Excellent Excellent Excellent

Table 1 (Continued)

Embodiment	8	9	10	11	12	13	14
Polyamide a)	N-46	N-46	N-46	N-46	N-46/6: 95/5	N-46/66: 90/10	N-46//N-66 90//10
(Relative viscosity)	(3.80)	(3.90)	(5.80)	(3.10)	(4.70)	(3.50)	(3.40)
Silicone oil b)	SF8428	SF8421	SH200	SH200	SH200	SH200	SH200
(Amount) (parts by wt.)	(10)	(11)	(12)	(5)	(10)	(8)	(10)
Friction coefficient	0.08	0.08	0.05	0.12	0.15	0.12	0.06
Limit PV (kg/cm ² .m/min.)	1,900	2,000	2,600	1,500	1,200	1,200	1,300
Tensile strength (kg/cm ²)	950	920	900	1,020	890	880	900
Elongation at break (%)	20	15	15	30	32	29	20
Flexural strength (kg/cm ²)	1,010	1,000	1,050	1,100	990	990	1,010
Flexural modulus (kg/cm ²)	29,200	29,300	29,500	30,000	28,800	28,700	29,000
Izod impact strength (kg.cm/cm notch)	7	7	8	7	8	8	7
Heat distortion temperature (°C)	170	172	170	170	165	166	165
(Load 18.6 kg/cm ²)							

Surface appearance of molded articles

Excellent Excellent Excellent Excellent Excellent Excellent

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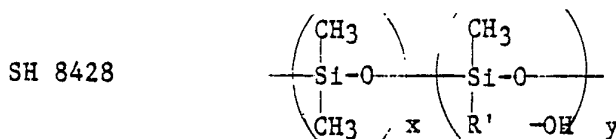
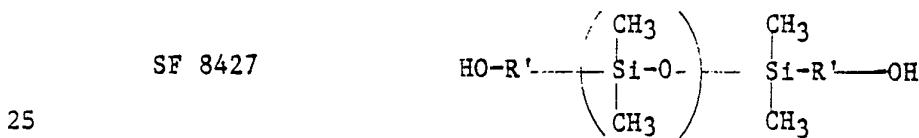
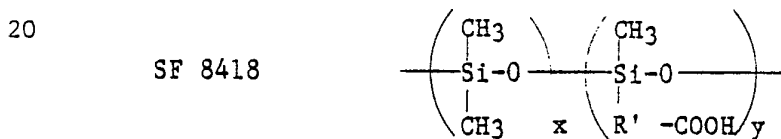
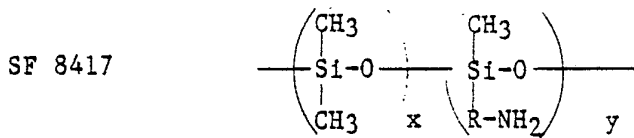
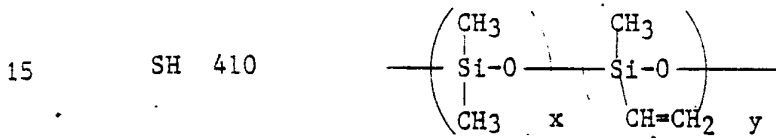
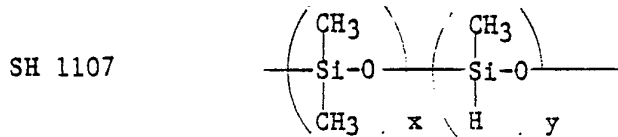
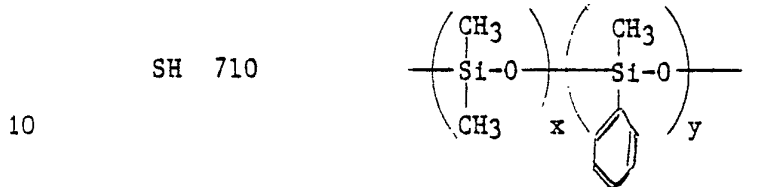
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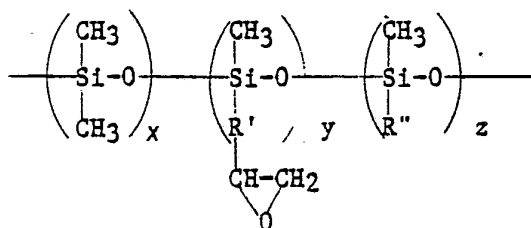
- a) N-4,6-polytetramethylene adipamide, N-4,6/6-poly(tetramethylene adipamide/caprolactam) copolymer (copolymerization ratio: 95/5 percents), N-4,6/6,6-poly(tetramethylene adipamide/hexamethylene adipamide) copolymer (copolymerization 90/10 percents by weight),
 5 N-4,6/N-6,6: polytetramethylene adipamide and polyhexamethylene adipamide (mixing ratio 90/10 percents by weight)

b) All the following are the grade names given by Toray Silicon K.K.



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SH 8421



CLAIMS

1. Polyamide resin composition containing 100 parts by weight of a polyamide with tetramethylene adipamide as main component and 2 to 20 parts by weight of silicon oil.
2. Polyamide resin composition according to claim 1 containing 3 to 18 parts by weight of silicon oil.
3. Polyamide resin composition according to one of the claims 1 and 2 containing 5 to 15 parts by weight of silicon oil.
4. Polyamide resin composition according to one of the claims 1-3 in which the silicon oil has a viscosity in the range of 100 to 50,000 centistokes.
5. Polyamide resin composition according to claim 4 in which the silicon oil has a viscosity in the range of 1,000 to 30,000 centistokes.
6. Polyamide resin composition according to one of the claims 1-5 in which the silicon oil has been chosen from the compounds represented by the general formula (1)-(12) in the description.
7. Molds mainly consisting of a polyamide composition according to one of the claims 1-6.
8. Process for the preparation of a polyamide resin composition with superior sliding characteristics by blending 2 to 20 parts by weight of silicon oil with 100 parts by weight of a polyamide with tetramethylene adipamide as main component.

INTERNATIONAL SEARCH REPORT

International Application No PCT/NL 85/00047

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ : C 08 L 77/00 // C 08 L 83:04		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁴	C 08 L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	Chemical Abstracts, volume 80, no. 22, 3 June 1974, Columbus, Ohio, (US) Kashio Junzo et al.: "Polyamide powdery composition for coating", see page 98, abstract no. 122569q & JP, A, 7328337 (TORAY INDUSTRIES) 31 August 1973 --	
A	Chemical Abstracts, volume 80, no. 10, 11 March 1974, Columbus, Ohio, (US) Ohba Tasaaki: "Holding by polymerization of lactoms", see pages 30,31, abstract no. 48814x & JP, A, 7251479 (TEIJIN) 25 December 1972	

<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
6th March 1986		09 APR 1986
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		M. VAN MOL 