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(54) **Bonded magnet moulding composition and bonded magnet.**

(57) This invention relates to compositions for the manufacture of magnets and magnets obtained by moulding said compositions. More particularly, it relates to bonded magnet moulding compositions with excellent magnetic properties, good mouldability and additionally superior heat stability during the moulding process, and the bonded magnets obtained therefrom. Specifically, a bonded magnetic moulding composition according to the invention comprises a polyamide type resin and magnetic or magnetisable material particles, having incorporated therein 0.3-2.0 weight% of a hydrazine derivative having a hindered phenolic hydroxyl group. The invention also includes the use of a hydrazine derivative containing a hindered phenolic group as an additive to a moulding composition for the moulding of bonded magnets.

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This invention relates to compositions for the manufacture of magnets and magnets obtained by moulding said compositions. More particularly, it relates to bonded magnet moulding compositions with excellent magnetic properties, good mouldability and additionally superior heat stability during the moulding process, and the bonded magnets obtained therefrom.

Bonded magnets made from compositions comprising organic polymer material consisting of thermoplastic resin and magnetic material are well known. With bonded magnet moulding compositions of this kind, products having a complex shape can be moulded by a plastic moulder such as an injection moulder, an extrusion moulder or a compression moulder without post-treatment, and this procedure is nowadays used for bonded magnet moulding in various applications. Moreover, because of the demand for downsizing and downweighting of electric products, auto-parts, etc. for electronic products, printers and others, it is highly desired to make bonded magnets of very high performance. In order to realize this aim, it is necessary to increase the content of the magnetic material while maintaining good mouldability.

For example, Japanese patent laid-open 1987-123702 describes a composition comprising magnetic powder surface-treated with a coupling agent and synthetic resin. In Japanese patent laid-open 1988-181403, the use of copolymers is disclosed. Japanese patent laid-open 1990-65103, describes the use of additivesetc. to try to improve the magnetic property and to improve the mouldability such as flowability. However there has not been any composition of which the content of the magnetic material is 65 % or more in volume ratio (corresponding to around 93 % or more when expressed by weight, depending on the substance used), having both heat stability and flowability, and the ability to give a strong mechanical strength to the moulded article, while maintaining the desired magnetic properties.

This invention offers a bonded magnet moulding composition which can be moulded particularly to a bonded magnet of thin thickness having high magnetic property by injection and/or extrusion moulding without deterioration of the flowability, the heat stability and the mechanical strength after the moulding, and also having improved magnetic properties resulting from a high density filling of the magnetic material.

After extensive research it has been found that the flowability and the heat stability in the moulding process, and the mechanical strength after the moulding can be remarkably improved by adding a hydrazine compound having a hindered phenolic structure to a bonded magnet moulding composition. The latter may comprise a polyamide type resin and magnetic material particles, the content of the hydrazine derivative in the said composition being 0.3-2.0 weight%, preferably 0.7-1.5 weight%. It has also been found that an excellent bonded magnet moulding composition having high magnetic property can be obtained with the magnetic material incorporated at a high density of 65 % or more of the volume ratio. Moreover, with the polyamide type resins which may be used in this invention, by adding 1-70 weight%, preferably 20-50 weight%, of polyamide copolymer to it, it has been found that a bonded magnet moulding composition having high magnetic property with further improved extrusion mouldability can be obtained.

The mechanism of the flowability improvement resulting from the addition of the divalent phenolic hydrazine compound having a hindered phenolic group is not known for certain but, in addition to the oxidation resistant action of the divalent hydrazine derivative it is considered that a mechanochemical amide substitution reaction may occur under high temperature and high shear. As a result, the molecular weight of the matrix resin is lowered, the flowability of the composition is increased the mouldability is improved, and moreover the high density filling of the magnetic material can be realized and therefore the magnetic property can be enhanced. Where a resin incorporated with a polyamide copolymer is used, the copolymer has lower crystallinity and longer crystallization time than the polyamide homopolymer, so that the moulding composition takes a long time for solidification in a die when it is processed by injection moulding, and thus the flowability during the processing is improved. When the composition is processed by extrusion moulding, the solidification time at the exit of a die is long, and thus a pressure elevation at the edge of the die can be reduced and a load on the screw can also be lightened. These desirable moulding conditions can be achieved even if a bonded magnet moulding composition which is filled with high density of the magnetic material is used. Consequently, according to the bonded magnet moulding composition of this invention, a bonded magnet with excellent magnetic property can be obtained.

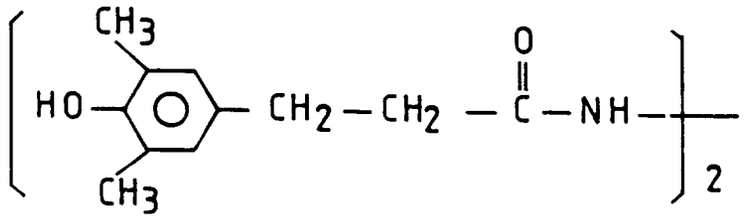
Suitable examples of the polyamide type resin to be used in this invention are 6-nylon, 6,6-nylon, 12-nylon, but others may also be used. A suitable polyamide copolymer which may be used in this invention is a copolymer of different polyamide type resins such as 6-nylon and 12-nylon, 6-nylon and 6,6-nylon.

The incorporated amount of the divalent phenolic hydrazine compound to be used in this invention, may be 0.3-2.0 weight%. If the incorporation amount is less than about 0.3 the desired heat stability and mouldability are not attained. On the other hand, if it is more, the magnetic property may not be attained to the level required for many applications.

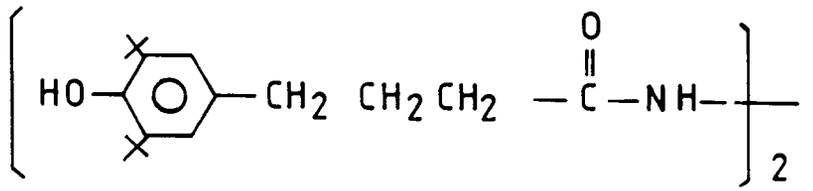
Suitable examples of the divalent phenolic hydrazine compound having a sterically hindered hydroxyl group are IRGANOX MD1024 (Ciba-Geigy product) shown by the below-listed formula 1, or N,N'-bis[3-(3,5-

di-t-butyl-4-hydroxyphenyl)alkanoyl]hydrazines shown by formula 2 and formula 3, in which X represents t-butyl.

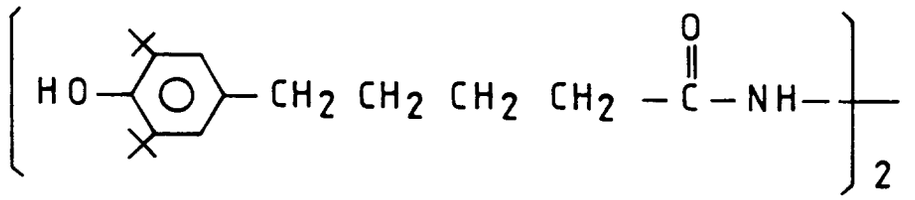
Formula 1



Formula 2



Formula 3



The magnetic material to be used in this invention can be magnetic or magnetizable material. Therefore the magnetic material does not need to be magnetized itself insofar as it can be magnetized by application of magnetic field during the production of the magnet or afterwards.

As examples of the magnetic material, ferrite materials such as barium ferrite ($BaO.6Fe_2O_3$) and strontium ferrite ($SrO6Fe_2O_3$) described in Japanese patent laid-open 1989-162301, intermetallic compounds of rare earth metals for the bonded magnet having high magnetic property (Sm, Ce, La, Y, Nd, Pr, Gd) with transition metals (Fe, Co, Ni, Zr,Hf, Cu, Ti), or intermetallic compounds comprising at least one of the rare earth metals and at least one of the transition metals based on neodymium-iron-boron, etc. can be used. Among these, the magnetic material comprising neodymium-iron-boron is particularly preferred for use according to this invention.

For the purposes of this invention, a lubricant, a lubrication oil, and other mould-processing auxiliaries can be added to the moulding compositions. As the lubricant, stearic acid, stearate, fatty acid amide and wax can be used and as for the lubricating oil, silicone oil can be used. It is preferable that these auxiliaries comprise 0.05-0.5 weight% of the mixture of the magnetic material and the matrix resin.

As raw material for the preparation of bonded magnet moulding of this invention, for example, 6,6-nylon pellets on the market can also be used as the substrate of the matrix resin, but it is preferable to use material in powder form before pelletizing for evenness of mixing and kneading.

Examples of this invention are shown hereinafter, but this invention is not limited by them.

Example 1

93.4 weight% of neodymium-iron-boron powder (GM product, MQ-P powder), 5.5 weight% of 12-nylon powder (Ube Kosan product, P-3014U) and 1.0 weight% of a hydrazine compound (Ciba-Geigy product, IRGANOX MD-1024) were placed in a Henschell mixer (Mitsuimiike Kako Product, FM10B) and were mixed for 1 minute.

Then 0.1 weight% of silicone oil (Bayer product, PN-200) was added to the mixture and they were again mixed for 1 minute. The mixture was taken out, was placed in a hopper of a same direction biaxial extruder (Toshiba product, TEM-35M), was kneaded at temperature of 230-250 °C, and a bonded magnet moulding composition in pellet form was prepared. The composition of this example is summarized in table 1.

For the evaluation of the heat stability, the bonded magnet moulding composition obtained was kneaded at 250 °C by using a labo-plastomill mixer (Toyoseiki Seisakusho product, 30C-150), it was measured by a torque elevation ratio, a value that a torque value after 10 minutes was divided by a torque value after 1 minute. Additionally, the viscosity of the pellets was measured with shear rate of 1216 sec-1 at 250 °C by using a capillary flow meter (Toyoseiki Seisakusho product, CAPIROGRAPH PM-C), and a bar flow was also evaluated by measuring a flow length with an injection pressure of 1400 kg/cm2 at 270 °C by a bar flow die having a bar channel shape of 10 mm wide and 1 mm deep byusing an injection moulder (Toshiba product, EPN-80).

In addition, the injection mouldability thereof was evaluated by ○ △ and X with a cylindrical bonded magnet of 24 mm inside diameter, 26mm outside diameter and 4 mm length by using an injection moulder (Toshiba product, EPN-80). ○ was that it could be moulded by general moulding condition, △ was that it could somehow be moulded by a high temperature and a high injection pressure, and X was that a satisfactory moulding could not be achieved even by a high temperature and a high injection pressure.

The magnetic property (BH)max of the cylindrical bonded magnet obtained was measured by a BH tracer.

The results were shown in the table 1 listed below. It was a high quality one with practical value on the heat stability, the injection mouldability and the magnetic property.

Example 2

A bonded magnet moulding composition was prepared in the similar manner to the example 1 by using the composition shown in the table 1 as the example 2.

As for the bonded magnet moulding composition obtained, it was evaluated in the similar manner to the example 1.

The results were shown in the table 1. It was a high quality one with practical value on the heat stability, the injection mouldability and the magnetic property.

Comparative example 1

A bonded magnet moulding composition was prepared in the similar manner to the example 1 by using the composition shown in the table 1 as the comparative example 1.

As for the bonded magnet moulding composition obtained, it was evaluated in the similar manner to the example 1.

The results are shown in the table 1, but its heat stability was inferior to the examples, though 10 times amount of silicone oil to the examples was used, both values of the viscosity and the bar flow were unfavourable, and it could not be made the injection moulding. Accordingly it was impossible to measure the magnetic property.

Comparative example 2

A bonded magnet moulding composition was prepared in the similar manner to the example 1 by using the composition shown in the table 1 as the comparative example 2.

As for the bonded magnet moulding composition obtained, it was evaluated in the similar manner to the example 1.

The results are shown in the table 1, but though a plasticizer was added, all of the heat stability, the viscosity and the bar flow were inferior to the examples, and the injection moulding was extremely difficult.

Example 3

A bonded magnet moulding composition was prepared in the similar manner to the example 1 by using the composition shown in the table 2 as the example 3.

As for the bonded magnet moulding composition obtained, as similar to the example 1, as the heat stability evaluation, it was measured by a torque elevation ratio, a value that a torque value after 10 minutes was divided by a torque value after 1 minute by using a labo-plastomill mixer (Toyoseiki Seisakusho product, 30C-150) by kneading at 250 °C. Additionally, the viscosity of the pellets was measured with shear rate of 1216 sec-1 at 250 °C by using a capillary flow meter (Toyoseiki Seisakusho product, CAPIROGRAPH PM-C).

An extrusion mouldability thereof was evaluated with a cylindrical bonded magnet of 20 mm outside diameter and 18 mm inside diameter by using a monoaxial extruder (Ikegai product, FS-40). ○ was that it could be moulded to a cylindrical shape by general moulding condition, and X was that the moulding could not be achieved by stoppage in the die.

The results are shown in the table 2, but it was a high quality one with practical value on the heat stability, the extrusion mouldability and the magnetic property.

Comparative example 3

A bonded magnet moulding composition was prepared in the similar manner to the example 1 by using the composition shown in the table 2 as the comparative example 3.

As for the bonded magnet moulding composition obtained, it was evaluated in the similar manner to the example 3.

The results are shown in the table 2, but its heat stability was inferior to the example, though 5 times amount of silicone oil to the example was used, the viscosity shown was an unfavourable value, and it could not be made the extrusion moulding. Accordingly it was impossible to measure the magnetic property.

Example 4

A bonded magnet moulding composition was prepared in the similar manner to the example 1 by using the composition containing a polyamide copolymer shown in the table 3 as the example 4.

As for the bonded magnet moulding composition obtained, as similar to the example 1, as the heat stability evaluation, it was measured by a torque elevation ratio, a value that a torque value after 10 minutes was divided by a torque value after 1 minute by kneading at 250 °C by using a labo-plastomill mixer (Toyoseiki Seisakusho product, 30C-150). Additionally, the viscosity of the pellets was measured with shear rate of 24.3 sec-1 at 210 °C by using a capillary flow meter (Toyoseiki Seisakusho product, CAPIROGRAPH PM-C).

An extrusion mouldability thereof was evaluated with an arcuate bonded magnet of 4.6 mm outside diameter, 3.6 mm inside diameter and 7.1 mm width by using a monoaxial extruder (Ikegai product, FS-40). ◎ was that one of the prefixed shape was moulded at high speed, ○ was that one of the prefixed shape was moulded at a low speed, △ was that though the composition was extruded through the die, the shape was not the prefixed one due to unevenness of the edge section and X was that the moulding could not be achieved by stoppage in the die.

The results are shown in the table 3, but it was a high quality one with practical value on the heat stability, the extrusion mouldability and the magnetic property.

Examples 5-7

Bonded magnet moulding compositions were prepared in the similar manner to the example 1 by using the compositions containing the polyamide copolymer shown in the table 3 as the examples 5-7.

As for the bonded magnet moulding compositions obtained, they were evaluated in the similar manner to the example 4.

The results are shown in the table 3. They were high quality with practical value on the heat stability, the injection mouldability and the magnetic property.

Comparative examples 4-5

Bonded magnet moulding compositions were prepared in the similar manner to the example 1 by using compositions shown in the table 3 as the comparative examples 4-5.

As for the bonded magnet moulding compositions obtained, they were evaluated in the similar manner to the example 4.

The results are shown in the table 3. One could not carry out the extrusion moulding, and as for the other, it could be only moulded to one having uneven edges, and therefore they had no practical value.

Table 1

	Example		Comparative example	
	1	2	1	2
Composition (weight%)				
neodymium-iron-boron powder	93.4	93.4	93.4	93.4
12-nylon	5.5	5.2	5.2	5.9
hydrazine compound[4)]	1.0	1.2	0.4	0.2
silicone oil	0.1	0.1	1.0	-
isostearic acid	-	-	-	0.5
Property				
torque elevation ratio[1)]	0.9	0.8	1.5	1.8
viscosity[2)] (k poise)	8	6	12	10
bar flow (cm)	8	9	5	6
injection mouldability[3)]	○	○	X	△
(BH)max (MGOe)	6.8	6.8	-	6.6

(Remarks) 1), 2), 3) and 4) in the table 1 mean the following respectively

1) It means a value that a torque value after 10 minutes is divided by a torque value after 1 minute by kneading at 250 °C by using a labo-plastomill mixer (Toyoseiki Seisakusho product, 30C-150).

2) It means a value obtained by measurement of the viscosity with shear rate of 1216 sec^{-1} at 250 °C by using a capillary flow meter (Toyoseiki Seisakusho product, CAPIROGRAPH PM-C).

3) ○ means that it could be moulded by general moulding condition, △ was that it could somehow be moulded by a high temperature and a high injection pressure, and X was that a satisfactory moulding could not be achieved even by a high temperature and a high injection pressure.

4) IRGANOX MD1024 (Ciba-Geigy product)

Table 2

	Example 3	Comparative example 3
Composition (weight%)		
neodymium-iron-boron powder	93.9	93.9
12-nylon	5.0	5.6
hydrazine compound[4)]	1.0	-
silicone oil	0.1	0.5
Property		
torque elevation ratio[1)]	0.8	2.2
viscosity[2)] (k poise)	9	15
extrusion mouldability[3)]	○	X
(BH)max (MGOe)	7.1	-

(Remarks) 1), 2), 3) and 4) in the table 1 mean the following respectively

1) It means a value that a torque value after 10 minutes is divided by a torque value after 1 minute by kneading at 250 °C by using a labo-plastomill mixer (Toyoseiki Seisakusho product, 30C-150).

2) It means a value obtained by measurement of the viscosity with shear rate of 1216 sec^{-1} at 250 °C by using a capillary flow meter (Toyoseiki Seisakusho product, CAPIROGRAPH PM-C).

3) ○ means that it could be moulded to a cylindrical shape by general moulding condition, and X means that the moulding could not be achieved by stoppage in the die.

4) IRGANOX MD1024 (Ciba-Geigy product)

Table 3

	Example				Comparative example	
	4	5	6	7	4	5
Composition (weight%)						
neodymium-iron-boron powder	93.9	93.6	94.9	94.8	93.9	93.9
12-nylon	3.8	2.4	2.8	1.8	5.4	5.1
6,12-nylon copolymer	1.3	2.5	1.0	1.9	-	-
hydrazine compound[4)]	1.0	1.2	1.2	1.2	0.2	0.5
silicone oil	0.1	0.3	0.1	0.3	0.5	0.5
Property						
torque elevation ratio[1)]	0.6	0.5	0.6	0.6	1.5	1.2
viscosity[2)] (k poise)	85	90	460	95	110	102
extrusion mouldability[3)]	○	◎	○	◎	X	△
extrusion speed (mm/sec)	2	4	1.5	4	-	-
(BH)max (MGOe)	7.1	7.0	8.0	7.9	-	-

(Remarks) 1), 2), 3) and 4) in the table 1 mean the following respectively

1) It means a value that a torque value after 10 minutes is divided by a torque value after 1 minute by kneading at 250 °C by using a labo-plastomill mixer (Toyoseiki Seisakusho product, 30C-150).

2) It means a value obtained by measurement of the viscosity with shear rate of 24.3 sec^{-1} at 210 °C by using a capillary flow meter (Toyoseiki Seisakusho product, CAPIROGRAPH PM-C).

3) ◎ means that one of the prefixed shape was moulded at high speed, ○ means that one of the prefixed shape was moulded at a low speed, △ means that though the composition was extruded through the die, the shape was not the prefixed one due to unevenness of the edge section and X was that the moulding could not be achieved by stoppage in the die.

4) IRGANOX MD1024 (Ciba-Geigy product) [0042]

The present invention, thus provides a bonded magnet moulding composition with good mouldability having improved magnetic property by filling high density of the magnetic material, and having the ability to be moulded by injection moulding and extrusion moulding. Additionally, the magnets obtained do not show deterioration of mechanical strength after the moulding by either injection moulding or extrusion moulding and have the high performance magnetic property similar to those obtained by compression moulding.

Claims

1. A bonded magnet moulding composition comprising a polyamide type resin and magnetic or magnetisable material particles, having incorporated therein 0.3-2.0 weight% of a hydrazine derivative having a hindered phenolic hydroxyl group.

2. A bonded magnet moulding composition according to claim 1 wherein the content of the hydrazine derivative is 0.7-1.5% by weight.

3. A bonded magnet moulding composition according to claim 1 or 2 wherein the polyamide type resin contains 1-70 weight%, especially 20-50%. of polyamide copolymer.

4. A bonded magnet moulding composition according to claim 1, 2 or 3 wherein the magnetic material particles consist of neodymium iron-boron.

5. A bonded magnetic moulding composition according to any of claims 1 to 4, in which the magnetic or magnetisable material comprises at least 65% of the composition by volume.

6. A bonded magnetic moulding composition according to any of the preceding claims in which the hydrazine derivative is a bis-dialkylhydroxy phenyl alkanoyl derivative.

7. A bonded magnetic moulding composition according to claim 6, in which the derivative is the compound of formula 1, 2 or 3 illustrated hereinbefore.

8. A bonded magnet obtained by moulding of a bonded magnet moulding composition comprising a polyamide type resin and magnetic material particles, wherein 0.3-2.0 weight% of a hydrazine compound having a hindered phenolic structure is incorporated in the bonded magnet moulding composition.

9. A bonded magnet obtained by moulding a composition according to any of claims 1-7.

10. The use of a hydrazine derivative containing a hindered phenolic group as an additive to a moulding composition for the moulding of bonded magnets.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 30 0006

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 374 813 (BASF AG) * page 3, line 51 * * page 4, line 1 - line 3 *	1,2,6	H01F1/08 H01F1/113 H01F1/053
A	* page 4, line 17 - line 19; claim 1 *	3	
A	PATENT ABSTRACTS OF JAPAN vol. 15, no. 405 (E-1122)16 October 1991 & JP-31 65 504 (KANEBO LTD) 17 July 1991 * abstract *	1,4	
A	PATENT ABSTRACTS OF JAPAN vol. 11, no. 004 (E-468)7 January 1987 & JP-61 179 506 (DAISERU HIYURUSU KK) 12 August 1986 * abstract *	1	
A	PATENT ABSTRACTS OF JAPAN vol. 16, no. 358 (C-0970)4 August 1992 & JP-41 10 347 (UBE IND LTD) 10 April 1992 * abstract *		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

H01F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17 MAY 1993	DECANNIERE L.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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