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(54) Permanent magnets.

(57) A flexible permanent magnetic composition comprising of (1) powdered magnetic ferrite and (2) a polyacrylic elastomer binder exhibits superior processing characteristics at lower energy-input levels than those experienced with commercial compositions evaluated. The composition of the present invention also can accept higher loadings of the magnetic powder and still be processed.

ACTORUM AG

PERMANENT MAGNETS

BACKGROUND OF THE INVENTION

Flexible permanent magnets have been used extensively in gasket assemblies for sealing the space between the door and cabinet of refrigerators, food freezers and like structures. Such magnets also have found extensive use in a variety of other applications, including use in advertising sheet materials that can be removably attached to an appropriate metal surface, as an attaching component in storm window framing, in motors, in sheet backing for carpeting to anchor the carpeting to steel flooring, as toy components, etc.

As described in U.S. Patent No. 2,959,832, such magnets may be made by incorporating a magnetic powder into an elastomer binder and shaping the composition into the desired configuration, followed by orientation of the particles of magnetic powder within the binder in order to enhance the potential magnetic properties of the composition. The resulting composition is subjected to a magnetizing field to magnetize the particles of magnetic powder within the composition.

The mixing operation can be carried out in any convenient manner, such as by mixing the components of the magnetic composition together in a Banbury mixer, on a roll mill or in an extruder. The method or methods which can be used for shaping the composition will depend to a significant degree on the configuration into which the composition is to be formed. For example, if thin sheets of the magnetic composition are desired, the sheets can be formed by a conventional calendering operation. Strip magnets of the type used in refrigerator gasket assemblies normally are formed as a continuous strip by extruding the magnetic composition through an appropriately-shaped extrusion die. Magnetization of the particles of magnetic material within the composition can be accomplished by subjecting the shaped product to a magnetic field of sufficient strength.

The amount of powdered magnetic material present in the magnetic composition will influence the strength of a magnet that can be formed from the composition. Usually, the larger the quantity of powered magnetic material in the composition, the greater will be the strength of a magnet which can be formed from the composition (provided that the degree of orientation of the magnetic particles is equal). However, as the quantity of powdered magnetic material in the composition is increased, the stiffness of the composition also increases and ultimately the composition may become friable and unable to be "worked" further. Also, the energy required for mixing or the pressure required for extrusion may become objectionably high as greater quantities of the magnetic powder are added to the composition.

SUMMARY OF THE INVENTION

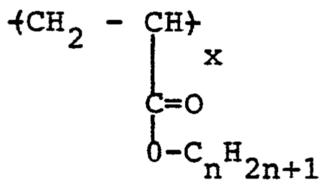
The present invention provides a magnetic composition that exhibits outstanding processing characteristics that enable the composition to be processed easily using less energy input and to be extruded at extrusion pressures lower than required with current commercial compositions containing comparable loadings of magnetic material The composition is able to accommodate higher loadings of the powdered magnetic material without losing its capability of being "worked" and shaped and, as a result of the possible higher loadings, can be formed into magnets of higher strengths.

In accordance with the present invention, a magnetic composition is provided that is comprised of (1) powdered magnetic material and (2) a polyacrylic elastomer binder for the magnetic material. Magnets formed from the composition not only can be of higher strength due to the higher loadings of magnetic powder that can be included in the composition, but also can be made into magnets that have a greater degree of flexibility than previously realized and which will withstand higher temperatures without exhibiting objectionable degradation.

DETAILED DESCRIPTION OF THE INVENTION

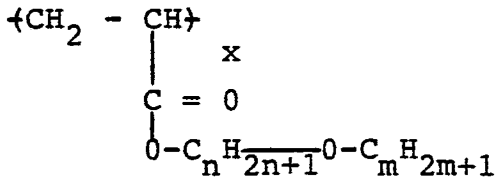
As indicated above, the magnetic composition of the present invention is comprised of (1) a finely-divided magnetic material and (2) polyacrylic elastomer binder for the magnetic material. The magnetic material can be combined with the polyacrylic elastomer component of the composition in any convenient manner, such as by mixing the components of the composition together in a Banbury mixer or on a roll mill. The mixed composition, usually is cubed or granulated to put it in a form that can be handled easily for further processing. The composition then is shaped into the desired configuration. If a flat thin sheet is desired, shaping can be accomplished on a calendering mill. If a magnet in the form of a strip is required, the cubed or granulated magnetic composition can be fed into a screw-type extruder and forced through an appropriately-shaped extrusion die to form a continuous strip of the magnetic composition of the desired cross-sectional configuration. The composition also can be shaped by injection molding or by shaping in conventional sectional molds. The shaped composition thereafter is exposed to a magnetizing field to magnetize the magnetic particles with the composition.

The binder component of the composition can be any polyacrylic elastomer that has a Mooney viscosity between 20 to 70, preferably between 25 to 60, when measured according to the procedure described in ASTM Designation No. 1646 after four minutes running time at 100°C. using the large rotor and with a one minute warm-up period and that is a polymer comprised of from 95 to 100 percent by weight of a backbone component having the structure:



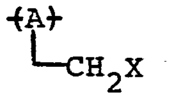
$$\left(CH_2-\underset{\substack{|\\C=O\\|\\O-C_nH_{2n+1}}}{CH}\right)_x$$

derived from an alkyl acrylate (such as ethyl acrylate, propyl acrylate, n-butyl acrylate, hexyl acrylate, heptyl acrylate and octyl acrylate) and where x is an integer and n is from 2 to 8, or having the structure



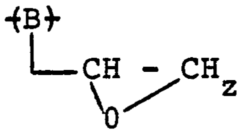
$$\left(CH_2-\underset{\substack{|\\C=O\\|\\O-C_nH_{2n+1}-O-C_mH_{2m+1}}}{CH}\right)_x$$

derived from an alkoxy acrylate (such as methoxy ethyl acrylate and ethoxy ethyl acrylate) and where x is an integer, n is 2 and m is 1 or 2. The polymer may contain up to 5 percent by weight of reactive functional groups that can function as cure cites. Among the reactive functional groups are reactive halogen groups having the structure

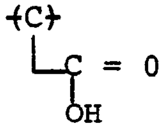


$$\underset{\llcorner CH_2X}{(A)}$$

where X is chlorine or bromine (such as results from the copolymerization of the alkyl acrylate or alkoxy acrylate with 2-chlorethyl vinyl ether), or reactive epoxy groups having the structure



(such as results from the copolymerization of the alkyl acrylate or alkoxy acrylate with an alkyl glycidyl ether), or reactive carboxyl groups having the structure



$\underset{\llcorner \mathrm{C}(=\mathrm{O})\mathrm{OH}}{-(\mathrm{C})-}$

(such as results from the copolymerization of the alkyl acrylate or alkoxy acrylate with acrylic acid or methacrylic acid) or reactive hydroxyl groups having the structure

$\underset{\mathrm{OH}}{\underset{|}{-(\mathrm{D})-}}$

(such as results from the copolymerization of the alkyl acrylate or alkoxy acrylate with an hydroxalkyl acrylate).

The magnetic component can be any anisotropic magnetizable material in fine particulate form, but preferably is a ferrite of barium, lead, or strontium, or a mixture thereof in a finely-divided state so that the individual particles desirably approach the size of the magnetic domains of the material. As used herein, a ferrite is defined as a material having the formula $MO.nFe_2O_3$ wherein M is barium, lead or strontium and n is an integer. Of the commercial ferrites, barium ferrite ($BaFe_{12}O_{19}$) is preferred. The particle size of the magnetic component desirably is within the size range of 0.5 to 10 microns with an average particle size preferably being 1 to 1.5 microns. Although commercial flexible permanent magnets currently being sold can contain as an upper limit only about 1,000 parts by weight of the magnetic component per 100 parts by weight of the binder component (since use of more than about 1000 parts by weight of the magnetic component per 100 parts by weight of binder produces a composition that is unable to be worked satisfactorily and that is objectionably friable and brittle), the composition of the present invention can accommodate up to about 1200 parts by weight of the magnetic material per 100 parts by weight of the polyacrylic binder component. As a result of the increased amount of magnetic material that can be incorporated into the composition, magnets of greater magnetic strength can be formed.

If desired, a small quantity of a processing aid for the polyacrylic binder component can be added to the composition. The processing aid should have a softening point below the temperature at which the magnetic composition is mixed and shaped to produce optimum results. Polyethylene homopolymers and copolymers of ethylene with an acrylic acid or vinyl acetate which have softening points when measured in accordance with the procedure described in ASTM Designation No. E-28 of between 60 to 120°C. are preferred processing aids. Desirably, from 1 to 15 parts by weight of such processing aid is used per 100 parts by weight of the polyacrylic elastomer in the magnetic composition.

The invention will be further understood by reference to the following examples.

EXAMPLES I-V

Magnetic compositions were formed having the following compositions:

	Parts by Weight				
Material	Ex. I	Ex. II	Ex. III	Ex. IV	Ex. V
Polyacrylic elastomer*	100.0	100.0	100.0	100.0	100.0
Ferrite powder**	700.0	765.0	830.0	945.0	1200.0

Material	Parts by Weight - contd. Ex. I	Ex. II	Ex. III	Ex. IV	Ex. V
Processing aid***	10.0	10.0	10.0	10.0	10.0
Volume percent ferrite	58.64	59.98	61.94	63.04	69.45

*Copolymer of 98 percent (by weight) ethyl acrylate and 2 percent (by weight) methacrylic acid

**Barium ferrite powder with average particle size between 1 to 1.5 microns and range of particle size between 0.5 to 10 microns

***Copolymer of ethylene and acrylic acid (Allied Chemical A-C 540A)

The ingredients were mixed together on a roll mill, sheeted off the mill and granulated. The granules were fed to a conventional extruder fitted with a heated die which produced a strip-type extrusion rectangular in cross-section. As the strip of material was discharged from the extrusion die, it was advanced through a magnetic field to magnetize the particles of ferrite in the composition. Various operating conditions employed in the manufacture of the strip materials and selected physical properties of the strip magnet formed are listed in Table I:

TABLE I

	Example				
Properties	I	II	III	IV	VI
Extrusion amperage (amps)	26	30	33	37	54
Die pressure (psi)	2600	2800	3600	3400	3800
Die temperature (C°)	155	157	158	164	180
Magnetic energy (gauss)	1680	1670	1720	1760	1930

TABLE I - contd.

Properties	I	II	III	IV	V
Yield stress (psi)	161	151	207	248	701
Elongation at break (%)	1420	1270	1280	483	412
Stress at break (psi)	183	123	166	659	610
Modulus (psi)	2170	2284	2852	3062	74,210

A typical commercial magnetic composition having the following composition served as a "control" was formed into a strip magnet as described in Examples I-V:

Materials	Parts by Weight
Chlorosulfonated polyethylene*	76.0
Polyisobutylene**	24.0
Barium ferrite***	1060.0
Volume percent ferrite	67.7

*Marketed by E.I. duPont de Nemours & Company as HYPALON 20 Rubber.

**Marketed by Enjay Company as Vistanex L-140.

***Barium ferrite powder with average particle size between 1 to 1.5 microns and range of particle size between 0.5 to 10 microns.

The "control" strip magnet had the following physical properties:

PROPERTIES OF CONTROL

Magnetic energy (gauss)	1775
Yield stress (psi)	840
Elongation @ break (%)	12.5
Stress @ break	950
Modulus (psi)	86,340

The invention is further illustrated by the following examples.

EXAMPLES VI-XIII

Magnetic compositions were formed using the following formulation:

Material	Parts by Weight
Polymer binder	100.0
Ferrite powder*	900.0

*Barium ferrite powder with average particle size between 1 to 1.5 microns and range of particle size between 0.5 to 10 microns.

The polymer binders used in the examples were:

Example	Polymer Binder
VI	Copolymer of 99.5 percent (by weight) ethyl acrylate and 0.5 percent (by weight) methacrylic acid.
VII	Polymer of 20 percent (by weight) ethyl acrylate, 78 percent (by weight) butyl acrylate and 2 percent (by weight) hydroxyethyl acrylate.
VIII	"
IX	Polymer of 98 percent (by weight) ethyl acrylate, 1.6 percent (by weight) vinyl benzyl chloride and 0.4 percent (by weight) methacrylic acid.
X	"
XI	Blend of 70 parts by weight of chlorosulfonated polyethylene (HYPALON 45) and 30 parts by weight of polyisobutylene (VISTANEX L-140).
XII	"
XIII	"

The compositions were mixed on an open mill. Mixing time for the polyacrylic elastomer binder compositions (Examples VI-X) was ten (10) minutes and mixing time for the chlorosulfonated polyethylene/polyisobutylene binder compositions was 20 minutes. Each composition was run through a capillary extrusion die in a constant load rheometer at the following conditions:

Die orifice	1/16 inch
Temperature	250°F.
Sample warm-up	15 minutes @ 250°F.
Sample time	5 seconds per sample

The data obtained is tabulated in Table II.

TABLE II

Example	Extrusion Pressure (psi)	Extrusion Mass (grams)	Extrusion Time (seconds)	Rate (grams/ minutes)
VI	400	8.37	80	6.28
VII	450	1.37	60	1.37
VIII	500	3.69	90	2.45
IX	400	6.28	75	5.02
X	450	7.56	35	12.96
XI	525	2.34	75	1.87
XII	625	3.18	50	3.18
XIII	650	3.72	30	7.44

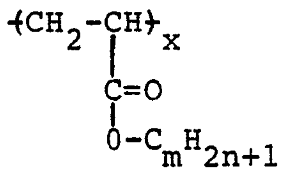
CLAIMS

1. A flexible permanent magnet composition comprising

a. finely-divided particles of a ferrite having the formula $MO.nFe_2O_2$ in which M is barium, lead or strontium and n is an integer, and

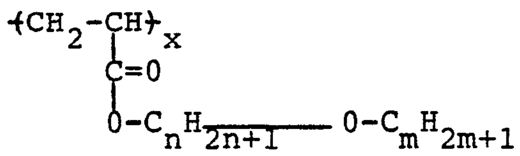
b. a polyacrylic elastomer having a Mooney viscosity between 20 and 70 when measured in accordance with the procedure of ASTM Designation 1646 with a 4 minute running time at 100°C. using the large rotor and with a 1 minute warm-up period,

said polyacrylic elastomer being a polymer comprised of from 95 to 100 percent by weight of a backbone component having the structure



$$\left(CH_2-\underset{\substack{| \\ C=O \\ | \\ O-C_mH_{2n+1}}}{CH} \right)_x$$

derived from an alkyl acrylate, where x is an integer and n is from 2 to 8, or having the structure



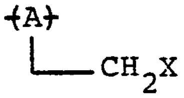
$$\left(CH_2-\underset{\substack{| \\ C=O \\ | \\ O-C_nH_{2n+1}\text{——}O-C_mH_{2m+1}}}{CH} \right)_x$$

derived from an alkyoxy acrylate, where x in an integer, n is 2 and m is 1 or 2,

said ferrite being present in an amount up to about 1200 parts by weight of said ferrite per 100 parts by weight of said polyacrylic elastomer.

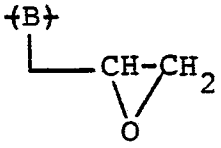
2. The composition of claim 1 wherein said polyacrylic elastomer polymer contains up to 5 percent by weight of reactive functional groups.

3. The composition of claim 2 wherein said reactive functional groups are reactive halogen groups having the structure

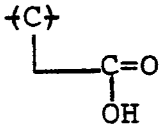

$-(\text{A})-\text{CH}_2\text{X}$

where X is chlorine or bromine.

4. The composition of claim 2 wherein said reactive functional groups are reactive epoxy groups having the structure



5. The composition of claim 2 wherein said reactive functional groups are reactive carboxyl groups having the structure


$-(\text{C})-\text{C}(=\text{O})\text{OH}$

6. The composition of claim 2 wherein said reactive functional groups are reactive hydroxyl groups having the structure


$-(\text{D})-\text{OH}$

7. The composition of claim 1 wherein said polyacrylic elastomer has a Mooney viscosity between 25 to 60 when measured in accordance with the procedure of ASTM Designation 1646 with a 4 minute running time at 100°C. using the large rotor and with a 1 minute warm-up period.

8. The composition of claim 1 wherein said finely-divided particles of ferrite have a particle size within the range of from 0.5 to 10 microns and an average particle size from 1 to 1.5 microns.

9. The composition of claims 1, 2, 3, 4, 5, 6, 7 or 8 wherein said ferrite is barium ferrite ($BaFe_{12}O_{19}$).

10. The composition of claims 1, 2, 3, 4, 5, 6, or 7 wherein said composition contains from 1 to 15 parts by weight of a polyethylene homopolymer or a copolymer of ethylene with an acrylic acid or vinyl acetate per 100 parts by weight of said polyacrylic elastomer.

European Patent
Office

EUROPEAN SEARCH REPORT

0080160
Application number

EP 82110609.3

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. 3)
A	US - A - 4 022 701 (SAWA et al.) * Totality * --	1	H 01 F 1/117 C 08 L 33/08 H 01 F 7/02
A	DE - B - 1 464 613 (THE B.F. GOODRICH CO.) * Totality * --	1,9	
A	DE - B - 1 302 093 (MINNESOTA MINING) * Totality * --	1,9	
A	US - A 3 257 586 (E. STEIN-GROEVER) * Totality * --	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
A	US - A - 3 602 986 (J.A. CONWICKE) * Column 1, line 26 - column 2, line 24; claim 3 * --	1,9	H 01 F 1/00 H 01 F 7/00 C 08 L 33/00
D,A	US - A - 2 959 832 (M. BAERMANN) --		
A	DE - A - 1 414 803 (THE B.F. GOODRICH CO.) --		
A	DE - A - 2 149 698 (COCHARDT GEB. MATTES) --		
A	DE - A - 2 248 533 (IOS) ----		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	24-02-1983	TSILIDIS

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document
T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
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