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(54) Title: RUBBER MASTERBATCHES

(57) Abstract: The present invention relates to a rubber masterbatch containing at least one hydrogenated nitrile polymer, at least two olefin-vinylacetate polymer and at least one processing aid. The present invention also relates to a curable rubber compound containing the rubber masterbatch and at least one vulcanization agent and at least one filler. Further, the present invention relates to a shaped article containing the curable rubber compound.



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RUBBER MASTERBATCHES

FIELD OF THE INVENTION

The present invention relates to a rubber masterbatch containing at least
5 one hydrogenated nitrile polymer, at least two olefin/vinylacetate and/or
olefin/acrylate polymers and at least one processing aid, wherein at least one of
the olefin/vinyl acetate and/or olefin/acrylate polymers is precrosslinked. The
present invention also relates to a curable rubber compound containing the rubber
masterbatch and at least one vulcanization agent and at least one filler. Further,
10 the present invention relates to a shaped article containing the curable rubber
compound.

BACKGROUND OF THE INVENTION

Hydrogenated nitrile rubbers (HNBR), prepared by the selective
15 hydrogenation of nitrile rubber (NBR, a co-polymer comprising at least one
conjugated diene, at least one unsaturated nitrile and optionally further
comonomers) are specialty rubbers which have very good heat resistance,
excellent ozone and chemical resistance, and excellent oil resistance. Coupled
with the high level of mechanical properties of the rubber (in particular the high
20 resistance to abrasion) it is not surprising that HNBR have found widespread use
in the automotive (seals, hoses, bearing pads) oil (stators, well head seals, valve
plates), electrical (cable sheathing), mechanical engineering (wheels, rollers) and
shipbuilding (pipe seals, couplings) industries, amongst others.

EP-A-0 471 250 discloses hydrogenated butadiene/ isoprene/ (meth)-
25 acrylonitrile copolymers, in particular copolymers containing 3.5 to 22% by weight
of copolymerized isoprene and 18 to 50% by weight of copolymerized acrylonitrile
or methacrylonitrile, and having a degree of hydrogenation, based on the C=C
double bonds of the polymer, of at least 85%, that is, an RDB not greater than
15%.

30 There are commercially available HNBR's that have good low temperature
properties. Therban[®] LT 2157 is a terpolymer, available from Lanxess, composed

of 21 wt% acrylonitrile, acrylate, and butadiene, that has a residual double bond content (RDB) of 5.5% and a glass transition temperature (T_g) of -38° C.

Therban[®] LT VP KA 8882 is similar, but differs in having an RDB of less than 0.9%, and, again, has a T_g of -38.° C.

- 5 WO-02/16441-A discloses a hydrogenated copolymer of an unsaturated nitrile, butadiene and isoprene, wherein the molar ratio of butadiene to isoprene is less than 3:1.

EP-A-0 151 691 discloses a blend of 95-5 wt.% of EVA and 5-95 wt.% of HNBR.

- 10 CA 2,436,742 discloses a polymer blend comprising at least one, preferably statistical, hydrogenated nitrile rubber, at least one, preferably statistical, hydrogenated nitrile terpolymer rubber, at least one, preferably binary, salt of a strong base and a weak acid comprising a group 1 metal, and at least one olefin/vinylacetate or olefin/acrylate rubber.

15

SUMMARY OF THE INVENTION

The present invention relates to a rubber masterbatch containing

(i) at least one, preferably statistical, hydrogenated nitrile polymer,

(ii) at least two olefin/vinyl acetate and/or olefin/acrylate polymers, wherein

- 20 at least one of the olefin/vinyl acetate and/or olefin/acrylate polymers has a gel content and a swelling index which is adjusted with gamma radiation and wherein the radiation adjusted polymer has a gel content of 40 to 80% based on the total mass of the olefin/vinyl acetate and/or olefin/acrylate polymer and a swelling index of 20 to 80 based on the gel, and

- 25 (iii) at least one processing aid.

The present invention also relates to a rubber masterbatch containing

(i) at least one, preferably statistical, hydrogenated nitrile terpolymer rubber,

(ii) at least two olefin/vinyl acetate and/or olefin/acrylate polymers, wherein

- 30 at least one of the olefin/vinyl acetate and/or olefin/acrylate polymers has a gel content and a swelling index which is adjusted with gamma radiation and wherein the radiation adjusted polymer has a gel content of 40 to 80% based on the total

mass of the olefin/vinyl acetate and/or olefin/acrylate polymer and a swelling index of 30 to 75 based on the gel, and

(iii) at least one processing aid.

In addition, the present invention relates to curable rubber compound
5 containing the rubber masterbatch and at least one filler, and at least one vulcanization agent.

Further, the present invention relates to a shaped article containing the curable rubber compound.

Rubber compounds containing rubber masterbatches according to the
10 present invention have improved processability due to lower compound Mooney viscosity and quicker Mooney relaxation times compared to rubber compounds conventionally prepared. Also, rubber compounds containing rubber masterbatches according to the present invention have improved physical properties, in particular, higher moduli or overall compound stiffness.

15

DESCRIPTION OF THE INVENTION

As used throughout this specification, the term "nitrile rubber", "nitrile polymer" or NBR is intended to have a broad meaning and is meant to encompass a copolymer having repeating units derived from at least one conjugated diene, at
20 least one alpha, beta-unsaturated nitrile and optionally further copolymerizable monomer(s).

As used throughout this specification, the term "nitrile terpolymer rubber" or "LT-NBR" is intended to have a broad meaning and is meant to encompass a copolymer having (a) repeating units derived from at least one conjugated diene,
25 (b) at least one alpha, beta-unsaturated nitrile, (c) repeating units derived from at least one further monomer selected from the group consisting of conjugated dienes, unsaturated carboxylic acids; alkyl esters of unsaturated carboxylic acids, alkoxyalkyl acrylates and ethylenically unsaturated monomers other than dienes and (d) optionally further copolymerizable monomer(s). If (a) and (c) are
30 conjugated dienes, it is understood that the nitrile terpolymer rubber contains repeating units derived from at least two different conjugated dienes.

As used throughout this specification, the term "hydrogenated" or HNBR is intended to have a broad meaning and is meant to encompass a NBR wherein at least 10 % of the residual C-C double bonds (RDB) present in the starting NBR are hydrogenated, preferably more than 50 % of the RDB present are

5 hydrogenated, more preferably more than 90 % of the RDB are hydrogenated, even more preferably more than 95 % of the RDB are hydrogenated and most preferably more than 99 % of the RDB are hydrogenated.

The conjugated diene may be any known conjugated diene preferably a C₄-C₆ conjugated diene. Preferred conjugated dienes include butadiene, isoprene,
10 piperylene, 2,3-dimethyl butadiene and mixtures thereof. Even more preferred C₄-C₆ conjugated dienes include butadiene, isoprene and mixtures thereof. The most preferred C₄-C₆ conjugated diene is butadiene.

The alpha, beta-unsaturated nitrile may be any known alpha, beta-unsaturated nitrile, preferably a C₃-C₅ alpha, beta-unsaturated nitrile. Preferred
15 C₃-C₅ alpha, beta-unsaturated nitriles include acrylonitrile, methacrylonitrile, ethacrylonitrile and mixtures thereof. The most preferred C₃-C₅ alpha, beta-unsaturated nitrile is acrylonitrile.

The unsaturated carboxylic acid may be any known unsaturated carboxylic acid copolymerizable with the other monomers, preferably a C₃-C₁₆ alpha, beta-unsaturated carboxylic acid. Preferred unsaturated carboxylic acids include acrylic
20 acid, methacrylic acid, itaconic acid and maleic acid and mixtures thereof.

The alkyl ester of an unsaturated carboxylic acid may be any known alkyl ester of an unsaturated carboxylic acid copolymerizable with the other monomers, preferably an alkyl ester of an C₃-C₁₆ alpha, beta-unsaturated carboxylic acid.
25 Preferred alkyl ester of an unsaturated carboxylic acid include alkyl esters of acrylic acid, methacrylic acid, itaconic acid and maleic acid and mixtures thereof, preferably methyl acrylate, ethylacrylate, butylacrylate, 2-ethylhexyl acrylate and octyl acrylate. Preferred alkyl esters include methyl, ethyl, propyl, butyl and octyl esters.

The alkoxyalkyl acrylate may be any known alkoxyalkyl acrylate copolymerizable with the other monomers, preferably methoxyethyl acrylate, ethoxyethyl acrylate and methoxyethoxyethyl acrylate and mixtures thereof

5 The ethylenically unsaturated monomer may be any known ethylenically unsaturated monomer copolymerizable with the other monomers, preferably allyl glycidyl ether, vinyl chloroacetate, ethylene, butene-1, isobutylene and mixtures thereof.

Preferably, the HNBR in the masterbatch according to the present invention contains in the range of from 40 to 85 weight percent of repeating units derived from one or more conjugated dienes and in the range of from 15 to 60 weight percent of repeating units derived from one or more unsaturated nitriles. More preferably, the HNBR contains in the range of from 60 to 75 weight percent of repeating units derived from one or more conjugated dienes and in the range of from 25 to 40 weight percent of repeating units derived from one or more
10 15 unsaturated nitriles. Most preferably, the HNBR contains in the range of from 60 to 70 weight percent of repeating units derived from one or more conjugated dienes and in the range of from 30 to 40 weight percent of repeating units derived from one or more unsaturated nitriles.

Preferably, the nitrile terpolymer rubber in the masterbatch according to the present invention is a hydrogenated alpha, beta-unsaturated nitrile/
20 butadiene/isoprene rubber. Preferably, the ratio of repeating units derived from butadiene to repeating units derived from isoprene (butadiene:isoprene ratio) is preferably below 3:1, more preferably below 2:1. The ratio can be as low as 0.1:1, but is preferably not less than 0.5:1. Good results are obtained with a ratio of 1:1
25 and the preferred range is 0.75:1 to 1:0.75.

The butadiene plus isoprene usually constitutes in the range of from 50 to 95% of the copolymer, and the nitrile usually constitutes in the range of from 5 to 50% of the copolymer. For the present invention the nitrile content does not normally exceed 36% and is preferably below 30%. The preferred lower limit on
30 the nitrile content is 15%, because copolymers with lower nitrile contents tend to lose their oil resistance. For applications where oil resistance is not of importance,

however, lower nitrile contents are acceptable, down to 10% or even 5%. For most purposes a nitrile content of 15 to 25% is preferred.

More preferably, the nitrile terpolymer rubber is a hydrogenated alpha, beta-unsaturated nitrile/butadiene/acrylate rubber. The combined butadiene and acrylate content constitutes a range of 50 to 95% of the terpolymer, while the nitrile is in the range of 5 to 50%. More preferably, the nitrile range is between 10 and 30%. Commercially available examples of such terpolymers include Therban® LT 2157 (21% nitrile content, 5.5% residual double bonds) and Therban® LT VP KA 8882 (21% nitrile content, 0.9 % maximum double bond content).

Optionally, according to the present invention, the hydrogenated nitrile polymer and/or the hydrogenated nitrile terpolymer rubber may further contain repeating units derived from one or more copolymerizable monomers. Repeating units derived from one or more copolymerizable monomers will replace either the nitrile or the diene portion of the nitrile rubber and it will be apparent to the skilled in the art that the above mentioned figures will have to be adjusted to result in 100 weight percent.

The olefin/vinylacetate polymers in the masterbatch according to the present invention may be any olefin/vinylacetate rubber known in the art.

The olefin may be any known olefin, preferably ethylene, propylene, butenes, pentenes, hexenes, heptenes, octenes and their higher homologues and mixtures thereof.

The olefin/vinylacetate rubber usually contains in the range of from 10-95 wt.%, preferably 10-80 wt%., of repeating units derived from the olefin monomer(s) and in the range of from 5-90 wt.%, preferably 20-90 wt.%, of repeating units derived from the vinylacetate. Preferred are olefin/vinylacetate rubbers available under the trade-name LEVAPREN® from Lanxess Deutschland GmbH.

The olefin/acrylate polymer may be any olefin/ acrylate rubber known in the art.

The olefin may be any known olefin, preferably ethylene, propylene, butenes, pentenes, hexenes, heptenes, octenes and their higher homologues and mixtures thereof.

5 The acrylate may be any known acrylate copolymerizable with the olefin, preferably acrylic acid and derivatives such as methacrylic acid and methylmethacrylate.

The olefin/acrylate rubber usually contains in the range of from 5-95 wt.%, preferably 10-80 wt%., of repeating units derived from the olefin monomer(s) and in the range of from 5-95 wt.%, preferably 20-90 wt.%, of repeating units derived
10 from the acrylate(s). Preferred are olefin/acrylate rubbers available under the trade-name VAMAC® from DuPont.

At least one of the olefin/vinylacetate and/or olefin/acrylate polymers in the masterbatch according to the present invention is a precrosslinked olefin/vinylacetate and/or a precrosslinked olefin/acrylate polymer prepared
15 according to United States Patent No. 6,399,671, the contents of which are herein incorporated by reference.

The precrosslinked polymers in the masterbatch according to the present invention are those synthesized from ethylene and vinyl acetate, from ethylene and the above-stated acrylates.

20 In the precrosslinked polymers, the mixture ratio of the monomers relative to each other is conventionally 0.1%-99.9%, preferably 5%-95%, more preferably 30%-80%.

The gel content and degree of swelling of the precrosslinked polymers in the masterbatch according to the present invention is established by ionizing
25 radiation. Treatment with γ radiation is preferably considered as the ionizing radiation.

The precrosslinked polymers useful in the present invention preferably have a gel content of 30 to 80%, more preferably of 40 to 70%. The swelling index is preferably 20 to 80, more preferably 40 to 60.

30 The gel content and swelling index of the precrosslinked polymers useful in the present invention are determined using the following method:

The sample is placed in methylene chloride, to which 1 g/l of Ionol had been added, such that there were 12.5 g of polymer per liter of solvent. The mixture is shaken for 6 hours at 140°C, and then centrifuged for 1 hour at 20,000 rpm, wherein the temperature was still maintained at 140°C. The sol solution was separated and may optionally be further investigated. The gel is first weighed while moist and the quantity of the dry gel obtained after drying to constant weight in a vacuum drying cabinet is determined.

The percentage gel content and the swelling index are calculated using the following formulae:

$$\text{Gel content} = \frac{\text{mass of dry gel}}{\text{total initial weight of sample}} \cdot 100$$

$$\text{Swelling index} = \frac{\text{mass of moist gel}}{\text{mass of dry gel}}$$

In order to be able to establish the gel content and degree of swelling of the precrosslinked polymers according to the masterbatch of the present invention, the treatment with ionizing γ radiation is performed at a radiation dose of 20 to 140, preferably of 60 to 120, more preferably of 70 to 100 kGy (kilogray).

Irradiation may be performed using any desired plant suitable for this purpose, for example with a 3.5 MCi ^{60}Co gamma plant (approx. 1.3 MeV). Apart from Co-60 radiation, radiation from the ^{137}Cs isotope is also suitable. The applied radiation dose may, for example, be measured using a photometric system from Far West Technology, USA and the film dosimeter supplied by this company. These film dosimeters contain a radiation-sensitive dye and the radiation dose is calculated on completion of the irradiation process from the change in the absorbance of said dye. These dosimeters are calibrated ex works against an internationally recognized standard.

Treatment with γ radiation may be performed in the conventional manner at temperatures of 0° to 130°, preferably of 10° to 120°, more preferably of 20 to 80°C. The most favorable temperature range may readily be determined by

appropriate preliminary testing. It is essential that the temperature range is selected such that adequate free radical mobility is ensured.

The precrosslinked olefin/vinylacetate and/or olefin/acrylate polymers according to the present invention are preferably produced by initially polymerizing
5 the monomers used in a conventional manner and then treating the resultant polymers with ionizing radiation.

It is possible in this connection to treat the precrosslinked polymers in the most varied forms, ranging from powders to large bales. It must merely be ensured that the γ radiation used sufficiently penetrates the polymers used.

10 In order to establish a desired gel content, it is preferred, once the polymers have been irradiated, to homogenize them in suitable apparatus (internal mixers, roll mills or co-kneaders). If the precrosslinked polymer is in finely divided form (for example powder or pellets), a powder mixer may also be used for homogenization. By means of this homogenization, it is possible to obtain a
15 product which is entirely uniform with regard to gel content, irrespective of the shape and size of the irradiated container.

The desired average gel content may, of course, also be established by blending with non-irradiated or more or less highly irradiated polymers, i.e. with polymers having different gel contents.

20 The amount of the individual polymers and/or rubbers present in the inventive masterbatch may vary in wide ranges and thus it is possible to tailor the properties of the final compound as well as the properties of the final shaped article. Preferably, the masterbatch contains in the range of from 5 to 50 wt.%, preferably from 10 to 40 wt.%, of at least one, preferably statistical, hydrogenated
25 nitrile rubber and/or in the range of from 5 to 50 wt.%, preferably from 10 to 40 wt.%, of at least one, preferably statistical, hydrogenated nitrile terpolymer rubber , and in the range of from 5 to 50 wt.%, preferably from 10 to 40 wt.%, of at least one olefin/vinylacetate rubbers and/or one or more olefin/acrylate rubbers and in the range of from 20 to 80 wt.%, preferably from 30 to 70 wt.%, of at least one
30 precrosslinked olefin/vinylacetate rubbers and/or precrosslinked olefin/acrylate rubbers .

The masterbatch according to the present invention further contains at least one processing aid. Preferably the masterbatch contain the range of from 0.1 to 5 wt.%, preferably from 0.2 to 1 wt.% of one or more organic fatty acids as an auxiliary product, preferably an unsaturated fatty acid having one, two or more carbon double bonds in the molecule which more preferably includes 10% by weight or more of a conjugated diene acid having at least one conjugated carbon-carbon double bond in its molecule. Preferably those fatty acids have in the range of from 8-22 carbon atoms, more preferably 12-18. Examples include stearic acid, palmitic acid and oleic acid and their calcium-, zinc-, magnesium-, potassium- and ammonium salts.

The Mooney viscosity of the polymers and/or rubbers in the masterbatch may vary in wide ranges and thus it is possible to tailor the properties of the final compound as well as the properties of the final shaped article. Preferably, the hydrogenated nitrile polymer and/or hydrogenated nitrile terpolymer may have a Mooney viscosity ML(1+4@ 100°C) of in the range of from 20 to 100 MU, preferably 40 to 80 MU. Preferably the olefin/vinyl acetate and/or olefin/acrylate polymer may have a Mooney viscosity ML (1+4@ 100°C) of in the range of from 10 to 90 MU, preferably 20 to 70 MU. Preferably the precrosslinked olefin/vinyl acetate and/or olefin/acrylate polymer may have a Mooney viscosity ML (1+4@ 100°C) of in the range of from 30 to 90 MU, preferably 40 to 70 MU.

The Mooney viscosity of the raw polymers, the rubber masterbatch and the cured rubber compound containing the inventive masterbatch can be determined using ASTM test D1646.

While it may not be preferred, the present inventive masterbatch may further contain up to 30 wt% of other polymers such as polyolefins, BR (polybutadiene), ABR (butadiene/acrylic acid-C₁-C₄-alkylester-copolymers), CR (polychloroprene), IR (polyisoprene), SBR (styrene/butadiene-copolymers) with styrene contents in the range of 1 to 60 wt%, EPDM (ethylene/propylene/diene-copolymers), FKM (fluoropolymers or fluororubbers), and mixtures of the given polymers. Careful blending with said other polymers often reduces cost of the polymer blend without sacrificing to much of the desired final properties of the

compound. The amount of other polymers will depend on the process condition to be applied during manufacture of shaped articles and the targeted final properties and is readily available by few preliminary experiments.

The masterbatch according to the present invention is prepared by mixing
5 at least one, preferably statistical, hydrogenated nitrile polymer and/or
hydrogenated nitrile terpolymer, at least two olefin/vinyl acetate and/or
olefin/acrylate polymers, wherein at least one of the olefin/vinyl acetate and/or
olefin/acrylate polymers has a gel content and a swelling index which is adjusted
with gamma radiation and wherein the radiation adjusted polymer has a gel
10 content of 40 to 80% based on the total mass of the olefin/vinyl acetate and/or
olefin/acrylate polymer and a swelling index of 20 to 80 based on the gel, and at
least one processing aid, then compounding the resulting mixture at a temperature
in the range of between 75 to 175°C to form a masterbatch.

In order to prepare a curable rubber compound containing the present
15 inventive masterbatch, preferably at least one filler and vulcanizing agent has to
be added to the masterbatch.

Suitable filler(s) may be an active or an inactive filler or a mixture thereof.
The filler(s) may be in particular:

- 20 - highly dispersed silicas, prepared e.g. by the precipitation of silicate
solutions or the flame hydrolysis of silicon halides, with specific surface
areas of in the range of from 5 to 1000 m²/g, and with primary particle
sizes of in the range of from 10 to 400 nm; the silicas can optionally
also be present as mixed oxides with other metal oxides such as those
of Al, Mg, Ca, Ba, Zn, Zr and Ti;
- 25 - synthetic silicates, such as aluminum silicate and alkaline earth metal
silicate like magnesium silicate or calcium silicate, with BET specific
surface areas in the range of from 20 to 400 m²/g and primary particle
diameters in the range of from 10 to 400 nm;
- 30 - natural silicates, such as kaolin and other naturally occurring silica;
- glass fibers and glass fiber products (matting, extrudates) or glass
microspheres;

- metal oxides, such as zinc oxide, calcium oxide, magnesium oxide and aluminum oxide;
- metal carbonates, such as magnesium carbonate, calcium carbonate and zinc carbonate;
- 5 - metal hydroxides, e.g. aluminum hydroxide and magnesium hydroxide;
- carbon blacks; the carbon blacks to be used here are prepared by the lamp black, furnace black or gas black process and have preferably BET (DIN 66 131) specific surface areas in the range of from 20 to 200 m²/g, e.g. SAF, ISAF, HAF, FEF or GPF carbon blacks;
- 10 - rubber gels, especially those based on polybutadiene, butadiene/styrene copolymers, butadiene/acrylonitrile copolymers and polychloroprene;
- large aspect ratio nanoclays such as Cloisite® or mixtures thereof.

15 Examples of preferred mineral fillers include silica, silicates, clay such as bentonite, gypsum, alumina, titanium dioxide, talc, mixtures of these, and the like. For many purposes, the preferred mineral is silica, especially silica made by carbon dioxide precipitation of sodium silicate. Dried amorphous silica particles suitable for use in accordance with the invention may have a mean agglomerate

20 particle size in the range of from 1 to 100 microns, preferably between 10 and 50 microns and most preferably between 10 and 25 microns. It is preferred that less than 10 percent by volume of the agglomerate particles are below 5 microns or over 50 microns in size. A suitable amorphous dried silica moreover usually has a

25 BET surface area, measured in accordance with DIN (Deutsche Industrie Norm) 66131, in the range from 50 and 450 square meters per gram and a DBP absorption, as measured in accordance with DIN 53601, in the range from 150 and 400 grams per 100 grams of silica, and a drying loss, as measured according to DIN ISO 787/11, of in the range of from 0 to 10 percent by weight. Suitable

30 silica fillers are available under the trademarks HiSil® 210, HiSil® 233 and HiSil® 243 from PPG Industries Inc. Also suitable are Vulkasil® S and Vulkasil® N, from Bayer AG.

Often, use of carbon black as a filler is advantageous. Usually, carbon black is present in the polymer blend in an amount of in the range of from 20 to 200 parts by weight, preferably 30 to 150 parts by weight, more preferably 40 to 100 parts by weight. Further, it might be advantageous to use a combination of
5 carbon black and mineral filler in the inventive rubber compound. In this combination the ratio of mineral fillers to carbon black is usually in the range of from 0.05 to 20, preferably 0.1 to 10.

Optionally, the present curable rubber compound containing the inventive masterbatch may further contains a carbodiimide, a polycarbodiimide or mixtures
10 thereof. The preferred carbodiimide is available commercially under the tradenames Rhenogran™ PCD-50 and Stabaxol™ P. This ingredient may be used in the present curable rubber compound in an amount in the range of from 0 to about 15 parts by weight, more preferably in the range of from 0 to about 10 parts by weight, even more preferably in the range of from about 2 to about 5 parts by
15 weight.

The rubber compound containing the inventive masterbatch further comprises at least one vulcanizing agent or curing system. The present invention is not limited to a special curing system; however, peroxide curing system(s) are preferred. Furthermore, the invention is not limited to a special peroxide curing
20 system. For example, inorganic or organic peroxides are suitable. Preferred peroxides include organic peroxides such as dialkylperoxides, ketalperoxides, aralkylperoxides, peroxide ethers, peroxide esters, such as di-tert.-butylperoxide, bis-(tert.-butylperoxyisopropyl)-benzene, dicumylperoxide, 2,5-dimethyl-2,5-di(tert.-butylperoxy)-hexane, 2,5-dimethyl-2,5-di(tert.-butylperoxy)-hexene-(3), 1,1-bis-(tert.-butylperoxy)-3,3,5-trimethyl-cyclohexane, benzoylperoxide, tert.-butyl-
25 cumylperoxide and tert.-butylperbenzoate. Usually the amount of neat peroxide in the cured rubber compound containing the masterbatch is in the range of from 1 to 6 phr, preferably from 1 to 3 phr. Subsequent curing is usually performed at a temperature in the range of from 100 to 200 °C, preferably 130 to 180 °C.
30 Peroxides might be applied advantageously with the aid of a carrier such as polymer or a clay. Suitable systems are commercially available, such as Poly-

dispersion T(VC) D-40 P from Rhein Chemie Rheinau GmbH, D (= polymerbound di-tert.-butylperoxy-isopropylbenzene).

The curable rubber compound according to the invention can contain further auxiliary products for rubbers, such as reaction accelerators, vulcanizing accelerators, vulcanizing acceleration auxiliaries, antioxidants, foaming agents, anti-aging agents, heat stabilizers, light stabilizers, ozone stabilizers, plasticizers, tackifiers, blowing agents, dyestuffs, pigments, waxes, extenders, organic acids, inhibitors, metal oxides, and activators such as triethanolamine, polyethylene glycol, hexanetriol, etc., which are known to the rubber industry. The rubber aids are used in conventional amounts, which depend inter alia on the intended use. Conventional amounts are e.g. from 0.1 to 50 phr. The ingredients of the rubber compound (the masterbatch, at least one vulcanizing agent and at least one filler) are often mixed together, suitably at an elevated temperature that may range from 25 °C to 200 °C.

Normally the mixing time does not exceed one hour and a time in the range from 2 to 30 minutes is usually adequate. The mixing of the rubbers, optionally the filler(s), optionally vulcanization agent, and/or further ingredients is suitably carried out in an internal mixer such as a Banbury mixer, or a Haake or Brabender internal mixer. A two roll mill mixer also provides a good dispersion of the compounds within the final product. An extruder also provides good mixing, and permits shorter mixing times. It is possible to carry out the mixing in two or more stages, and the mixing can be done in different apparatus, for example one stage in an internal mixer and one stage in an extruder. However, it should be taken care that no unwanted pre-crosslinking (= scorch) occurs during the mixing stage. For compounding and vulcanization see also: Encyclopedia of Polymer Science and Engineering, Vol. 4, p. 66 et seq. (Compounding) and Vol. 17, p. 666 et seq. (Vulcanization).

The masterbatch and the curable rubber compound according to the present invention are very well suited for the manufacture of a shaped article, such as a seal, hose, bearing pad, stator, well head seal, valve plate, cable

sheathing, wheel roller, pipe seal, in place gaskets or footwear component. Furthermore, they are very well suited for wire and cable production.

The masterbatch provides a compound possessing enhanced processability due to lower compound Mooney viscosity and quicker Mooney relaxation times

- 5 compared to rubber compounds conventionally prepared. Also, rubber compounds containing rubber masterbatches according to the present invention have improved physical properties, in particular, higher moduli or overall compound stiffness.

10 EXAMPLES

List of Compounding Ingredients

Levapren® 600 HV - ethylene vinyl acetate copolymer containing 60% by weight vinyl acetate available from Lanxess Deutschland GmbH.

- 15 Levapren® 700 HV - ethylene vinyl acetate copolymer containing 70% by weight vinyl acetate available from Lanxess Deutschland GmbH.

Levapren® VP KA 8815- precrosslinked ethylene vinyl acetate copolymer containing 60% by weight vinyl acetate available from Lanxess Deutschland GmbH.

- 20 Therban® A 3907 - hydrogenated acrylonitrile butadiene rubber containing 39% acrylonitrile and less than 0.9% residual double bonds. It is available from Lanxess Deutschland GmbH.

- Therban® LT VP KA 8882 - hydrogenated acrylonitrile butadiene rubber containing 21% acrylonitrile and less than 0.9% residual double bonds. It is
25 available from Lanxess Deutschland GmbH.

Carbon black N774 and N990 are both available from Cabot Corp..

Elastomag™ 170 Powder is magnesium oxide available from Morton International.

- 30 Naugard™ 445 is p-dicumyl diphenylamine and is available through Crompton Corp..

Plasthall™ TOTM is a trioctyl trimellitate from The C.P. Hall Co., Inc..

Rhenogran™ PCD-50 is a polycarbodiimide from Rhein Chemie Corp..

Stearic Acid Emersol™ 132 NF is stearic acid available from Acme-Hardesty Co..

TP-759 is an ether/ester based plasticizer available from Morton
5 International.

Vulkanox™ ZMB-2/C5 is the zinc salt of 4- and 5-methyl mercaptobenzimidazole (ZMMBI) and is available from Lanxess Deutschland GmbH.

Zinc Oxide (Kadox™ 920) is available from St. Lawrence Chem. Inc.

10 TAIC-DLC-A is triallyl isocyanurate (72% by weight) on a silicon dioxide carrier available from Natrochem, Inc..

Vulcup™ 40KE is a bis 2-(t-butyl-peroxy) diisopropylbenzene (40% on Burgess clay) available from Geo Specialty Chemicals, Inc..

15 Description of Tests

Compound Mooney Viscosity and Relaxation

The compound Mooney viscosity was determined at 100°C using a large rotor. The sample was preheated within the rotor cavity for one minute and then, subjected to the shearing action of the viscometer disk rotating at 2 rpm for a
20 period of 4 minutes. The torque in Mooney units was immediately recorded at that time. The sample was then allowed to relax for a period of 4 minutes in order to acquire information about the relaxation behavior of the rubber compound. The slope, intercept and area under the relaxation curve are all recorded. The tests were compliant with ASTM D-1646.

25 **Compound Mooney Scorch**

The compound Mooney scorch was measured using a large rotor and a temperature of 135°C. The time at which the Mooney viscosity increases 5 Mooney units from the minimum value was recorded as t05 in minutes. The test was run in compliance with ASTM D-1646.

Rheometry

A Moving Die Rheometer (MDR 2000(E)) was used in order to follow the vulcanization behavior of the rubber samples. The platens were set at 180°C and a frequency of oscillation of 1.7 Hz coupled with a 1° arc were applied to the sample for a time of 30 minutes. This test procedure complies with ASTM D-5289.

Hardness

Hardness measurements were carried out according to ASTM D-2240 using an A-2 type durometer at 23°C.

10 Stress-strain

Tensile slabs were prepared by curing the rubber samples for 12 minutes at 180°C. Standard die C dumbbells were died out afterwards for testing. Testing was carried out at 23°C and the procedure complies with ASTM D-412 Method A.

Tear Resistance

15 Die B and die C geometries were cut out of a tensile sheet which was cured for 12 minutes at 180°C. The test complies with ASTM D-624.

Compression Set

Solid compression buttons were prepared by curing the rubber samples 17 minutes at 180°C. Afterwards, the buttons were compressed 25% in a compression set jig and placed in a hot air oven set at 150°C for 70 and 168 hours. The test procedure complies with ASTM D-395 (Method B).

Stress Strain Liquid Immersion Aging

25 Die C tensile rubber samples were exposed to Service Fluid 105 (SF 105) for a period of 70 and 168 hours at 150°C. Testing afterwards was carried out according to ASTM D-471.

Temperature Retraction

Low temperature stiffening effects in the tension mode was characterized using the temperature retraction technique. This method conforms to ASTM D 1329.

Masterbatch Mixing Procedure

The present inventive masterbatches containing the ingredients listed in Table 1 were mixed according to the following procedure. An internal Banbury type mixer with tangential rotors and a mixing capacity of 1.57 liters was employed. The rotor speed was initially set at 77 rpm and the water was set for cooling at 30°C. A batch factor of 73% was used. At time 0, all three polymers and the stearic acid were added into the mixing chamber and the ram was lowered. The ram was raised after 2 minutes to perform a sweep and then lowered for the remainder of the mix. The mix was dumped after 5 minutes of total mixing time. Temperatures did not surpass 125°C using this method. Scale up methods of such mixes may require the lowering of the rotor speed during the mix in order to prevent the temperature from exceeding 125°C.

The dumped masterbatch blend was then placed on a 10" by 20" two roll mill with the cooling water set at 30°C. The masterbatch was banded on the mill and refined by using 3/4 cuts. Six endwise passes was also performed to ensure maximum dispersive mixing of the polymers within the masterbatch.

Table 1: Masterbatch Formulations

Ingredient	Levatherm	Levatherm LT	Levatherm LT II
Levapren 700 HV	20	20	25
Levapren VP KA 8815	50	50	55
Therban A 3907	30	0	0
Therban LT VP KA 8882	0	30	20
Stearic Acid Emersol 132 NF	0.5	0.5	0.5
Specific Gravity (g/cm ³)	1.02	1.02	1.03

20 Compounding Mixing Procedure

The mixing of the rubber compound ingredients given in Table 2 was completed in two stages. In the first stage, an internal BR-82 Banbury mixer with tangential rotors turning at 77 rpm was used. The mixing chamber has a volume of 1.6 liters and the water was set for cooling at 30°C. The fill factor was 0.73. At

time 0, the inventive masterbatches or the Levapren® and Therban® polymers used for comparison were added to the mixing chamber and allowed to mix for 1 minute. At 1 minute, the carbon black, magnesium oxide, antioxidants (diphenylamine, ZMMBI and polycarbodiimide), TOTM and TP-759 plasticizers, 5 stearic acid and zinc oxide were all added to the mixer. Mixing continued for another 2 minutes. At 3 minutes a sweep was performed. After 5 minutes, the mix was dumped and final mixing temperatures were recorded. A 10" by 20" two roll mill was used for the second stage of mixing. It was cooled by water set at 30°C. After banding of the masterbatch material, both the TAIC and peroxide 10 were added and incorporated into the mix. The use of 3/4 cuts helped to homogenize the ingredients throughout and along the mill roll. Finally, 6 endwise passes were carried out to optimize dispersion of all ingredients in the mix.

TABLE 2: COMPOUND FORMULATIONS

INGREDIENTS	Ex. 1	Comp. Ex. 2	Ex. 3	Comp. Ex. 4	Ex. 5	Comp. Ex. 6
LEVAPREN 700 HV	0	20	0	20	0	25
LEVAPREN VP KA 8815	0	50	0	50	0	55
LEVATHERM	100.5	0	0	0	0	0
LEVATHERM LT	0	0	100.5	0	0	0
LEVATHERM LT II	0	0	0	0	100.5	0
THERBAN A 3907	0	30	0	0	0	0
THERBAN LT VP KA 8882	0	0	0	30	0	20
CARBON BLACK, N 774	40	40	40	40	40	40
CARBON BLACK, N 990	60	60	60	60	60	60
ELASTOMAG 170 POWDER	3	3	3	3	3	3
NAUGARD 445	1.1	1.1	1.1	1.1	1.1	1.1
PLASTHALL TOTM	5	5	5	5	5	5
RHENOGRAN PCD-50	4	4	4	4	4	4
STEARIC ACID EMERSOL 132 NF	1	1.5	1	1.5	1	1.5
TP - 759	5	5	5	5	5	5
VULKANOX ZMB-2/C5 (ZMMBI)	0.5	0.5	0.5	0.5	0.5	0.5
ZINC OXIDE (KADOX 920)	3	3	3	3	3	3
TAIC-DLC-A	1.75	1.75	1.75	1.75	1.75	1.75
VULCUP 40KE	5	5	5	5	5	5
PHRS	229.85	229.85	229.85	229.85	229.85	229.85
Specific Gravity	1.304	1.305	1.304	1.307	1.311	1.314

TABLE 3: COMPOUND MOONEY SCORCH (large rotor, 135°C)

PROPERTY	Ex. 1	Comp. Ex. 2	Ex. 3	Comp. Ex. 4	Ex. 5	Comp. Ex. 6
t Value t05 (min)	14.34	13.81	13.5	14.03	14.63	14.97

TABLE 4: COMPOUND MOONEY VISCOSITY (ML 1+4@100°C, 4 min relaxation time (80% decay))						
PROPERTY	Ex. 1	Comp. Ex. 2	Ex. 3	Comp. Ex. 4	Ex. 5	Comp. Ex. 6
Mooney Viscosity (MU)	48.51	50.09	45.86	48.52	44.3	46.4
Time to Decay (min)	0.05	0.06	0.07	0.09	0.07	0.08
Slope (lgM/lgs)	-0.5531	-0.4981	-0.4593	-0.4065	-0.5125	-0.4644
Intercept (MU)	17.4	18.6	17.3	18.8	17.5	18.5
Area Under Curve	411.9	543.1	587.5	787.5	483.4	615.8

TABLE 5: MDR CURE CHARACTERISTICS (1.7 Hz, 180°C, 1° arc, 30 min run)

PROPERTY	Ex. 1	Comp. Ex. 2	Ex. 3	Comp. Ex. 4	Ex. 5	Comp. Ex. 6
MH (dN.m)	27.33	25.95	23.33	23.56	23.45	23.15
ML (dN.m)	1.57	1.59	1.65	1.86	1.43	1.54
Delta MH-ML (dN.m)	25.76	24.36	21.68	21.7	22.02	21.61
ts 1 (min)	0.48	0.48	0.54	0.54	0.54	0.54
ts 2 (min)	0.6	0.63	0.69	0.72	0.69	0.69
t' 10 (min)	0.66	0.67	0.71	0.72	0.71	0.71
t' 25 (min)	1.04	1.05	1.14	1.15	1.11	1.11
t' 50 (min)	1.79	1.79	1.95	1.95	1.87	1.85
t' 90 (min)	4.93	4.82	5.13	5.1	4.96	4.92
t' 95 (min)	6.26	6.1	6.46	6.41	6.28	6.25
Delta t'50 - t'10 (min)	1.13	1.12	1.24	1.23	1.16	1.14

TABLE 6: STRESS STRAIN (die C)

PROPERTY	Ex. 1	Comp. Ex. 2	Ex. 3	Comp. Ex. 4	Ex. 5	Comp. Ex. 6
Test Temperature (°C)	23	23	23	23	23	23
Hardness Shore A2 (pts.)	66	65	61	60	62	61
Ultimate Tensile (MPa)	13.34	13.63	13.61	14.3	13.39	14.28
Ultimate Elongation (%)	211	208	220	215	199	219
Stress @ 25 (MPa)	1.72	1.53	1.15	1.13	1.21	1.15
Stress @ 50 (MPa)	3.07	2.81	2.07	2.06	2.27	2.16
Stress @ 100 (MPa)	6.89	6.72	5.38	5.64	6.14	5.82
Stress @ 200 (MPa)	12.99	13.33	12.81	13.54		13.57
Tear Strength (kN/m) Die C	23.22	22.72	21.51	21.47	21.75	21.14
Tear Strength (kN/m) Die B	46.16	47.91	40.99	42.97	50.28	45.76

TABLE 7: COMPRESSION SET -METHOD B (buttons, 25% compression, 150°C hot air)

PROPERTY	Ex. 1	Comp. Ex. 2	Ex. 3	Comp. Ex. 4	Ex. 5	Comp. Ex. 6
Compression Set (%) 70 hrs	24.72	23.58	18.59	18.52	17.49	16.84
Compression Set (%) 168 hrs	33.66	30.38	25.64	25.04	24.83	22.61

TABLE 8: STRESS STRAIN LIQUID IMMERSION (SF105, 70 hrs at 150°C)

PROPERTY	Ex. 1	Comp. Ex. 2	Ex. 3	Comp. Ex. 4	Ex. 5	Comp. Ex. 6
Chg. Hard. Shore A2 (pts.)	-7	-8	-12	-10	-13	-12
Chg. Ulti. Tens. (%)	-10	-4	-6	-10	-12	-13
Chg. Ulti. Elong. (%)	-30	-22	-17	-17	-11	-18
Change Stress @ 25 (%)	-26	-25	-34	-33	-43	-36
Change Stress @ 50 (%)	-12	-11	-23	-18	-31	-24
Change Stress @ 100 (%)	9	7	-4	-3	-16	-8
Wt. Change (%)	9.3	9.5	12.2	12.6	13.2	13
Vol. Change (%)	14.6	15	19.3	19.8	20.7	20.6

TABLE 9: STRESS STRAIN LIQUID IMMERSION (SF105, 168 hrs at 150°C)

PROPERTY	Ex. 1	Comp. Ex. 2	Ex. 3	Comp. Ex. 4	Ex. 5	Comp. Ex. 6
Chg. Hard. Shore A2 (pts.)	-8	-7	-11	-12	-12	-13
Chg. Ulti. Tens. (%)	-2	-5	-14	-12	-14	-21
Chg. Ulti. Elong. (%)	-24	-27	-29	-19	-19	-26
Change Stress @ 25 (%)	-30	-25	-36	-41	-39	-42
Change Stress @ 50 (%)	-16	-10	-20	-28	-23	-29
Change Stress @ 100 (%)	3	13	5	-8	-5	-11
Wt. Change (%)	10.6	10	13.2	13.2	13.8	13.6
Vol. Change (%)	17.1	16	20.5	20.9	21.8	21.2

TABLE 10: TEMPERATURE RETRACTION

PROPERTY	Ex. 1	Comp. Ex. 2	Ex. 3	Comp. Ex. 4	Ex. 5	Comp. Ex. 6
TR 10 (°C)	-23.5	-23	-28.1	-28.6	-27.2	-27.2
TR 30 (°C)	-16.2	-15.4	-20.7	-21.8	-19.7	-20.1
TR 50 (°C)	-11.1	-10.1	-14.5	-15.8	-13.5	-13.9
TR 70 (°C)	-5.8	-4.9	-8.7	-9.8	-7.6	-7.8

Table 3 illustrates that the compounds prepared with the rubber masterbatch (Ex, 1, 3 and 5) still possess excellent scorch safety compared to the ones produced conventionally (Ex. 2, 4 and 6). Extra mixing of elastomers is sometimes a cause for a concern especially if degradation effects could arise.

Table 4 clearly shows the improvement in compound Mooney viscosity comparing Ex.1 to Ex.2, Ex. 3 to Ex. 4 and finally Ex. 5 to Ex. 6. A lower compound Mooney viscosity translates to easier processing for compression, transfer or injection molding. The quicker relaxation times illustrated by the lower time to decay, the more negative Mooney slopes, the lower intercept values and finally the smaller area under the relaxation curve are all indicative of a material possessing better processability characteristics.

The rheometry data in Table 5 clearly shows that a lower minimum torque is acquired when using the rubber masterbatch material (Exs. 1, 3 and 5) versus the conventionally mixed material (Exs. 2, 4 and 6). These results correlate with

the decreased compound Mooney viscosity and hence are indicative of better processability. The maximum torques and delta torques are slightly higher (Ex. 1 vs Ex. 2 and Ex. 5 vs Ex. 6) for the rubber masterbatch produced compounds versus the conventionally made ones. Cure characteristics are essentially
5 identical between all rubber examples.

The physical property results shown in table 6 clearly demonstrate that hardness and moduli (up to 200% elongation) do increase in the case of using the rubber masterbatch (Exs. 1, 3 and 5) versus the convention mixes (Exs. 2, 4 and 6). The ensuing increased compound stiffness has a very little effect on both
10 tensile strength and elongation. Tear strengths remain quite high for compounds which possess improved stiffness.

Table 7 illustrates that the compression set values are only slightly influenced by using the rubber masterbatch technology.

Tables 8 and 9 illustrate that the rubber masterbatch produced compounds
15 age in a similar manner as the conventional prepared ones in service fluid 105.

Table 10 illustrates that low temperature properties are not harmed in using the rubber masterbatch compounds versus the conventionally mixed compounds.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that
20 purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

CLAIMS:

1. A rubber masterbatch comprising:
 - (i) at least one hydrogenated nitrile rubber;
 - 5 (ii) at least two olefin/vinyl acetate and/or olefin/acrylate polymers, wherein at least one of the olefin/vinyl acetate and/or olefin/acrylate polymers has a gel content and a swelling index which is adjusted with gamma radiation and wherein the radiation adjusted polymer has a gel content of 40 to 80% based on the total mass of the olefin/vinyl acetate and/or olefin/acrylate polymer and a swelling index
10 of 20 to 80 based on the gel; and,
 - (iii) at least one processing aid.
2. A rubber masterbatch comprising:
 - (i) at least one hydrogenated nitrile rubber,
 - 15 (ii) at least two olefin/vinyl acetate polymers, wherein at least one of the olefin/vinyl acetate polymers has a gel content and a swelling index which is adjusted with gamma radiation and wherein the radiation adjusted polymer has a gel content of 40 to 80% based on the total mass of the olefin/vinyl acetate polymer and a swelling index of 20 to 80 based on the gel; and,
 - 20 (iii) at least one processing aid.
3. A rubber masterbatch according to Claim 2, wherein the olefin/vinyl acetate polymers having a gel content and a swelling index which is adjusted with gamma radiation and wherein the radiation adjusted polymer has a gel content of 40 to
25 80% based on the total mass of the olefin/vinyl acetate polymer and a swelling index of 20 to 80 based on the gel is a precrosslinked olefin/vinyl acetate polymer.
4. A rubber masterbatch according to any one of Claims 1 to 3, wherein the processing aid is a fatty acid.

5. A rubber masterbatch according to Claim 4, wherein the fatty acid is stearic acid.
6. A rubber masterbatch comprising:
 - 5 (i) at least one hydrogenated nitrile terpolymer rubber,
 - (ii) at least two olefin/vinyl acetate and/or olefin/acrylate polymers, wherein at least one of the olefin/vinyl acetate and/or olefin/acrylate polymers has a gel content and a swelling index which is adjusted with gamma radiation and wherein the radiation adjusted polymer has a gel content of 40 to 80% based on the total
10 mass of the olefin/vinyl acetate and/or olefin/acrylate polymer and a swelling index of 20 to 80 based on the gel, and
 - (iii) at least one processing aid.
7. A curable rubber compound comprising the rubber masterbatch according
15 to any one of Claims 1 to 5 and at least one vulcanization agent and at least one filler.
8. A curable rubber compound comprising the rubber masterbatch according to Claim 6 and at least one vulcanization agent and at least one filler.
20
9. A curable rubber compound according to Claim 7 wherein the vulcanization agent is a peroxide.
10. A curable rubber compound according to Claim 8 wherein the vulcanization
25 agent is a peroxide.
11. A shaped article comprising a curable rubber compound according to Claim 7.
- 30 12. A shaped article comprising a curable rubber compound according to Claim 8.

13. A shaped article according to Claim 11 in the form of a seal, gasket, belt, hose, bearing pad, stator, well head seal, valve plate, cable sheathing, wheel roller, in place gasket or pipe seal.

5

14. A shaped article according to Claim 12 in the form of a seal, gasket, belt, hose, bearing pad, stator, well head seal, valve plate, cable sheathing, wheel roller, in place gasket or pipe seal.

- 10 15. A process for preparing a rubber masterbatch comprising mixing
- (i) at least one hydrogenated nitrile rubber,
 - (ii) at least two olefin/vinyl acetate and/or olefin/acrylate polymers, wherein at least one of the olefin/vinyl acetate and/or olefin/acrylate polymers has a gel content and a swelling index which is adjusted with gamma radiation and wherein
- 15 the radiation adjusted polymer has a gel content of 40 to 80% based on the total mass of the olefin/vinyl acetate and/or olefin/acrylate polymer and a swelling index of 20 to 80 based on the gel, and,
- (iii) at least one processing aid and
- compounding the resulting mixture at a temperature in the range of 75 to 175°C.

20

16. A process for preparing a rubber masterbatch comprising mixing
- (i) at least one hydrogenated nitrile terpolymer rubber,
 - (ii) at least two olefin/vinyl acetate and/or olefin/acrylate polymers, wherein at least one of the olefin/vinyl acetate and/or olefin/acrylate polymers has a gel
- 25 content and a swelling index which is adjusted with gamma radiation and wherein the radiation adjusted polymer has a gel content of 40 to 80% based on the total mass of the olefin/vinyl acetate and/or olefin/acrylate polymer and a swelling index of 30 to 75 based on the gel, and
- (iii) at least one processing aid; and
- 30 compounding the resulting mixture at a temperature in the range of 75 to 175°C.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2005/001887

A. CLASSIFICATION OF SUBJECT MATTER

IPC: *C08L 15/00* (2006.01) , *C08L 31/04* (2006.01) , *C08L 9/02* (2006.01) , *C08J 3/28* (2006.01) , *C08F 36/08* (2006.01) , *C08F 36/06* (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C08L; C08J; C08F (2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)

DWPI/Delphion; PlusPat database; Esp@cenet; Canadian Patent database- full text plus bibliography; Google (rubber AND nitrile AND olefin AND vinylacetate), (rubber AND nitrile AND olefin AND acrylate), (rubber AND nitrile AND hydrogenated AND olefin), (rubber AND nitrile AND hydrogenated AND vinylacetate), (rubber AND nitrile AND hydrogenated AND acrylate), (masterbatch AND "acrylate OR vinylacetate"), all keywords searched with related terms.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	CA 2436742 A1 (BAYER INC.) 26 December 2004 (26-12-2004) see the whole document	1-16
A	CA 2292158 A1 (BAYER INC.) 15 June 2001 (15-06-2001) see the whole document	1-10, 15-16
A	EP 0 531 788 A1 (BAYER AG) 17 March 1993 (17-03-1993) see abstract and claim 1	1-16
A	EP 0 272 071 A1 (BICC PUBLIC LIMITED COMPANY) 22 June 1988 (22-06-1988) see abstract, Example 1 and claim 1	1-16

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents :	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2005/001887

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant	Relevant to claim No.
A	JP 02160850A2 (FUJIKURA LTD) 20 June 1990 (20-06-1990) see abstract	1-16
A	US 4,675,248 (BAYER AG) 23 June 1987 (23-06-1987) see abstract, column 1, lines 10-15 & lines 48-62, column 2, line 1, line 21 & lines 27-28, and example	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/CA2005/001887

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