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(54) Title: IMPROVED ASPHALT MATERIAL

(57) Abstract: Asphalt product comprising Z1) from 90 wt% to 98 wt% of mineral aggregate; Z2) From 2 wt% to 10 wt% of a bitumen composition comprising: T1) from 99 wt% to 75 wt% of bitumen, and T2) from 1 wt% to 25 wt% of polymer composition comprising the following components, A) 5-35% by weight of a propylene homopolymer; B) 20-50% by weight; of an ethylene homopolymer; and C) 30-60% by weight of a terpolymer of ethylene, propylene and 1-butene derived units.

TITLE

IMPROVED ASPHALT MATERIAL

FIELD OF THE INVENTION

[0001] The present disclosure relates an asphalt composition having improved features. The asphalt composition comprises mineral aggregate and a mixture comprising bitumen and polymer compositions.

BACKGROUND OF THE INVENTION

[0002] Asphalt is a mixture of bitumen with mineral aggregate and optionally various additives.

[0003] The most important part of asphalt is therefore bitumen.

[0004] Polymer compositions that can be used to modify bitumen, are already known in the art.

[0005] Published European patent application EP-A-411627 describes polymer compositions developed to be used in roofing applications. Said polymer compositions comprise two fractions, one of which is made up of a propylene homopolymer, and the other of a propylene-ethylene copolymer.

[0006] According to said patent application, the polymer compositions with the best properties for the use in bituminous mixtures for roofing must have an intrinsic viscosity (I.V.) ranging from 0.5 to 1.5 dl/g for both the above mentioned polymer fractions.

[0007] Published European patent application EP-A-592852 describes mixtures of bitumen and polymer compositions containing:

[0008] A) 10-40 parts by weight of a propylene homopolymer or a copolymer of propylene with up to 10% by weight of comonomer(s);

[0009] B) 0-20 parts by weight of a copolymer fraction containing over 55 wt% ethylene units, which is insoluble in xylene at room temperature;

[0010] C) 50-80 parts by weight of a copolymer fraction of ethylene with propylene or higher α-olefins, said copolymer fraction being soluble in xylene at room temperature, and having an intrinsic viscosity in tetrahydronaphthaline at 135°C greater than 1.5 and up to 2.2 dl/g.

[0011] Such compositions achieve an improved set of properties, in particular flexibility at low temperature, resistance to penetration and softening, and ductility.

[0012] The applicant found that the properties of asphalt can be improved by using a particular bitumen composition.

SUMMARY OF THE INVENTION

[0013] Object of the present disclosure is an asphalt product comprising:

[0014] Z1) from 90 wt% to 98 wt% of mineral aggregate;

[0015] Z2) From 2 wt% to 10 wt% of a bitumen composition comprising:

[0016] T1) from 99 wt% to 75 wt% of bitumen , and

[0017] T2) from 1 wt% to 25 wt% of polymer composition comprising the following components,

[0018] A) 5-35% by weight of a propylene homopolymer containing 10% by weight or less of a fraction soluble in xylene at 25°C (XS_A), the amount of the fraction XS_A being referred to the weight of A);

[0019] B) 20-50% by weight; of an ethylene homopolymer having 5% by weight or less of a fraction soluble in xylene at 25°C (XS_B) referred to the weight of (B); and

[0020] C) 30-60% by weight of a terpolymer, wherein the terpolymer contains ethylene, propylene and 1-butene derived units containing from 45% to 65% by weight of ethylene units; and from 15% to 38% by weight of 1-butene units; and containing from 30% to 85% by weight of a fraction soluble in xylene at 25°C (XS_C), the amount of ethylene units; 1-butene units and the fraction XS_C being referred to the weight of (C);

[0021] the amounts of (A), (B) and (C) being referred to the total weight of (A) + (B) + (C), the sum of the amount of (A) + (B) + (C) being 100 wt%;

[0022] the amounts, wt%, of T1 +T2 being 100 wt%.

DETAILED DESCRIPTION OF THE INVENTION

[0023] Object of the present disclosure is an asphalt product comprising:

[0024] Z1) from 90 wt% to 98 wt%; preferably from 93 wt% to 97 wt%; more preferably from 96 wt% to 94 wt% of mineral aggregate;

[0025] Z2) From 2 wt% to 10 wt%; preferably from 3 wt% to 7 wt%; more preferably from 4 wt% to 6 wt% of a bitumen composition comprising:

[0026] T1) from 99 wt% to 75 wt% preferably from 98 wt% to 80 wt%; more preferably from 97 wt% to 90 wt% even more preferably from 97 wt% to 92 wt% of bitumen; and

[0027] T2) from 1 wt% to 25 wt%; preferably from 2 wt% to 20 wt%; more preferably from 3 wt% to 10 wt% even more preferably from 3 wt% to 8 wt% of polymer composition comprising the following components;

[0028] A) 5-35% by weight; preferably 10-30 % by weight; more preferably 15-23%by weight of a propylene homopolymer containing 10% by weight or less preferably 8 wt% or less more preferably 6 wt% or less of a fraction soluble in xylene at 25°C (XS_A), the amount of the fraction XS_A being referred to the weight of A);

[0029] B) 20-50% by weight; preferably 25-45% by weight; more preferably 30-40 % by weight an ethylene homopolymer having 5% by weight or less; preferably 4 wt% or less; more preferably 3 wt% or less of a fraction soluble in xylene at 25°C (XS_B), the amount of the fraction XS_B being referred to the weight of (B); and

[0030] C) 30-60% by weight; preferably 35-55% by weight; more preferably 40-50 % by weight of a terpolymer of ethylene, propylene and 1-butene containing from 45% to 65% by weight preferably from 48 % to 62 % by weight; more preferably from 50 % to 60 % by weight of ethylene units; and from 15% to 38%; preferably from 18 % to 33 % by weight, more preferably from 20 % to 30 % by weight of 1-butene units; and containing from 30% to 85%; preferably from 35% to 50% by weight of a fraction soluble in xylene at 25°C (XS_C), both the amount of ethylene units and of the fraction XS_C being referred to the weight of (C);

[0031] the amounts of (A), (B) and (C) being referred to the total weight of (A) + (B) + (C), the sum of the amount of (A) + (B) + (C) being 100.

[0032] Mineral aggregate component Z1) typically is composed of sand, gravel, limestone, crushed stone, slag, and mixtures thereof. The mineral aggregate particles include calcium based aggregates, for example, limestone, siliceous based aggregates and mixtures thereof.

[0033] Component Z2) comprises bitumen T1) and a polymer composition T2).

[0034] Useful bitumens (T1) include solid, semi-solid or viscous distillation residues of the petroleum refinery process, consisting predominantly of high molecular weight hydrocarbons, the structure of which can be partially altered, for example by oxidation.

[0035] Polymer composition T2) comprises components A), B) and C).

[0036] Component (A) preferably has the melt flow rate (230°C/2.16 kg) ranging between 50 and 200 g/10 min; more preferably between 80 and 170 g/10 min.

[0037] The ethylene homopolymer (B) may contain up to 5% by weight preferably up to 3% by weight of comonomer units. When comonomer units are present, they derive from one or more comonomers selected from C_3 to C_8 alpha-olefins. Specific examples of such alpha-olefin comonomers are propylene, butene-1, pentene-1, 4-methylpentene-1, hexene-1 and octene-1, preferably propylene or 1-butene. Preferably the ethylene homopolymer (B) does not contain additional comonomer units.

[0038] The ethylene homopolymer (B) preferably has a melt flow rate (230°C/2.16 kg) comprised between 0.1 and 50 g/10 min. preferably comprised between 0.1 and 30 g/10 min; more preferably comprised between 0.1 and 10 g/10 min.

[0039] Preferably the ethylene homopolymer (B) may have a density (determined according to ISO 1183 at 23°C) of from 0.940 to 0.965 g/cm^3.

[0040] Components (A)+ (B) blended together preferably have the melt flow rate (230°C/2.16 kg) comprised between 0.1 and 70 g/10 min. preferably between 1 and 50 g/10 min; more preferably between 8 and 40 g/10 min.

[0041] Preferably the polyolefin composition (A)+(B)+(C) has a melt flow rate (230°C/2.16 kg) comprised between 0.5 to 25 g/10min preferably from 0.8 to 20.0g/10min; even more preferably from 1.0 to 18.0g/10min..

[0042] Preferably the xylene soluble fraction at 25° C of the polyolefin composition (A+B+C) has an intrinsic viscosity [η] (measured in tetrahydronaphthalene at 135 °C) comprised between 2.4 and 3.5 dl/g, preferably the intrinsic viscosity is comprised between 2.5 and 3.3 dl/g.

[0043] For the present disclosure, the term "copolymer" means polymer containing two kinds of comonomers, such as propylene and ethylene or ethylene and 1-butene and the term "terpolymer" means polymer containing three kinds of comonomers, such as propylene, ethylene and 1-butene

[0044] It has been found that the polyolefin composition can be prepared by a sequential polymerization, comprising at least three sequential steps, wherein components (A), (B) and (C) are prepared in separate subsequent steps, operating in each step, except the first step, in the presence of the polymer formed and the catalyst used in the preceding step. The catalyst is added only in the first step, however its activity is such that it is still active for all the subsequent steps.

[0045] The polymerization, which can be continuous or batch, is carried out following known techniques and operating in liquid phase, in the presence or not of inert diluent, or in gas phase, or by mixed liquid-gas techniques. It is preferable to carry out the polymerization in gas phase.

[0046] Reaction time, pressure and temperature relative to the polymerization steps are not critical, however it is best if the temperature is from 50 to 100 °C. The pressure can be atmospheric or higher.

[0047] The regulation of the molecular weight is carried out by using known regulators, hydrogen in particular.

[0048] The said polymerizations are preferably carried out in the presence of a Ziegler-Natta catalyst. Typically a Ziegler-Natta catalyst comprises the product of the reaction of an organometallic compound of group 1, 2 or 13 of the Periodic Table of elements with a transition metal compound of groups 4 to 10 of the Periodic Table of Elements (new notation). In particular, the transition metal compound can be selected among compounds of Ti, V, Zr, Cr and Hf and is preferably supported on $MgCl_2$.

[0049] Particularly preferred catalysts comprise the product of the reaction of said organometallic compound of group 1, 2 or 13 of the Periodic Table of elements, with a solid catalyst component comprising a Ti compound and an electron donor compound supported on $MgCl_2$.

[0050] Preferred organometallic compounds are the aluminum alkyl compounds.

[0051] Thus, in a preferred embodiment, the polymer composition of the present invention is obtainable by using a Ziegler-Natta polymerization catalyst, more preferably a Ziegler-Natta catalyst supported on $MgCl_2$, even more preferably a Ziegler-Natta catalyst comprising the product of reaction of:

1) a solid catalyst component comprising a Ti compound and an electron donor (internal electron-donor) supported on $MgCl_2$;

2) an aluminum alkyl compound (cocatalyst); and, optionally,

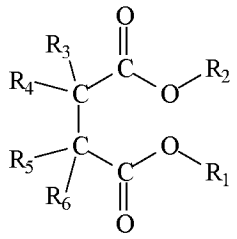
3) an electron-donor compound (external electron-donor).

[0052] The solid catalyst component (1) contains as electron-donor a compound generally selected among the ethers, ketones, lactones, compounds containing N, P and/or S atoms, and mono- and dicarboxylic acid esters.

[0053] Catalysts having the above mentioned characteristics are well known in the patent literature; particularly advantageous are the catalysts described in US patent 4,399,054 and European patent 45977.

[0054] Particularly suited among the said electron-donor compounds are phthalic acid esters, preferably diisobutyl phthalate, and succinic acid esters.

[0055] Suitable succinic acid esters are represented by the formula (I):



(I)

[0056] wherein the radicals R_1 and R_2, equal to or different from each other, are a C_1-C_{20} linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl group, optionally containing heteroatoms; the radicals R_3 to R_6 equal to or different from each other, are hydrogen or a C_1-C_{20} linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl group, optionally containing heteroatoms, and the radicals R_3 to R_6 which are joined to the same carbon atom can be linked together to form a cycle.

[0057] R_1 and R_2 are preferably C_1-C_8 alkyl, cycloalkyl, aryl, arylalkyl and alkylaryl groups. Particularly preferred are the compounds in which R_1 and R_2 are selected from primary alkyls and in particular branched primary alkyls. Examples of suitable R_1 and R_2 groups are methyl, ethyl, n-propyl, n-butyl, isobutyl, neopentyl, 2-ethylhexyl. Particularly preferred are ethyl, isobutyl, and neopentyl.

[0058] One of the preferred groups of compounds described by the formula (I) is that in which R_3 to R_5 are hydrogen and R_6 is a branched alkyl, cycloalkyl, aryl, arylalkyl and alkylaryl radical having from 3 to 10 carbon atoms. Another preferred group of compounds within those of formula (I) is that in which at least two radicals from R_3 to R_6 are different from hydrogen and are selected from C_1-C_{20} linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl

group, optionally containing heteroatoms. Particularly preferred are the compounds in which the two radicals different from hydrogen are linked to the same carbon atom. Furthermore, also the compounds in which at least two radicals different from hydrogen are linked to different carbon atoms, that is R_3 and R_5 or R_4 and R_6 are particularly preferred.

[0059] Other electron-donors particularly suited are the 1,3-diethers, as illustrated in published European patent applications EP-A-361 493 and 728769.

[0060] As cocatalysts (2), one preferably uses the trialkyl aluminum compounds, such as Al-triethyl, Al-triisobutyl and Al-tri-n-butyl.

[0061] The electron-donor compounds (3) that can be used as external electron-donors (added to the Al-alkyl compound) comprise the aromatic acid esters (such as alkylic benzoates), heterocyclic compounds (such as the 2,2,6,6-tetramethylpiperidine and the 2,6-diisopropylpiperidine), and in particular silicon compounds containing at least one Si-OR bond (where R is a hydrocarbon radical).

[0062] Examples of the said silicon compounds are those of formula $R^1_aR^2_bSi(OR^3)_c$, where a and b are integer numbers from 0 to 2, c is an integer from 1 to 3 and the sum (a+b+c) is 4; R^1, R^2 and R^3 are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms optionally containing heteroatoms.

[0063] Useful examples of silicon compounds are $(tert\text{-}butyl)_2Si(OCH_3)_2$, $(cyclohexyl)(methyl)Si(OCH_3)_2$, $(phenyl)_2Si(OCH_3)_2$ and $(cyclopentyl)_2Si(OCH_3)_2$.

[0064] The previously said 1,3- diethers are also suitable to be used as external donors. In the case that the internal donor is one of the said 1,3-diethers, the external donor can be omitted.

[0065] The catalysts may be precontacted with small quantities of olefin (prepolymerization), maintaining the catalyst in supension in a hydrocarbon solvent, and polymerizing at temperatures from room to 60 °C, thus producing a quantity of polymer from 0.5 to 3 times the weight of the catalyst.

[0066] The operation can also take place in liquid monomer, producing, in this case, a quantity of polymer up to 1000 times the weight of the catalyst.

[0067] Moreover component Z2) may contain at least one other type of polymer, hereinafter identified as component (T3), in addition to the polymer composition (T2).

[0068] For example, T2 may comprise, as component (T3), one or more olefinic or nonolefinic polymers. In particular, such additional polymers (T3) can be selected from the group

consisting of amorphous or atactic polymers (in particular amorphous polyolefins such as amorphous polypropylene), styrene-butadiene-styrene (SBS) copolymers, ethylene polyvinyl acetate, low or high density polyethylene, and other polyolefins, in particular isotactic polypropylene and ethylene-propylene random copolymers.

[0069] Generally the said additional polymers (T3) are added, for example, in quantities greater than or equal to 0.5%, preferably from 0.5 to 30%, more preferably from 0.5 to 23% by weight with respect to the weight of T2. Even when the said additional polymers are present, the total quantity of component T2 and T3, in other words the amount of T2+T3, in the bituminous mixture is less than or equal to 40%, preferably 25% by weight with respect to the total weight of the mixture.

[0070] The asphalt product object of the present disclosure can be obtained according the known methods.

[0071] The polymer composition (T2) and all the other described components are incorporated in the bitumen T1) according to known methods.

[0072] Preferably the mixing process is carried out at a temperature from 120 to 250°C; more preferably from 130°C to 180°C.

[0073] The asphalt according to the present disclosure shows improved features in terms of density, voids, stability and flow.

[0074] The following examples are given in order to illustrate, but not limit the present disclosure.

EXAMPLES

CHARACTERIZATIONS

[0075] Xylene-soluble (XS) Fraction at 25 °C

[0073] Solubility in xylene: Determined as follows:

[0074] 2.5 g of polymer and 250 ml of xylene are introduced in a glass flask equipped with a refrigerator and a magnetic stirrer. The temperature is raised in 30 minutes up to the boiling point of the solvent. The resulting clear solution is then kept under reflux and stirred for 30 minutes. The closed flask is then kept for 30 minutes in a bath of ice and water, then in a thermostatic water bath at 25 °C for 30 minutes. The resulting solid is filtered on quick filtering paper. 100 ml of the filtered liquid is poured in a previously weighed aluminum container, which is heated on a heating plate

under nitrogen flow to remove the solvent by evaporation. The container is then kept on an oven at 80 °C under vacuum until a constant weight is obtained. The weight percentage of polymer soluble in xylene at room temperature is then calculated.

[0076] The content of the xylene-soluble fraction is expressed as a percentage of the original 2.5 grams and then, by the difference (complementary to 100%), the xylene insoluble percentage (%);

[0077] XS of components B) and C) have been calculated by using the formula;

[0078] $XS_{tot}=WaXS_A+WbXS_B+WcXS_C$

[0079] wherein Wa, Wb and Wc are the relative amount of components A, B and C, respectively, and (A+B+C=1).

[0080] **Melt Flow Rate (MFR)**

[0081] Measured according to ISO 1133 at 230°C with a load of 2.16 kg, unless otherwise specified.

[0082] **Intrinsic Viscosity (IV)**

[0083] The sample is dissolved in tetrahydronaphthalene at 135 °C and then poured into a capillary viscometer. The viscometer tube (Ubbelohde type) is surrounded by a cylindrical glass jacket; this setup allows for temperature control with a circulating thermostatic liquid. The downward passage of the meniscus is timed by a photoelectric device.

[0084] The passage of the meniscus in front of the upper lamp starts the counter which has a quartz crystal oscillator. The meniscus stops the counter as it passes the lower lamp and the efflux time is registered: this is converted into a value of intrinsic viscosity through Huggins' equation (Huggins, M.L., J. Am. Chem. Soc., 1942, 64, 2716) provided that the flow time of the pure solvent is known at the same experimental conditions (same viscometer and same temperature). One single polymer solution is used to determine [η].

[0085] **Comonomer (C_2 and C_4) Content**

[0086] The content of comonomers was determined by infrared (IR) spectroscopy by collecting the IR spectrum of the sample vs. an air background with a Fourier transform infrared spectrometer (FTIR). The instrument data acquisition parameters were:

purge time: 30 seconds minimum

collect time: 3 minutes minimum

apodization: Happ-Genzel

resolution: 2 cm-1.

[0087] Sample Preparation - Using a hydraulic press, a thick sheet was obtained by compression molding about 1 g of sample between two aluminum foil sheets. A small portion was cut from the resulting sheet to mold a film. The film thickness was set in order to have a maximum absorbance of the CH2 absorption band at ~720 cm-1 of 1.3 a.u. (% Transmittance > 5%). The molding conditions were carried out at a temperature of about 180 ± 10 °C (356 °F) and a pressure of about 10 kg/cm2 (142.2 psi) for about one minute. The pressure was then released, the sample was removed from the press and cooled to room temperature. The spectrum of the pressed film sample was recorded as a function of absorbance vs. wavenumbers (cm-1). The following measurements were used to calculate ethylene (C2) and 1-butene (C4) contents:

[0088] Area (At) of the combination absorption bands between 4482 and 3950 cm-1, which is used for spectrometric normalization of film thickness.

[0089] Area (AC2) of the absorption band due to methylenic sequences (CH2 rocking vibration) in a range of 660-790 cm-1 after a proper digital subtraction of an isotactic polypropylene (IPP) and a C2C4 references spectrum.

[0090] The factor of subtraction (FCRC4) between the spectrum of the polymer sample and the C2C4 reference spectrum: The reference spectrum is obtained by performing a digital subtraction of a linear polyethylene from a C2C4 copolymer in order to extract the C4 band (ethyl group at ~771 cm-1).

[0091] The ratio AC2/At is calibrated by analyzing ethylene-propylene standard copolymers of known compositions, as determined by NMR spectroscopy.

[0092] The assignments of the spectra, triad distribution and composition were made according to Kakugo ("Carbon-13 NMR determination of monomer sequence distribution in ethylene-propylene copolymers prepared with δ-titanium trichloride- diethylaluminum chloride," M. Kakugo, Y. Naito, K. Mizunuma and T. Miyatake, Macromolecules, 1982, 15, 1150).

[0093] In order to calculate the ethylene (C2) and 1-butene (C4) content, calibration curves were obtained by using samples of known amounts of ethylene and 1-butene that were detectable by 13C NMR.

[0094] Calibration for ethylene – A calibration curve was obtained by plotting AC2/At versus ethylene molar percent (%C2m), and the coefficients aC2, bC2 and cC2 were then calculated via linear regression.

[0095] Calibration for 1-butene – A calibration curve was obtained by plotting FCRC4/At versus butane molar percent (%C4m), and the coefficients aC4, bC4 and CC4 were then calculated via linear regression.

[0096] The spectra of the unknown samples are recorded and then (At), (AC2) and (FCRC4) of the unknown sample are calculated.

[0097] The ethylene content (% molar fraction C2m) of the sample was calculated as follows:

$$\%C2m = -b_{C2} + \frac{\sqrt{b_{C2}^2 - 4 \cdot a_{C2} \cdot (c_{C2} - \frac{A_{C2}}{A_t})}}{2 \cdot a_{C2}}$$

[0098] The 1-butene content (% molar fraction C4m) of the sample was calculated as follows:

$$\%C4m = -b_{C4} + \frac{\sqrt{b_{C4}^2 - 4 \cdot a_{C4} \cdot (c_{C4} - \frac{FCR_{C4}}{A_t})}}{2 \cdot a_{C4}}$$

[0099] where aC4, bC4, cC4 aC2, bC2, cC2 are the coefficients of the two calibrations.

Changes from mol% to wt% are calculated by using molecular weights of the compound(s).

[0100] Amount (wt%) of comonomer of components B-C are calculated by using the following relationship:

[0101] $Com_{tot}=WaCom_A+WbCom_B+WcCom_C$

[0102] wherein Wa, Wb and Wc are the relative amount of components A, B and C, respectively, and (A+B+C=1).

[0103] Com_{tot}, Com_A, Com_B and ComC are the amounts of comonomer in the total composition (tot) and in components A-C.

[0104] Example 1 - Preparation of the Polyolefin Composition component T2

[0105] Catalyst precursor:

[0106] The solid catalyst component used in the polymerization was a Ziegler-Natta catalyst component supported on magnesium chloride ($MgCl_2$) containing titanium and diisobutylphthalate as an internal donor and prepared as follows. An initial amount of microspheroidal

$MgCl_2 \cdot 2.8C_2H_5OH$ was prepared according to Example 2 of U.S. Pat. No. 4,399,054, but operating at 3,000 rpm instead of 10,000 rpm. The resulting adduct was subjected to thermal dealcoholation at increasing temperatures from 30-130 °C in a nitrogen current until the molar alcohol content per mol of Mg was about 1.16. Into a 1000 mL four-necked round flask, purged with nitrogen, 500 mL of $TiCl_4$ were introduced at 0 °C. While stirring, 30 grams of the microspheroidal $MgCl_2 \cdot 1.16C_2H_5OH$ adduct (prepared as described above) were added. The temperature was raised to 120 °C and kept at this value for 60 minutes. During the temperature increase, an amount of diisobutylphthalate was added to produce a Mg/ diisobutylphthalate molar ratio of about 18. After 60 minutes, the stirring was stopped, the liquid siphoned off and the treatment with TiCl4 was repeated at 100 °C for 1 hour in the presence of an amount of diisobutylphthalate to produce a Mg/ diisobutylphthalate molar ratio of about 27. The stirring was then stopped, the liquid siphoned off and the treatment with $TiCl_4$ was repeated at 100 °C for 30 min. After sedimentation and siphoning at 85 °C, the solid was washed six times with anhydrous hexane (6 x 100 ml) at 60 °C.

[0107] Catalyst system and prepolymerization:

[0108] Before introducing it into the polymerization reactors, the solid catalyst component described above was contacted at 30 °C for 9 minutes with aluminum triethyl (TEAL) and dicyclopentyldimethoxysilane (DCPMS) at a TEAL/DCPMS weight ratio of about 15 and in such a quantity that the TEAL/solid catalyst component weight ratio was about 4.

[0109] The catalyst system was then subjected to prepolymerization by maintaining it in a liquid propylene suspension at 50 °C for about 75 minutes before introducing it into the first polymerization reactor.

[0110] Polymerization

[0111] The polymerization was carried out in continuous mode in a series of three gas-phase reactors equipped with devices to transfer the product from the first reactor to the second one. A propylene-based polymer (A) was produced in the first gas phase polymerization reactor by feeding the prepolymerized catalyst system, hydrogen the molecular weight regulator) and propylene, all in the gas state, in a continuous and constant flow. The propylene-based polymer (A) coming from the first reactor was discharged in a continuous flow and, after having been purged of unreacted monomers, was introduced, in a continuous flow, into the second gas phase reactor, together with quantitatively constant flows of hydrogen and ethylene, all in the gas state. In the second reactor a copolymer of ethylene (B) was produced. The product coming from the second reactor was

discharged in a continuous flow and, after having been purged of unreacted monomers, is introduced, in a continuous flow, into the third gas phase reactor, together with quantitatively constant flows of hydrogen, ethylene and propylene, all in the gas state. In the third reactor an ethylene-propylene polymer (C) was produced. Polymerization conditions, molar ratio of the reactants and compositions of the resulting copolymers are shown in Table 1. The polymer particles exiting the third reactor were subjected to a steam treatment to remove the reactive monomers and volatile substances and then dried. Thereafter the polymer particles were mixed with a stabilizing additive composition in a twin screw extruder Berstorff ZE 25 (length/diameter ratio of screws: 34) and extruded under a nitrogen atmosphere in the following conditions:

Rotation speed: 250 rpm;

Extruder output: 15 kg/hour;

Melt temperature: 245 °C.

The stabilizing additive composition comprised the following components:

- 0.1% by weight of Irganox® 1010;
- 0.1% by weight of Irgafos® 168; and
- 0.04% by weight of DHT-4A (hydrotalcite);

where all percentage amounts refer to the total weight of the polymer and stabilizing additive composition.

[0112] Irganox® 1010 is 2,2-bis[3-[,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl)-1-oxopropoxy]methyl]-1,3-propanediyl-3,5-bis(1,1-dimethylethyl)-4-hydroxybenzene-propanoate, and Irgafos® 168 is tris(2,4-di-tert.-butylphenyl)phosphite. The characteristics of the polymer composition, reported in Table 2, are obtained from measurements carried out on the extruded polymer, which constitutes the stabilized ethylene polymer composition according to certain embodiments disclosed herein.

Table 1 – Polymerization conditions

Example		Example 1
1st Reactor – component (A)		
Temperature	°C	60
Pressure	barg	16
H_2/C_3-	mol.	0.16
Split	wt%	20
Xylene soluble of (A) (XS_A)	wt%	4.6

2nd Reactor – component (B)		
Temperature	°C	80
Pressure	barg	18
H_2/C_2-	mol.	1.04
C_4-/(C_2- + C_4-)	mol.	0
C_2-/(C_2- + C_3-)	mol.	0.96
Split	wt%	35
3rd Reactor – component (C)		
Temperature	°C	67
Pressure	barg	16
H_2/C_2-	mol.	0.16
C_3-/(C_2- + C_3-)	mol.	0.42
C_4-/(C_2- + C_4-)		0.41
Split	wt%	45

Notes: C_2- = ethylene (IR); C3- = propylene (IR); C_4- = 1-butene (IR); split = amount of polymer produced in the concerned reactor. * Calculated values.

The features of the polymer of Example 1 are reported in Table 2

Table 2

Example		1
component A		
C_2 content	wt%	0
XSA	wt%	4.6
MFR	g/10 min	110
split	wt%	20
component B		
XSB*	wt%	1.7
C_2 content*	wt%	100
C_4 content*	wt%	0
split	wt%	35
MFR	g/10 min	17.4
Component C		
XSC*	wt%	39.5
C_2 content*	wt%	55.0
C_4 content*	wt%	23
split	wt%	45
total composition		
MFR	g/10 min	0.9
IV on soluble in Xylene at 25°C	dl/g	2.75

C_2 = ethylene ; C_4 = 1-butene;

* calculated

[0113] Bitumen from the polymer of example 1 and comparative example 2

[0114] The polymer of example 1 and comparative example 2 have been blended with bitumen. The blends contain 5% of the polymers of example 1 (T2) and comparative example 2 (T2) and 95% of bitumen (T1). The two compositions are marked as B1 e B2. Comparative example 2 is a commercial polymer ***SBS sold by Kraton for bitumen mixtures***.

[0115] Asphalt

[0116] Samples of different amount of B1 and B2 have been mixed with sand, stone and gravel to obtain asphalt. The feature of the asphalt obtained has measured and the results are reported on table 3.

Table 3

	Amount* wt%	Marshall Flow mm	Density ρ_sea Kg/dm^3	Voids Vv. %void
B1-1	**5.06**	**4.8**	**2.38**	**3.25**
B1-2	**4.58**	3.7	2.38	4.17
B1-3	**4.31**	4.1	2.39	4.17
B1-4	**3.93**	2.6	2.37	6.44
B2-1	**5.15**	8.35	2.39	2.63
B2-2	**4.67**	5.9	2.41	3.00
B2-3	**4.43**	4.6	2.42	3.52
B2-4	**4.01**	4.0	2.39	4.92

*The amounts of B1 and B2 are measured by ligand extraction according to UNI EN 12697 – 1 - 2012 (Bituminous mixtures - Test methods for hot mix asphalt - Part 1: Soluble binder content)

Density has been measured according to EN 12697-5 - 2018;

Voids have bene measured according to EN 12687-8;

Stability and Flow have bene measured according to EN 12697-34 - 2012

CLAIMS

What is claimed is:

1. Asphalt product comprising

Z1) from 90 wt% to 98 wt% of mineral aggregate;

Z2) From 2 wt% to 10 wt% of a bitumen composition comprising:

T1) from 99 wt% to 75 wt% of bitumen , and

T2) from 1 wt% to 25 wt% of polymer composition comprising the following components,

A) 5-35% by weight of a propylene homopolymer containing 10% by weight or less of a fraction soluble in xylene at 25°C (XS_A) the amount of of the fraction XS_A being referred to the weight of A);

B) 20-50% by weight; of an ethylene homopolymer having 5% by weight or less of a fraction soluble in xylene at 25°C (XS_B) referred to the weight of (B); and

C) 30-60% by weight of a terpolymer of ethylene, propylene and 1-butene derived units containing from 45% to 65% by weight of ethylene units; and from 15% to 38% by weight of 1-butene units; and containing from 30% to 85% by weight of a fraction soluble in xylene at 25°C (XS_C), the amount of ethylene units; 1-butene units and the fraction XS_C being referred to the weight of (C);

the amounts of (A), (B) and (C) being referred to the total weight of (A) + (B) + (C), the sum of the amount of (A) + (B) + (C) being 100 wt%.

2. Asphalt product according to claim 1 wherein in component T2):
Component A ranges from 10 % by weight to 30 % by weight;
Component B ranges from 25 % by weight to 45 % by weight; and
Component C ranges from 35 % by weight to 55 % by weight;

3. Asphalt product according to claims 1 or 2 wherein in component T2):
Component A ranges from 15 % by weight to 23 % by weight;
Component B ranges from 30 % by weight to 40 % by weight; and
Component C ranges from 40 % by weight to 50 % by weight.

4. Asphalt product according to anyone of claims 1-3 wherein in component T2) component A) has the fraction soluble in xylene at 25°C (XS_A) of 8 wt% or less.

5. Asphalt product according to anyone of claims 1-3 wherein in component T2) component B) is an ethylene homopolymer having 4 wt% or less of a fraction soluble in xylene at 25°C (XS_B).
6. Asphalt product according to anyone of claims 1-5 wherein in component T2) component C) is terpolymer of ethylene, propylene and 1-butene containing from 48 % to 62 % by weight; of ethylene units; and from 18 % to 33 % by weight of 1-butene units.
7. Asphalt product according to anyone of claims 1-6 wherein in component T2) component (A) has the melt flow rate (230°C/2.16 kg) ranging between 50 and 200 g/10 min.
8. Asphalt product according to anyone of claims 1-7 wherein in component T2) component (B) has the melt flow rate (230°C/2.16 kg) ranging between 0.1 and 70 g/10 min.
9. Asphalt product according to anyone of claims 1-8 wherein component T2) component (A) has the melt flow rate (230°C/2.16 kg) ranging between 80 and 170 g/10 min;.
10. Asphalt product according to anyone of claims 1-9 wherein in component T2) component (B) has the melt flow rate (230°C/2.16 kg) ranging between 0.1 and 30 g/10 min.
11. Asphalt product according to anyone of claims 1-10 wherein component T2) the ethylene homopolymer component (B) has a density (determined according to ISO 1183 at 23°C) of from 0.940 to 0.965 g/cm^3.
12. Asphalt product according to anyone of claims 1-11 wherein component T2) has a melt flow rate (230°C/2.16 kg) comprised between from 0.8 to 20.0g/10min.
13. Asphalt product according to anyone of claims 1-12 wherein T1 ranges from 98 wt% to 80 wt%; and T2 ranges from 2 wt% to 20 wt%.
14. Asphalt product according to anyone of claims 1-12 wherein T1 ranges from 97 wt% to 90 wt%; and T2 ranges from 3 wt% to 10 wt%.
15. Asphalt product according to anyone of claims 1-12 wherein T1 ranges from from 97 wt% to 92 wt%; and T2 ranges from 3 wt% to 8 wt%.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L95/00 C08L23/06 C08L23/12 C08L23/18 C08L23/20
E01C7/18 E01C7/30
ADD.
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)
E01C C08L

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"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

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Date of the actual completion of the international search	Date of mailing of the international search report
16 June 2021	24/06/2021

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	olde Scheper, Bernd

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