Title: COMPOSITIONS OF POLYMERIC ASPHALT EMULSION, PROCESS FOR OBTAINING POLYMERIC ASPHALT EMULSION, USE OF THE SAME IN SURFACES

Abstract: The present invention relates to a composition and utilization of organic chemical compounds and polymers to prepare polymeric asphalt emulsions, as well as the process for obtaining these polymeric asphalt emulsions. The polymeric asphalt emulsions according to the present invention presents better mechanical properties than the conventional asphalt emulsions used in pavements and any other bearing surfaces.
COMPOSITIONS OF POLYMERIC ASPHALT EMULSION, PROCESS FOR
OBTAINING POLYMERIC ASPHALT EMULSION, USE OF THE SAME IN SURFACES

FIELD OF THE INVENTION
The present invention relates to compositions of polymeric asphalt emulsions, characterized by presenting better physical-chemical properties than conventional asphalt emulsions. The present invention relates specifically to compositions of asphalt emulsions containing chemical compounds, polymers and an asphalt binder, which can be used in construction or maintenance of highways, roads, sidewalks, parking lots, airport runways and service roads and any other rolling surfaces.

BACKGROUND OF THE INVENTION
Asphalt emulsions are dispersions containing an oil phase, characterized by an asphalt binder and by an aqueous phase, characterized by water and one or more emulsifying agent as, for example, in a non-restrictive way, primary amines, secondary amines, diamines or polyamines, besides other components, such as acid adjuvants, forming a stable dispersion for a certain period of time after the use of an industrialization process using a mechanical mill.

The particle size of an asphalt emulsion is in the range from 0.1 to 20 microns and an average size of about 1 micron and may vary with changes in the parameters of the production process.

The asphalt emulsions can be applied at room temperature due to its liquid physical state due to the emulsification process, providing reduction on storage, transport and utilization costs, since it is not necessary to maintain these high temperature processes in order to enable the field application.

When an asphalt emulsion comes into contact with an aggregate it begins the process of the emulsion breaking, which consists in the separation of the emulsified asphalt binder from the aqueous phase, allowing the coating of the aggregate with a film of asphalt. The water evaporates and is released to the environment. The breaking of the emulsion occurs by the phenomenon known as coagulation or flocculation of asphalt particles dispersed in the aqueous medium and its rate of breakage depends upon of the chemical composition of the emulsifier and its quantity present in the composition. Breaks can be fast, medium or slow.

It's widely known that polymers can be added to the asphalt binder or to the aqueous phase of the asphalt emulsions, in order to obtain residual asphalt with improved mechanical properties. As an example there is the patent US 5.795.929, which comprises one asphalt composition prepared from bitumen (asphalt), copolymers of styrene and butadiene linear and nonlinear, cross-linking agents and emulsifiers. However, the
modification processes of asphalt binders by those polymers are extremely time consuming and laborious, requiring a long time of stirring with heating and an effective milling process for dispersing such polymers and obtaining a relatively homogeneous polymeric asphalt binder.

Polymers are large molecules formed by chemical bonds of many repeating units chemically known as monomers. Among the mechanical properties of asphalt binders, can be highlighted in a non restrictive way, resistance to wheel tracks, fatigue resistance and crack resistance. In general, conventional asphalt emulsions do not have at the same time all the ideal qualities and the addition of polymers to the asphalt binders or even to the aqueous phase of the asphalt emulsions allows favorably changes in their mechanical properties, forming polymeric asphalt emulsions compositions that have improved mechanical properties compared to conventional asphalt emulsions.

Therefore, the addition of polymers to asphalt binders or to the aqueous phase of the asphalt emulsions is often performed to increase their flexibility and can also increase the cohesion and elastic recovery of asphalt. Examples of polymers commonly used in polymeric asphalt emulsions are: styrene butadiene rubbers, block copolymers of styrene butadiene and natural latex.

Until now, many polymeric asphalt emulsions compositions were made, for example, the patent US 6,706,787 that describes a method for preparing an asphalt emulsion composition comprised by the preparation of a synthetic polymer aqueous emulsion and an asphalt mixture and mixing the aqueous emulsion asphalt/polymer with reclaimed rubber particles wherein the ratio of polymer/rubber particles is from about 1:2 to about 1:20 by weight, respectively, at room temperature. The final composition may also contain one or more solids selected from a rheological agent, gilsonite, carbon black, active clay surface and polymer fibers, and mixtures of these. Another example is the patent US 5,811,477, which describes a method for preparing an asphalt emulsion composition characterized by mixing an aqueous asphalt emulsion, water, rubber latex and a solid mixture composition comprising reclaimed rubber particles that passes through a mesh number 40 U.S. sieve and one or more solid additions selected from the group consisting of a rheological agent, gilsonite, carbon black, active clay surface and polymer fibers and mixtures of these, and wherein the ratio of latex rubber/rubber particles is from about 1:1 to about 1:10 by weight, respectively, and mixing the components at substantially room temperature. However, none of these is similar to the composition as claimed by the present invention. We discovered a organic chemical compound capable of accelerate the reaction of polymers based in compositions of ethylene vinyl acetate, polyethylene, alpha-polyolefins, olefin polymers functionalized by epoxy or carboxyl
groups and/or mixtures thereof for modifying the asphalt binder and that is totally compatible with the asphalt emulsion formulations, allowing to improve the elastic recovery and the other mechanical properties of the asphalt binder used in the asphalt emulsions production process.

The patent WO2010/039998 describes an acid modified asphalt binder, which is combined with a solution of an emulsifier to produce emulsified asphalt binder. The acid modified asphalt binder may be formed by combining an asphalt binder, an acid based on phosphorous acid and, optionally, a modifying polymer. The emulsifier solution can be produced by forming an aqueous solution of an amine and a phosphor based acid, which form an aqueous solution comprising an amine phosphate. The emulsified asphalt binder can be combined with an aggregate to form a paving material. This patent discloses the use of a phosphorus-based acid in order to obtain an acid modified asphalt binder, which is not a object of the present invention.

The patent US 7,951,858 discloses about new bituminous products, as well as new aqueous emulsions of bituminous products, mixtures of these products with coated granules, useful for application of sealing, construction and maintenance of pavements, driveways and sidewalks, floors, bike paths, parking lots and runways. It cites the use of random or block copolymer(s) of ethylene oxide/propylene oxide but it does not contemplate the use of such polymers in order to increase the elastic recovery of the asphalt binders, a mechanical property very desirable in polymeric asphalt binders and polymeric asphalt emulsions.

The presence of one or more organic compounds in the asphalt according to the present invention can also increase the aggregates coating film by the polymer modified asphalt binder and improve the workability of the asphalt mixture during spreading and compacting.

**OBJECT OF INVENTION**

It is an object of this invention to provide a organic chemical formulation to prepare polymeric asphalt emulsions containing polymers based in compositions of ethylene vinyl acetate, polyethylene, alpha-polyolefins, olefin polymers functionalized by epoxy or carboxyl groups and/or mixtures thereof. This formulation is capable of increasing the rate of reaction of said polymers with an asphalt binder, resulting in the increase of elastic recovery of the asphalt binder that will be used to prepare polymeric asphalt emulsions with improved mechanical properties.

It is also an object of the present invention the process of using the organic chemical compound to prepare polymeric asphalt emulsions based on compositions of ethylene vinyl acetate, polyethylene, alpha-polyolefins, olefin polymers functionalized by
epoxy or carboxyl groups and/or mixtures thereof.

These polymeric asphalt emulsion compositions obtained by the said process can be used in construction or maintenance of highways, roads, sidewalks, parking lots, airport runways and service roads and any other rolling surfaces.

SUMMARY OF THE INVENTION

The present invention relates to a polymer modified asphalt, which uses polymers based on compositions of ethylene vinyl acetate, polyethylene, alpha-polyolefins, olefin polymers functionalized by epoxy or carboxyl groups and/or mixtures thereof together with an organic chemical compound capable of accelerate the reaction between those polymers with the asphalt binder and provide compatibility of the polymer modified asphalt with an emulsification process, obtaining at the end an polymeric asphalt emulsion stable and ready for use.

The present invention relates to the use of a polymer added to the asphalt binder, a catalyst agent and a subsequent emulsification process, obtaining at the end an polymeric asphalt emulsion but, differently than which is presented in the current state of the art, uses one or more polymers based on compositions of ethylene vinyl acetate, polyethylene, alpha-polyolefins, olefin polymers functionalized by epoxy or carboxyl groups and/or mixtures thereof, which are reacted with a organic chemical compound, with substantial advantages, both in mechanical and physical performance and cost reduction.

The present invention includes the organic chemical formulation, the resulting polymeric asphalt emulsion and also includes the components formulation and emulsification processes. These polymers asphalt emulsions compositions can be anionic, cationic, nonionic or amphoterically and fast, medium or slow settings.

Composition of polymeric asphalt emulsion, comprising one polymer modified asphalt; one or more organic chemical compounds; emulsifiers; and water; wherein said composition is capable of accelerate the reaction between polymers of ethylene vinyl acetate, polyethylene, alpha-polyolefins, olefin polymers functionalized by epoxy or carboxyl groups and/or mixtures thereof and the asphalt binder to be used as the bituminous phase of polymeric asphalt emulsions.

Process to obtain polymeric asphalt emulsions comprising the addition to the asphalt in solid, molten, dissolved or dispersed state of one or more organical chemical compounds; addition to the asphalt in solid, molten, dissolved or dispersed state of one or more polymers of ethylene vinyl acetate, polyethylene, alpha-polyolefins, olefin polymers functionalized by epoxy or carboxyl groups and/or mixtures thereof; optionally, add one or more components in the asphalt chosen among adhesion promoters agents, fluxing
agents, talc, carbon black and used scrap tires powder where the order of addition between them and those organic chemical compounds or mixture of those is irrelevant; mix, preferably under mild agitation, by any mechanical process during a period of time and certain temperature; preparing the aqueous phase and adjust the temperature; add one or more components in the aqueous phase chosen among emulsifiers and acid adjuvants, where the order of addition between them is irrelevant; adjust the temperature of the obtained mixture to a certain range; perform the mechanical milling of the previously obtained mixtures by any mechanical means during a period of time and obtain a polymeric asphalt emulsion ready for use.

The polymeric asphalt composition described in the present invention has the advantage of providing, besides the increase of reaction speed between polymers and the asphalt binder, the compatibility between the polymer modified asphalt binder with the emulsification process, because it does not use inorganic acids as polymers catalysts, obtaining a stable polymeric asphalt emulsion ready for use.

The presente invention also relates to the use of the polymeric asphalt emulsions in surfaces.

**DETAILED DESCRIPTION OF THE INVENTION**

Asphalt or asphalt binder is manufactured during the distillation and refining petroleum process as a bottom column product. Due to different origins and processes of petroleum refining and distillation, the resulting asphalt can have a wide range of properties and characteristics. In the present invention, the term asphalt does not only refer to the petroleum product obtained by direct distillation or by distillation at low pressures, particularly known as asphalt cement, but also the product coming from the extraction of tar and bituminous sands, synthetic asphalt, tar, petroleum resins and/or paraffinic hydrocarbons and mixtures among them.

Asphalt is widely used in the field of pavement due to various aspects, among them can be mentioned, in a non restrictive manner: acts as a binder, promoting a strong union between aggregates by coating its surface; has high resistance to physical and chemical agents and thus high durability; has waterproofing action; can be used heated, known as hot asphalt or emulsified, known as asphalt emulsion.

In order to adequately cover the stone aggregates, it is necessary that the asphalt binder presents a sufficient low viscosity in order to permit their proper and homogeneous mixing with aggregates, which may be achieved by a heating process, dilution or by a process of emulsifying the asphalt binder.

The emulsification process of the asphalt binder results in obtaining asphalt emulsions, which are characterized by emulsions oil in water (O/W) type and can be
defined as a stable dispersion of water and asphalt, as well as other components. Due to the fact that asphalt has a high viscosity and a nonpolar nature, the asphalt and water does not form an emulsion by simply mixing the two compounds, making it necessary to use an auxiliary component, the emulsifier, so the asphalt emulsion remains stable. The emulsifier acts reducing the surface tension, allowing the globules of asphalt to remain suspended in water to form a mixture stable for a certain period of time after the use of a stirring process by mechanical mill.

The amount of asphalt binder typically used for the preparation of an asphalt emulsion is 60 to 70% by weight and of water is from 30 to 40% by weight, based on the final weight of the asphalt emulsion, though these proportions can vary depending on the specification of the project.

Asphalt emulsions are mostly used at room temperature, without the application of heat, which, besides providing energy savings both in storage, transportation and application, has a great environmental advantage as well as in occupational health, because there is not emissions of polycyclic aromatic hydrocarbons and other toxic known to be compounds present in the asphalt binder during its use at high temperatures.

In road applications with increasing traffic volume conditions and increasing vehicle weight per rolling axle, heavy traffic corridors and extreme climatic variations, has been increasingly necessary to use modifiers of the properties of asphalt, in order to improve its performance and durability. Thus, it is widely known that polymers can be added to the asphalt binder, in order to obtain asphalt mixtures with improved mechanical properties. Among the mechanical properties of asphalt binders may be mentioned the resistance to tracks wheels, fatigue and cracking.

Polymers are macromolecules formed by the chemical bond of several repeating units chemically termed monomers. The homopolymers are comprised of only one type of monomer and copolymers have at least two monomers in their structure. In general, conventional asphalt binders do not have both the set of ideal qualities and the addition of polymers to these asphalt binders allows favorably modify its mechanical properties, forming polymer modified asphalt compositions having improved mechanical properties relative to unmodified asphalt binders.

Therefore, the addition of polymers to asphalt binders is often performed to increase its flexibility, and can also increase its cohesion and elastic recovery. Examples of polymers commonly used in asphalt modification are: styrene butadiene rubbers, block copolymers of styrene-butadiene, styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS), styrene-ethylene-butadiene-styrene (SEBS), acrylonitrile-butadiene-styrene (ABS) copolymers of ethylene vinyl acetate, polyethylene, alpha-polyolefins, olefin
polymers functionalized by epoxy or carboxyl groups such as terpolymers of ethylene/alkyl acrylate/glycidyl methacrylate, terpolymers of ethylene/n-butyl acrylate/glycidyl methacrylate, copolymers of ethylene alkyl acrylate and/or mixtures thereof.

It is of great interest that polymer modified asphalts be subjected to an emulsification process, resulting in an polymeric asphalt emulsion which, due to its liquid physical state obtained by the emulsification process, provides cost savings in storage, transport and utilization, as it is not necessary to maintain high temperatures in these processes so as to enable the coating of the aggregates, so these can be used at room temperature and thus obtaining at the end an asphalt mixture with improved mechanical properties.

Several attempts have been made to emulsify polymer modified asphalt binders based on polymer compositions of ethylene vinyl acetate, polyethylene, alpha-polyolefins, olefin polymers functionalized by epoxy or carboxyl groups and/or mixtures thereof, but the incompatibility between the inorganic acids used to accelerate the reaction of those polymers with asphalt and the traditionally used emulsifiers into the emulsification process resulted in unstable and heterogeneous asphalt emulsions, with sedimentation phenomena and consequent break, preventing the practical application of the same.

The organic chemical compounds according to the present invention are capable of promote the reaction of polymers based on compositions of ethylene vinyl acetate, polyethylene, alpha-polyolefins, olefin polymers functionalized by epoxy or carboxyl groups and/or mixtures thereof with asphalt binders thereby obtaining a modified asphalt binder with improved physical and mechanical properties, resulting in a significant increase in elastic recovery and softening point, as well as a reduction in the penetration of modified asphalt to be used as bituminous phase of the polymeric asphalt emulsion.

Furthermore, these organic chemical compounds according to the present invention shown to be fully compatible with the anionic, cationic, nonionic or amphoteric emulsifiers, as well presented total compatibility with the emulsification processes, allowing to obtain stable and homogeneous polymeric asphalt emulsions ready for use.

The compositions described in this invention comprise at least one organic chemical compound, which is the result of reaction between:

(i) a functional group among the compounds (1) to (2) or mixture thereof:

\[
\begin{align*}
R1 & \quad N \\
N & \quad R1
\end{align*}
\]
wherein

R₁ represents H, H₂, CH₃, CH₂CH₃, (CH₂CH₂NH)ₓH, (CH₂CH₂OH)ᵧ or
CH₂CH₂NHCH₂CH₂OH;

x = 1 to 10;
y = 1 to 3;

(ii) at least one fatty acid or mixture of fatty acids and/or an fatty acid ester and/or
fatty acid chloride;

Certain molecules having at least one functional group from (1) to (2), correspond,
but not as a restricted form, to N,N-diethylethanolamine (DEEA), N,N-
dimethylethanolamine (DMEA), N-methyldiethanolamine (MDEA), N-methylethanolamine
(NMEA).

Examples of fatty acids that may be used for this reaction are the saturated or
unsaturated carboxylic acids with at least 5 carbon atoms, such as linear monoacids like
lauric, myristic, oleic, stearic, linoleic or linolenic acids, branched monoacids like 2-ethyl
hexanoic acid, linear diacids such as glutaric, adipic, pimelic, suberic, azelaic, sebacic,
undecanedioic, dodecanedioic, brassylic, tetradecanedioic, pentadecanedioic, thapsic, or
octadecanedioic acids, branched diacids like 3,3-dimethylglutaric acid and undecylenic,
myristoleic, palmitoleic, oleic, linoleic, linolenic, ricinoleic, eicosenoic or docosenoic acids
(found on pine, corn, sunflower, soybean, raisin seeds, linen or jojoba) or animal origin
like eicosapentaenoic or docosahexaenoic acids (found in fish oils).

The reaction of fatty acids with compounds from (1) to (2), for example, alkyl
amines, amines, amino alcohols, secondary alkyl alkanolamides or amidoamines, results
in soap surfactants (for example N,N-diethyl ethanol ammonium stearate). Another
example of fatty acids reaction with compounds from (1) to (2), at higher temperatures,
are secondary alkyl alkanolamines (for example N-methylethanolamine) that reacts with
fatty acids in equimolar proportions, resulting in amide, also with significant amounts of
amine ester and amide. One more example are the tertiary alkyl alkanolamines, that
reacts with fatty acids and results in amine esters only.

In one aspect, this invention relates to the process for preparing polymeric asphalt
emulsions comprising at least the use of an organic chemical compound capable of
accelerate the reaction of polymers of ethylene vinyl acetate, polyethylene, alpha-
polyolefins, olefin polymers functionalized by epoxy or carboxyl groups and/or mixtures
thereof with asphalt binders promoting a significant increase in elastic recovery and softening point, as well as a reduction in the penetration of modified asphalt to be used as bituminous phase of the polymeric asphalt emulsion, comprising the following steps:

(i) addition to the asphalt in solid, molten, dissolved or dispersed state of one or more organic chemical compounds capable of accelerate the reaction between the polymer and the asphalt binder;

(ii) addition to the asphalt in solid, molten, dissolved or dispersed state of one or more polymers of ethylene vinyl acetate, polyethylene, alpha-polyolefins, olefin polymers functionalized by epoxy or carboxyl groups where the order of addition between them and those organic chemical compounds or mixture of those is irrelevant;

(iii) Optionally, add one or more components in the asphalt, such as adhesion promoters agents, fluxing agents, talc, carbon black and used scrap tires powder, where the order of addition between them and those organic chemical compounds or mixture of those is irrelevant;

(iv) Mix the components of steps (i), (ii) and (iii), preferably under mild agitation, by any mechanical process during a period of time sufficient to obtain a homogeneous mixture, and this period of time usually varies from 1 minute to several hours, normally from 1 to 120 minutes, with temperatures between 120°C to 190°C;

(v) Prepare the aqueous phase and adjust the temperature between 30 to 90 °C, preferably between 40 to 50 °C;

(vi) Add one or more components in the aqueous phase chosen between the emulsifiers and acid adjuvants, where the order of addition between them is irrelevant;

(vii) Adjust the temperature of the obtained mixture in the step (iv) to a range between 120°C to 190°C, preferably between 150°C to 160°C;

(viii) Perform the mechanical milling of the mixtures obtained in steps (vi) e (vii) by any mechanical way for a period of time sufficient to obtain a homogeneous mixture; and

(ix) Obtain a polymeric asphalt emulsion ready for use.

Non restrictives examples of asphalt emulsions which can be obtained through the process described above are anionic, cationic, nonionic or amphoteric emulsions of the type fast, medium or slow settings, microsurfacing emulsions and emulsified asphalt slurry seal.

Non limiting examples of the anionic emulsifiers that can be used in the present invention includes sarcosinates, alkyl sulfates, alkyl ether sulfates, ether sulfosuccinates, alkyl ether phosphates, alkyl sulfonates, alkyl isethionates and all its salts and derivatives; sulfonic acids, tall oil fatty acids, fatty acids and their salts; salts of esters of sulfur fatty acid and mixture between them.
Non restrictives examples of cationic emulsifiers that can be used in the present invention includes alkylamines salts, alkanolamines, quaternary ammonium salts, amine oxides, polyethyleneamines, ligninamines, fatty amines, fatty diamines, fatty polyamines and adducts of these compounds with ethylene oxide and/or propylene oxide and mixture of these. The cationic emulsifiers are highly polar and thus have a higher affinity with water, providing asphalt emulsions with greater stability when mixed with the aggregates.

Non limiting examples of the amphoteric emulsifiers that can be used in the present invention includes lignosulfonates and their salts, betaines and their derivatives, glycinates and their derivatives and mixture of these.

Non restrictives examples of nonionic emulsifiers that can be used in the present invention includes alkylphenols and adducts of these compounds with ethylene oxide and/or propylene oxide; amine oxides and mixtures between them.

One or more organic chemical compounds in accordance with the present invention can be added to a continuous flow of the asphalt by any types of continuous process, for example, using a direct injection and/or a static mixer in the production process.

The addition of one or more organic chemical compounds may occur before, after or concurrently with the other necessary or desired components for modification of asphalt binder such as adhesion promoters or fluxing agents.

The amount of one or more organic chemical compounds according to the present invention must be added in the range from 0.0001% to 10.0% based on total weight of the polymer modified asphalt, preferably from 0.01% to 1.0%.

Non limitative examples of polymers used in the present invention are: copolymers of ethylene vinyl acetate, polyethylene, alpha-polyolefins, olefin polymers functionalized by epoxy or carboxyl groups such as terpolymers of ethylene/alkyl acrylate/glycidyl methacrylate, terpolymers of ethylene/n-butyl acrylate/glycidyl methacrylate, copolymers of ethylene alkyl acrylate and/or mixtures thereof for modifying the asphalt binder to be used in asphalt emulsions. The polymer composition according to the present invention can be present in the asphalt in any quantity sufficient to achieve improvements in mechanical properties of asphalt binders and/or polymeric asphalt emulsions, preferably in amounts of 0.001% to 10% based on total weight of the asphalt binder.

Can be highlighted among the acid adjuvants, in a non restricted way, sulfuric acid, hydrochloric acid, nitric acid, boric acid, phosphonic acids, anhydrides of these acids and mixtures thereof. In a non-limiting modality, the proportion of acid adjuvants is preferably in the range of 0.01% to 1.0% based on total weight of the polymeric asphalt emulsion.
Among the fluxing agents mentioned above, may be highlighted in a non-restrictive way, epoxidized fatty acids from vegetable or animal sources; esterified fatty acids of vegetable or animal sources, petroleum cuts with aromatic, naphthenic-aromatic, naphthenic-paraffinic and paraffinic character.

The main application for the polymeric asphalt emulsions presented in this invention, but not restricted, is the construction or maintenance of highways, roads, sidewalks, parking lots, airport runways, service roads, waterproof membranes, aged asphalt mixtures recycling and any other bearing surfaces.

Thus, and in accordance with another aspect, the invention relates to a surface that is coated in whole or in part with a asphalt mixture comprising a polymeric asphalt emulsion and/or aggregates and, as described above, said surface is generally a rolling surface, such as roads, parking lots, bridges, roads, highways, airport runways or any similar rolling surface, and also any surface requiring asphalt coating or asphalt, such as walks, sidewalks, parks, roofs, walls and similar.

Below are described Examples of application of the present invention, non-limitative, in an only illustrative character:

**EXAMPLE 1**

A. Preparation of the polymer modified asphalt binder

A.1) 656 Kg of asphalt cement (CAP 50/70) were heated at 165°C - 170°C in an industrial mixing tank;

A.2) Added 12.3 kg of a acrylic ester, ethylene and glycidyl methacrylate terpolymer;

A.3) The mixture was subjected to mechanical stirring for 1.5 hours under constant temperature of 160°C;

A.4) Added 1.7 kg of the organic chemical product GEMUL® XR, provided by the same applicant of this invention patent;

A.5) The obtained mixture was subjected to mechanical stirring for 30 minutes under the temperature of 160°C;

A.6) The obtained mixture was reserved and kept under temperature of 160°C.

After the polymer modified asphalt binder manufacturing process, tests were carried out as described below with the results:

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Unity</th>
<th>Method</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration (100g, 5s, 25°C)</td>
<td>0.1mm</td>
<td>NBR 6576</td>
<td>51.3</td>
</tr>
<tr>
<td>Softening Point</td>
<td>°C</td>
<td>NBR 6550</td>
<td>54</td>
</tr>
<tr>
<td>Brookfield Viscosity at 135°C, SP 21, 20 rpm</td>
<td>cP</td>
<td>NBR 15184</td>
<td>963</td>
</tr>
<tr>
<td>Brookfield Viscosity at 150°C, SP 21, 50 rpm</td>
<td>cP</td>
<td>NBR 15184</td>
<td>462</td>
</tr>
</tbody>
</table>
Table I: tests results performed on the polymer modified asphalt binder prepared in steps A.1 to A.6

<table>
<thead>
<tr>
<th>Test</th>
<th>Unity</th>
<th>Method</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saybolt-Furol Viscosity, at 50°C</td>
<td>s</td>
<td>NBR 14491</td>
<td>137</td>
</tr>
<tr>
<td>Sedimentation</td>
<td>% weight</td>
<td>NBR 6570</td>
<td>0.9</td>
</tr>
<tr>
<td>Sieve test 0,84 mm</td>
<td>% weight</td>
<td>NBR 14393</td>
<td>0.03</td>
</tr>
<tr>
<td>Particle Charge</td>
<td>-</td>
<td>NBR 6567</td>
<td>Positive</td>
</tr>
<tr>
<td>PH</td>
<td></td>
<td>NBR 6299</td>
<td>2.3</td>
</tr>
<tr>
<td>Dry Residue</td>
<td>% weight</td>
<td>NBR 14376</td>
<td>67.3</td>
</tr>
<tr>
<td>Demulsibility</td>
<td>% weight</td>
<td>NBR 6569</td>
<td>70</td>
</tr>
</tbody>
</table>
EXAMPLE 2

A. Preparation of the polymer modified asphalt binder

A.1) 978 Kg of asphalt cement (CAP 50/70) were heated at 165°C - 170°C in a industrial mixing tank;

A.2) Added 19 kg of a acrylic ester, ethylene and glycidyl methacrylate terpolymer;

A.3) The mixture was subjected to mechanical stirring for 1.5 hours under constant temperature of 160°C;

A.4) Added 3.0 kg of the organic chemical product GEMUL® XR, provided by the same applicant of this invention patent;

A.5) The obtained mixture was subjected to mechanical stirring for 30 minutes under the temperature of 160°C;

A.6) The obtained mixture was reserved and kept under temperature of 160°C.

After the polymer modified asphalt binder manufacturing process, tests were carried out as described below with the results:

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Unity</th>
<th>Method</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration (100g, 5s, 25°C)</td>
<td>0.1mm</td>
<td>NBR 6576</td>
<td>50</td>
</tr>
<tr>
<td>Softening Point</td>
<td>°C</td>
<td>NBR 6560</td>
<td>56</td>
</tr>
<tr>
<td>Brookfield Viscosity at 135°C, SP 21, 20 rpm</td>
<td>cP</td>
<td>NBR 15184</td>
<td>1015</td>
</tr>
<tr>
<td>Brookfield Viscosity at 150°C, SP 21, 50 rpm</td>
<td>cP</td>
<td>NBR 15184</td>
<td>481</td>
</tr>
<tr>
<td>Brookfield Viscosity at 177°C, SP 21, 100 rpm</td>
<td>cP</td>
<td>NBR 15184</td>
<td>171</td>
</tr>
<tr>
<td>Flash Point</td>
<td>°C</td>
<td>NBR 11341</td>
<td>240</td>
</tr>
<tr>
<td>Phase separation test</td>
<td>°C</td>
<td>NBR 15166</td>
<td>1.5</td>
</tr>
<tr>
<td>Elastic Recovery, 25°C, 20 cm</td>
<td>%</td>
<td>NBR 15086</td>
<td>79</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Unity</th>
<th>Method</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tests in RTFOT Residue at 163°C, 85 minutes:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass change</td>
<td>%</td>
<td>NBR 15235</td>
<td>0.21</td>
</tr>
<tr>
<td>Softening Point change</td>
<td>°C</td>
<td>NBR 6560</td>
<td>+4.0</td>
</tr>
<tr>
<td>Percent of the Original Penetration</td>
<td>%</td>
<td>NBR 6576</td>
<td>75</td>
</tr>
<tr>
<td>Percent of the Original Elastic Recovery at 25°C</td>
<td>%</td>
<td>NBR 15086</td>
<td>85</td>
</tr>
</tbody>
</table>

Table III: tests results performed on the polymer modified asphalt binder prepared in steps A.1 to A.6
B) Preparation of the aqueous phase

B.1) Weighed 6.5 kg of water at room temperature;

B.2) Slowly added, under stirring, 3.0 Kg of industrial hydrochloric acid 33%;

B.3) The obtained solution was heated until 40°C;

B.4) 2.5 Kg of tallow fatty diamine was added;

B.5) pH of the aqueous phase was not adjusted because it presented the measuring value of to 1.2;

C) Preparation of the RR-1C-E (ref. ANP) polymeric asphalt emulsion

C.1) The temperatures of the polymer modified asphalt prepared according to item A were adjusted to 150°C e of the aqueous phase prepared according to item B to 41°C;

C.2) A milling under pressure in a colloidal Mill was started with the polymer modified asphalt prepared according to item A and the aqueous phase prepared according to item B;

C.3) Was measured at the mill outlet the temperature of the polymeric asphalt emulsion produced and was obtained as a result the temperature of 82°C;

C.4) The same temperature parameters of the aqueous and asphalt phases as well as the mill pressure were maintained constant throughout the manufacturing process;

C.5) Obtained a homogeneous polymeric asphalt emulsion, stable and ready for use.

After the polymeric asphalt emulsion manufacturing process, tests were carried out as described below with the results:

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Unity</th>
<th>Method</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saybolt-Furol Viscosity, at 50°C</td>
<td>s</td>
<td>NBR 14491</td>
<td>18</td>
</tr>
<tr>
<td>Sedimentation</td>
<td>% weight</td>
<td>NBR 6570</td>
<td>1.2</td>
</tr>
<tr>
<td>Sieve test 0.84 mm</td>
<td>% weight</td>
<td>NBR 14393</td>
<td>0.05</td>
</tr>
<tr>
<td>Particle Charge</td>
<td>-</td>
<td>NBR 6567</td>
<td>Positive</td>
</tr>
<tr>
<td>pH</td>
<td>-</td>
<td>NBR 6299</td>
<td>2.0</td>
</tr>
<tr>
<td>Dry Residue</td>
<td>% weight</td>
<td>NBR 14376</td>
<td>62.3</td>
</tr>
<tr>
<td>Demulsibility</td>
<td>% weight</td>
<td>NBR 6569</td>
<td>70</td>
</tr>
</tbody>
</table>

Tests for the emulsion residue obtained by ABNT NBR 14896:

| Penetration (100g, 5s, 25°C) | 0.1mm | NBR 6576 | 50 |
| Softening Point              | °C    | NBR 6560 | 59 |
| Brookfield Viscosity at 135°C, SP 21, 20 rpm | cP | NBR 15184 | 1008 |
| Elastic Recovery, 25°C, 20 cm | % | NBR 15086 | 76 |

Table IV: tests results performed on the polymeric asphalt emulsion prepared in steps C.1 to C.5
CLAIMS

1. Polymeric asphalt compositions, characterized by:
   (i) polymer modified asphalt;
   (ii) one or more organic chemical compounds;
   (iii) emulsifiers; and
   (iv) water.

2. Composition according to claim 1, characterized by the organic chemical compounds are composed by:
   (a) The reaction result between one of the compounds among (1) to (2) or mixture thereof:

   \[
   \begin{align*}
   &R_1-N-N-R_1 \quad (1) \\
   &R_1-N \quad (2)
   \end{align*}
   \]

   wherein
   \( R_1 \) represents \( H, H_2, CH_3, CH_2CH_3, (CH_2CH_2NH)_xH, (CH_2CH_2OH)_y \) or \( CH_2CH_2NHCH_2CH_2OH \);
   \( x = 1 \) to 10;
   \( y = 1 \) to 3; and
   (b) at least one fatty acid or mixture of fatty acids and/or an fatty acid ester and/or fatty acid chloride;

3. Compositions according to claim 1, characterized by result in a stable polymeric asphalt emulsion.

4. Compositions according to claim 1, characterized by the polymer modified asphalt be modified by a terpolymer of ethylene, methyl acrylate and glycidyl methacrylate.

5. Compositions according to claim 1, characterized by the polymer modified asphalt be modified by a terpolymer of ethylene, butyl acrylate and glycidyl methacrylate.

6. Compositions according to claim 1, characterized by the polymer modified asphalt be modified by a terpolymer of ethylene, ethyl acrylate and / or 2-ethylhexyl acrylate and glycidyl methacrylate.

7. Compositions according to claim 1, characterized by the polymer modified asphalt be modified by one or more polymers of ethylene vinyl acetate, polyethylene,
alpha-polyolefins, olefin polymers functionalized by epoxy or carboxyl groups or mixtures thereof.

8. Compositions according to claims 1 to 7, characterized by the polymer or mixture of polymers promotes a increase in elastic recovery and softening point, as well as a reduction in the penetration of the modified asphalt.

9. Compositions according to claims 1 and 2, characterized by the amount of one or more organic chemical compounds be in the range of 0.0001% to 10.0% by weight based on total weight of the polymer modified asphalt.

10. Compositions according to claims 1 and 2, characterized by the amount of one or more organic chemical compounds be preferentially in the range of 0.01% a 1.0% by weight based on total weight of the polymer modified asphalt.

11. Compositions according to claim 1, characterized by the emulsifiers be cationic.

12. Compositions according to claim 1, characterized by the emulsifiers be anionic.

13. Compositions according to claim 1, characterized by the emulsifiers be nonionic.

14. Compositions according to claim 1, characterized by the emulsifiers be amphoteric.

15. Compositions according to claims 1 to 14, characterized by comprising additionally aggregates.

16. Compositions according to claim 15, characterized by that the aggregates are not limited in its chemical nature, shape or size and may be the products of quarries, recovered aggregates from the previous asphalt mixtures, milled or recycled asphalt, construction products and mixture of any of the above.

17. Compositions according to claims 1 to 16, characterized by comprising additionally volume of voids.

18. Compositions according to claims 1 to 8, characterized by comprising additionally one or more components in the asphalt chosen among adhesion promoters agents, fluxing agents, talc, carbon black and used scrap tires powder.

19. Process for obtaining polymeric asphalt emulsions, characterized by comprising the following steps:

   (i) Add to the asphalt in solid, molten, dissolved or dispersed state one or more organic chemical compounds;

   (ii) Add to the asphalt in solid, molten, dissolved or dispersed state one or more polymers of ethylene vinyl acetate, polyethylene, alpha-polyolefins, olefin polymers functionalized by epoxy or carboxyl groups or mixtures thereof;
(iii) Optionally, add one or more components in the asphalt selected from adhesion promoters agents, fluxing agents, talc, carbon black and used scrap tires powder, where the order of addition between them and those organic chemical compounds or mixture of those is irrelevant;

(iv) Mix the components obtained in steps (i), (ii) and (iii), preferably under mild agitation, by any mechanical process during a period of time between 1 minute to several hours and temperature range of 120°C to 190°C;

(v) Prepare the aqueous phase and adjust the temperature between 30 to 90°C;

(vi) Add one or more components to the aqueous phase selected from emulsifiers and acid adjuvants, where the order of addition between them is irrelevant;

(vii) Adjust the temperature of the mixture obtained in step (iv) to a range between 120°C to 190°C;

(viii) Perform a mechanical milling of the mixtures obtained in steps (vi) e (vii) by any mechanical process during a period of time between 1 minute and several hours; and

(ix) Obtain a polymeric asphalt emulsion ready for use.

20. Process, according to claim 19, characterized by the step (iv) be carried out preferentially during a period of time between 1 to 120 minutes.

21. Process, according to claim 19, characterized by the step (v) be carried out preferentially in temperatures between 40 to 50°C.

22. Process, according to claim 19, characterized by the step (vii) be carried out preferentially in temperatures between 150°C to 160°C.

23. Process, according to claim 19, characterized by the step (viii) be carried out preferentially with milling under pressure.

24. Process, according to claim 19, characterized by at least one or more organic chemical compounds are added to a continuous flow of the asphalt by any continuous process, for example, using a direct injection and/or a static mixer.

25. Process, according to claims 19 to 24, characterized by in the step (i) at least one or more organic chemical compounds are added before, concomitantly or after the step (viii).

26. Use of compositions according to claims 1 to 18, characterized by the construction or maintenance of highways, roads, sidewalks, parking lots, bridges, airport runways, sidewalks, parks, roofs, walls, service roads, waterproof membranes, asphalt recycling and any other bearing surfaces.

27. Use of polymeric asphalt emulsions, obtained by the process of claims 19 to 25, characterized by the construction or maintenance of highways, roads, sidewalks,
parking lots, bridges, airport runways, sidewalks, parks, roofs, walls, service roads, waterproof membranes, asphalt recycling and any other bearing surfaces.

28. Surface, characterized by being coated, in whole or in part with a composition according to claims 1 to 18.

29. Surface, characterized by being coated, in whole or in part with a polymeric asphalt emulsion obtained by the process of claims 19 to 25.

30. Surface, according to claims 28 and 29, characterized as a bearing surface.
**INTERNATIONAL SEARCH REPORT**

**PCT/BR2013/000437**

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C08L95/00 C08K5/20 E01C7/24 E01C7/35

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)

C08L C08K EOIC

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**

<table>
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<th>Relevant to claim No.</th>
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<td>X</td>
<td>Anonymous: &quot;Basic Asphalt Emulsion manual; MS-19; 4th Edition&quot;</td>
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<td>In: &quot;Basic Asphalt Emulsion manual; MS-19; 4th Edition&quot;,</td>
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<td></td>
<td>1 February 2008 (2008-02-01), Asphalt Institute, Lexington, Kentucky; USA,</td>
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<td></td>
<td>XP055100940, ISBN: 978-1-93-415456-4, page i-iii, v-xi, 1-3-5-12, the whole document</td>
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<td>US 5 795 929 A (GRUBBA WILLIAM E [US])</td>
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<td>18 August 1998 (1998-08-18), cited in the application on column 6, line 10 - line 45; claims 1-19; examples 1-4</td>
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</table>

**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

**E** earlier application or patent but published on or after the international filing date

**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)

**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

**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

**X** document of particular relevance: the claimed invention cannot be considered novel or, if it were, cannot be considered to involve an inventive step when the document is taken alone

**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

**A** document member of the same patent family

**Date of the actual completion of the international search**

11 February 2014

**Date of mailing of the international search report**

19/02/2014

**Name and mailing address of the ISA**

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

**Authorized officer**

ol de Scheper, Bernd
This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. □ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. □ Claims Nos.:
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. □ Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. □ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. X As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. □ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. □ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: 

Remark on Protest

□ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

□ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

□ No protest accompanied the payment of additional search fees.
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Form PCT/ISA/210 (continuation of second sheet) (April 2005)
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<td>US 5795929</td>
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This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-18, 26, 28 (completely); 30 (partially)
   Polymeric asphalt composition, its use and a surface coated therewith

2. claims: 19-25, 27, 29 (completely); 30 (partially)
   Process for obtaining polymeric asphalt emulsions, its use and a surface coated therewith