The present invention refers to a process for obtaining butadiene-styrene copolymers (SBR) that are prepared by aqueous emulsion polymerization technology, at high temperature, having differentiated rheological properties and which is particularly directed to the industry of manufacturing chewing gum and bubble gum. The present invention also refers to a rheology modifying agent for said butadiene-styrene copolymers, which are derived from the emulsion polymerization process. The present invention also refers to the SBR rubber product, mixture or composition having differentiated rheological properties that is obtained after the step of coagulating butadiene-styrene copolymer (SBR) latex.
The present invention refers to a process for obtaining butadiene-styrene copolymers (SBR) that are prepared by aqueous emulsion polymerization technology, at high temperatures, having differentiated rheological properties and that are particularly directed to the industry of manufacturing chewing gum and bubble gum. The present invention also refers to a rheology modifying agent for said butadiene-styrene copolymers, which are derived from the emulsion polymerization process. The present invention also refers to the SBR rubber product, mixture or composition having differentiated rheological properties that is obtained after the step of coagulating butadiene-styrene copolymer (SBR) latex.

The application of said product, composition or mixture to processes of producing chewing gum and bubble gum will reduce processing time, energy, and size of equipments used therein. Additionally, the present invention refers to a gum base prepared from the SBR composition of the present invention, as well as to said chewing gum and bubble gum, which are made from said gum base.

BACKGROUND OF THE INVENTION

In accordance with EP Patent 1 098 571, chewing gum generally comprises a portion of water-insoluble gum base and a water-soluble portion comprising several additives and, typically,
flavoring agents, which are soluble in water. Said water-soluble portion together with the flavoring agent dissolves in the mouth, during chewing, while the gum base portion is retained therein.

Elastomer is one of the main ingredients of insoluble gum base, and is, therefore, one of the main ingredients of the final product, i.e., the chewing gum and the bubble gum. Elastomer is an important component of gum base, as it constitutes the insoluble and elastic body thereof. Said elastomer must have rheological properties that facilitate the step of adding gum ingredients and resiliency capable of recovering from the deformation caused by chewing.

Synthetic butadiene-styrene copolymers (SBR), polyisobutylene, isobutylene-isoprene copolymers and natural elastomers, such as natural rubber, chiclet, balata, gutta-percha, etc., are elastomers suitable for application to chewing gum base.

Butadiene-styrene rubbers (SBR) are synthetic elastomers widely used as gum base in chewing gum and in bubble gum. However, in spite of their lower costs of production and commercialization, the use of SBR in the manufacture of soft chewing gums is still limited. This is due to the fact that its physical properties do not meet industry requirements.

In accordance with US Patent No. 5,093,136, SBR elastomers require their combination with rosin esters for achieving film-forming properties, particularly in the preparation of gum base for bubble gum. Nevertheless, said US Patent 5,093.136 teaches that gum base produced from said combination is still rigid,
difficult to chew and requires a significant amount of energy to prepare as well as the addition of a large amount of other additives, such as softeners and fillers into its composition, in order to obtain a texture suitable for use as chewing gum.

Depending on the type of gum to be manufactured, a gum base may comprise, in addition to SBR, other elastomers or synthetic or natural resins, such as polyisobutylene, isobutylene-isoprene copolymers, polyvinyl acetate, vinyl acetate-vinyl laurate copolymers, guayule, balata, chiclet, etc. US Patent No. 3,984,574 refers to a chewing gum comprising a gum base having a combination of an elastomer with polyvinyl acetate. US Patent No. 5,093,136 refers to a bubble gum comprising a co-mixture of an SBR gum base and a polyisobutylene gum base. US Patent No. 4,352,822 teaches that polyvinyl acetate resin may also be used as anti-adherent agent in the preparation of a bubble gum.

When the rubber used in preparing gum base is SBR, the amount of styrene in aqueous emulsion that is added to the polymerization reactor is critical. US Patent No. 6,399,721 teaches that in the manufacture of soft chewing gum, the styrene content in SBR ranges from 1 to 12 weight percent and in the preparation of bubble gum, styrene content in SBR may be as high as about 50 weight percent.

As a rule, insoluble gum base comprises one or more elastomers, one or more fillers, one or more solvents/plasticizers for the elastomer, waxes, resins, fats, oils, softeners, emulsifiers, texturizers, and other additives such as antioxidants, stabilizers, dye, bleachers, etc. Mainly, a gum base
comprises between 5-95 weight percent of chewing gum composition, preferably between 10-50 weight percent and, more usually, between 15-35 weight percent of chewing gum.

Typically a gum base comprises from about 0 to about 75 weight percent, preferably 5 to 45 weight percent, more preferably 10 to 30 weight percent of the gum base of a plasticizer compound for the elastomer selected from natural rosin esters, such as partially hydrogenated glycerol ester of rosin, polymerized glycerol ester of rosin, partially dimerized glycerol ester of rosin, glycerol ester of rosin, partially hydrogenated pentaerythritol esters of rosin, etc.

Waxes, if used, include those synthetic and natural waxes and comprise up to 30 weight percent of gum base.

Softeners/emulsifiers are present in amounts ranging from 0.5 to 40 weight percent gum base and are selected from hydrogenated and partially hydrogenated vegetable oils, cocoa butter, glycerin monostearate, glycerin triacetate, lecithin, mono-, di-, and triglycerides, acetylated glycerides and fatty acids, e.g., stearic, palmitic, oleic and linoleic acids, or mixtures thereof.

Fillers/texturizers typically used comprise magnesium and calcium carbonates, ground calcareo and silicates, such as magnesium and aluminum silicates, clay, alumina, talc, titanium oxide, monocalcium phosphite, dicalcium phosphite and tricalcium phosphite, cellulose polymers. Fillers are present in the gum in a concentration of about 1 to about 65 weight percent of the gum.
In the preparation of the gum base it is important that the elastomer portion and all other components be thoroughly mixed so that the gum base shows a homogenous phase and retains appropriate resiliency.

In the process for preparing gum base, the technical drawback resides in the mixture of ingredients or additives, most of which are solid, into rubber or elastomers, once they confer to the rubber its adequate final form as chewing gum or as bubble gum. In this way, the following are the two most widely used processes: batch process in an open mixer, such as Sigma mixer, and continuous process in extruders, as disclosed in EP Patent 1 098 571. Said batch process is mainly used by the industry, although there are some systems capable of producing the final product in a continuous process using extruders.

Although batch process is laborious, difficult to operate, time- and energy consuming and produces chewing gum of varied consistency, said gum preparation method is the one most commercially used nowadays.

Due to the difficulties in melting and homogeneously dispersing the solid elastomers with the remaining components that make up a gum base composition, the addition of the components that comprise the gum base is carried out in a balanced and sequential form. Therefore, the conventional batch process for preparing chewing gum and bubble gum typically comprises the following three steps: preparation of the so-called pre-base,
preparation of the gum base itself and preparation of chewing gum or gum for final bubble gum.

Said first two steps are necessary due to the high viscosity of the rubber that does not allow for a single-step addition of formulation components and consequent required plasticization so as to form a homogeneous elastic body having no lumps or protuberances.

The preparation step of the so-called pre-base comprises plasticizing solid components in an open mixer, such as a Sigma mixer. Typically, the elastomer that may comprise a butadiene-styrene copolymer (SBR) or a combination of SBR with other synthetic or natural elastomers is dispersed into a plasticizer with or without other gum base ingredients. Mixing is carried out at high and constant temperatures. Depending on the formulation, said mixture is maintained in the mixer during an extended time period of up to 8 hours so that a perfect plasticization of the copolymer is obtained.

Typically, the second step of gum base preparation consists in adding, in an open mixer heated at temperatures in the range of 60°C to 120°C, a variety of additives, such as texturizing agents, fillers, plasticizer, etc., to said pre-base prepared in accordance with the above-description. Said additives are added in a balanced and sequential mode so that a completely melted and homogeneous mass is obtained at temperatures ranging from 80°C to 90°C. Said mass is the melted gum base, which is discharged from
the mixer and sent to lined pans for preparation of the chewing gum or bubble gum.

The third step consists of forming the final chewing gum or bubble gum that comprises adding sweeteners and flavorings to the gum base.

Therefore, the conventional technology for the manufacture of chewing gums and bubble gums depends on synthetic elastomeric materials that allow solid additives to be incorporated in an easy and economic way.

In accordance with US Patent 6,399,721, apart from the drawbacks outlined above, many other disadvantages can still be found when butadiene-styrene rubber (SBR) is used as the elastic body of chewing gum. SBR rubber does not provide for a soft and elastic mastication, and these features limit its use in gum base formulations. Therefore, the Applicant, who is a manufacturer of SBR rubbers and well acquainted with the needs of the industry of gum base, chewing gum and bubble gum is making an effort to improve the physical and mastication properties of SBR rubbers, such as hardness/softness, elasticity and tenacity.

Elastomers can generally be prepared by emulsion, suspension, slurry or mass polymerization. However, emulsion and suspension polymerization techniques are most widely used due to the easy control of reaction medium viscosity and high conversion of monomers compared to other techniques. Polymerization can be performed as batch, continuous and (semi-continuous) batch feed processes, wherein one or more components of the reaction can be
added during polymerization. Reaction temperatures are usually in the range of -10°C to about 100°C, preferably in the range of 5°C to 80°C. Polymerization is preferably effected in the absence of air or oxygen.

Aqueous emulsion polymerization is the preferred method used for the preparation of butadiene-styrene copolymers (SBR). Emulsion polymerization can be initiated by free-radical generating agents, such as: organic peroxides and hydroperoxides, such as benzoyl peroxide, dicumyl peroxides, t-butyl peroxide, cumyl hydroperoxide, p-menthane hydroperoxide, etc; azo-compounds such as azobisisobutyronitrile, azobisisobutylamidine, azobisisobutylamidine, etc.; persulfates, such as ammonium, potassium and sodium persulfates; and ultraviolet light. Free-radical initiating or generating compounds are usually combined with redox systems or the ultraviolet light with photosensitive agents, such as benzophenone and organic diazo compounds.

Typical emulsion polymerization employs, as initiators, persulfate salts or organic peroxides, including a redox system, water adjusted to the desired pH with acids or bases, usually buffered with inorganic salts, and further, anionic, cationic or nonanionic surface active agents. Further it should be pointed out that the state of the art relative to emulsion polymerization discloses the use of chain transfer agents as an optional reaction component. Conventionally used agents are, for example, mercaptans.
The final product of emulsion polymerization is in a latex form and must then be subjected to a coagulation process so that rubber or solid elastomer is obtained. Typical coagulation processes use polyvalent metal salts and alcohols, such as, for example: magnesium sulfate, calcium chloride, methanol, and isopropanol. Agglomeration techniques are also employed. The resulting polymer is usually washed and dried.

As a rule, products derived from said polymerization do not exhibit per se rheological properties suitable for direct use in certain industrial fields. Therefore additives must be added thereto in order to achieve the desired results.

SBR elastomers, following the conventional synthesis steps of emulsion polymerization and coagulation of the latex, generally present a Mooney viscosity range that is not ideal for chewing gum industries.

Rubbers or elastomers produced according to the art are solid materials generally having diluted solution viscosity (DSV) higher than 0.5 when measured at 0.4% by weight of polymer solution in methylethylketone. They further present an amount of gel or insolubles varying from 0% to 60% by weight of rubber or elastomer.

Mooney viscosity (ML 1 + 4 @ 100°C) of SBR rubbers useful for manufacturing gums prepared in accordance with conventional aqueous emulsion polymerization processes typically varies from about 40 to 80.
US Patent No. 4,489,099 discloses Vitamin E/DLTDP (dilauryl thiodipropionate) stabilizer system for SBR chewing gums. In accordance with Examples 1 to 13, samples of a dry SBR rubber (Plioflex™ 1027) having styrene concentration ranging from 22% to 25%, about 22% of solids and a Mooney viscosity ranging from 53 to 86 were tested for the action of the stabilizer system in aging test. Therefore, it may be noted that said '099 patent teaches the use of unstable SBR rubbers having a high standard viscosity in preparing gums.

US Patent 6,399,721 refers to a process for synthesis of butadiene-styrene rubber that is particularly useful in the manufacture of gum base and chewing gum, the process comprising aqueous emulsion copolymerization of styrene and 1,3-butadiene, at temperatures in the range of 1°C to 70°C. Said copolymerization begins with an initiator system that comprises: (a) a free radical generator; (b) a reducing agent selected from the group consisting of ascorbic acid, isoascorbic acid, and ascorbic acid derivatives; and (c) a water soluble metal salt of iron, copper, nickel, tin, vanadium, manganese, chromium, or silver.

In accordance with the Example of '721 patent, the aqueous emulsion polymerization process for preparing SBR takes places under cold temperature conditions. Temperature is maintained constant at 5°C. The dry SBR rubber derived from the coagulated latex has a styrene content of 5%, a Mooney viscosity of 80, and a final torque value RPA t80 of 0.082 minutes. In spite of long
relaxation time, Mooney viscosity of 80 of the SBR rubber is not an ideal value range for use in manufacturing gums.

US Patent Nos. 6,399,721 and 4,489,099 teach the use of butadiene-styrene copolymers (SBR) having Mooney viscosity varying from 50 to 80. Those skilled in the art recognize that SBR rubbers exhibiting said Mooney viscosity range are difficult to process since they do not have the softness required to be applied as gum base and chewing gum. In this way, the applicant has researched so as to provide the chewing gum industry with a family of new butadiene-styrene copolymers, i.e., SBR rubbers having improved properties, which are ready to form an elastic body of homogeneous phase gum base, and have constant and suitable differentiated rheological properties, where the final product is free from lumps and other irregularities.

PURPOSE OF THE INVENTION

Therefore, in order to solve the drawbacks mentioned above, there is a need to develop novel SBR copolymers having differentiated rheological properties that will meet the chewing gum and bubble gum manufacturers' requirements in particular. To this effect, a new process for preparing butadiene-styrene copolymers having differentiated rheological properties has been developed. These properties permit the elimination of the so-called step of preparing pre-base required by conventional processes, whereby time and costs in the production of chewing and bubble gums will be reduced.
DETAILED DESCRIPTION OF THE INVENTION

It has been surprisingly discovered that synthesis of high molecular weight butadiene-styrene copolymers (SBR), followed by plasticization of the rubber by adding to the latex, prior to coagulation, an agent called rheology modifier for copolymer or SBR rubber, produces an SBR rubber product, mixture or composition having differentiated rheological properties, which is ready to be immediately applied to the manufacture of gum base without the drawbacks posed by the conventional art. The SBR composition, prepared in accordance with the present invention, allows for easy dispersion and incorporation of several ingredients of the gum base into the batch process for preparing said gum base.

One of the most important features of the present invention resides in the elimination of the so-called pre-base preparation step that is widely known for being time-consuming, laborious and expensive for chewing gum industry.

The new process of the present invention is characterized by controlling the molecular weight of the resulting copolymer, more particularly, the Mooney viscosity of the latex that, in the course of hot aqueous emulsion polymerization process, at temperatures in the range of 40°C to 65°C, preferably in the range of 45°C to 60°C, should be maintained in the range of 80 to 120, preferably between 85-110; by a total solids content that is maintained in the range of 20% to 40%, preferably 22% to 30%; and by including a novel process step that comprises introducing to the latex, prior to the coagulation step, a rheology modifying
agent for copolymer. After said coagulation step, the final product is in the form of a solid SBR rubber composition having a highly reduced Mooney viscosity ranging from 30-45.

Said rheology modifying agent for copolymer can be directly added to the latex-containing tank, or to the latex stream flowing towards the coagulation tank, at a flow rate of 150 to 500 kg/h. Addition of said modifying agent is preferably effected directly to the latex-containing tank and in batches.

The new emulsion polymerization process for preparing the SBR rubber composition having differentiated rheological properties is characterized by comprising the following steps:

1- purging the reactor with gaseous nitrogen to completely remove oxygen from the medium, which would inhibit initiation of said process and the reaction progress;

2- adding an emulsifier preheated at temperatures in the range of 40°C-60°C;

3- adding monomers (styrene and butadiene) and the chain transfer agent;

4- adding a previously prepared free radical initiator solution;

5- polymerizing at temperatures in the range of 40°C to 65°C until an SBR copolymer latex is formed, the Mooney viscosity of which is controlled to be within the range of 80-120, and the total solids content is maintained in the range of 20-40%;

6- stopping polymerization, after 60%-80% conversion of monomers, by adding a reaction shortstop;
7- removing unreacted butadiene and styrene monomers;
8- treating the resulting SBR copolymer latex with the rheology modifying agent prepared in accordance with the invention;
9- coagulating the latex by adding coagulants, such as aqueous solutions of inorganic salts to the coagulation container; and
10- washing and drying said SBR copolymer, the Mooney viscosity of which ranges from 30-45.

Preparation of the emulsifier or emulsifying mixture is carried out in a closed container that is inerted with nitrogen. The surface active agents used in the emulsifier are those typically employed in food industry and, consequently, approved by Health Agencies. Soaps typically used are salts of fatty acids obtained from animal or vegetable fats or waxes such as oleic acid, palmitic acid, stearic acid, and linoleic acid. Sodium or potassium salts of said fatty acids are widely used, such as, for example, sodium oleate, potassium oleate, sodium palmitate, potassium palmitate. The water used is demineralized water, since the presence of ions may cause insolubilization of the surface active agent or emulsifier, whereby deviations in the reaction progress and/or destabilization of the formed latex may occur. Water is preheated to 60°C to 70°C prior to the addition of said surface active agent thus improving dissolution kinetics of the surface active agent. Said surface active agent is present in the range of 1.0 to 8.0 parts per hundred parts of monomer (phm),
preferably in the range of 2.0 to 6.0 phm. After said surface active agent is completely solubilized, a dispersing agent is added until complete solubilization thereof.

The dispersing agent that is a dioctyl sulfo succinic acid salt acts in stabilizing the formed latex and is present in concentrations ranging from 0.1 to 2.5 phm, preferably 0.7 to 1.5 phm. Finally, a pH buffer in concentrations ranging from 0.2 to 1.5 phm, preferably 0.5 to 1.0 phm is added. Sodium phosphate, sodium acetate and sodium bicarbonate are the most widely utilized and preferred compounds for the present invention. The final pH of the emulsifying mixture must be set to 10 to 11.5. Generally, phosphoric acid is used for pH decrease and sodium hydroxide for pH increase. Said emulsifying mixture is maintained at a temperature of 60°C to 70°C.

Free radical generators, which can be used in the process of the present invention, are those widely known in the art. The concentration of free radicals generators, in accordance with the present invention, is in the range of 0.015 to 1.5 phm, preferably 0.1 to 0.8 phm.

Chain transfer agent is present in the reaction mixture in an amount of 0.01 to 1.0 phm, preferably 0.05 to 0.6 phm, more preferably, 0.1 to 0.2 phm, and is selected from alkyl and/or arylalkyl mercaptans, such as n-octyl mercaptan, n-dodecyl mercaptan, t-octyl mercaptan, t-dodecyl mercaptan, tridecyl mercaptan, tetradecyl mercaptan, hexadecyl mercaptan and the like;
and mixtures thereof. The preferred chain transfer agents are t-
dodecyl mercaptan and n-dodecyl mercaptan.

Chain shortstops used in the process of the present invention
are those typically used in conventional polymerization processes. Said chain shortstops are present in concentrations ranging from
0.015 to 15 phm, preferably 0.1 to 8 phm.

The amount of styrene in the aqueous emulsion typically
varies from about 1 phm to about 60 phm, and the amount of 1,3-
butadiene varies from about 40 phm to 99 phm. This corresponds, in
the SBR, to a chain comprising about 1 weight percent to 50 weight
percent styrene and about 50 to 99 weight percent butadiene.

In accordance with the present invention, SBR useful for
preparing a gum base suitable for bubble gum can have a styrene
content of 1 weight percent to 50 weight percent, preferably in
the range of 45 weight percent to 50 weight percent, while in the
preparation of soft chewing gums, in contrast with techniques
known from the state of the art, the amount of styrene in the SBR
rubber may vary from 1 to 30 weight percent, preferably 20 to 25
weight percent.

The product formed in the reactor is latex that must be
subjected to a coagulation process in order to become a solid
polymer. Said coagulation process consists of adding salts of
metals having valences greater or equal to two, the preferred
salts being calcium chloride, magnesium chloride or aluminum
sulfate. Said salts insolubilize the surface active agent, thereby
destabilizing particles and enhancing coalescence between said
particles. A mixture of mineral salts with monovalent salts, such as, for example, sulfuric acid and sodium chloride, may also be used. After coagulation, the polymer is washed and dried.

The rheology modifying agent for copolymer of the present invention consists of an emulsion or a mixture melted at a temperature ranging from 60ºC to 100ºC, preferably between 80ºC and 90ºC, comprising:

a) 0.1 to 50 weight percent softener based on the dry rubber; and

b) 0.1 to 5 weight percent antioxidant based on the dry rubber.

Antioxidant and softener compounds or substances used in the present invention are the ones approved by Health Agencies.

Representatives of softener compounds are synthetic waxes, such as, for example, polyethylene wax; natural waxes, such as, for example, candelilla, carnauba, rice bran waxes and mixtures thereof; and those derived from petroleum, such as microcrystalline and paraffin waxes and mixtures thereof. Said softener may also comprise hydrogenated or partially hydrogenated vegetable oils, glycerin monostearate, glycerin triacetate, lecithin, mono-, di- and triglycerides, fatty acids, such as, for example, stearic, palmitic, oleic, linoleic acids, and mixtures thereof. Said softener preferably consists of a melted mixture comprising 0.1 to 50% glycerin monostearate and 0.1 to 50% wax.

Representatives of antioxidants are the natural and synthetic ones that are commonly used and approved by Health Agencies, such as...
as, beta-carotenes, acidulants, such as, for example, Vitamin C, tocopherol (Vitamin E), propyl gallate, butyl hydroxyanisole (BHA), and hydroxytoluene butyl (BHT), the latter being preferably used.

Emulsion of the rheology modifying agent is obtained by mixing said softener with the antioxidant, followed by adding said emulsifying agent which is one selected from those used in the polymerization process. Concentration of said softener in the emulsion will vary from 5 weight percent to 70 weight percent of the total mixture, preferably from 10 weight percent to 50 weight percent. Concentration of the emulsifying agent in the emulsion ranges from 0.05% to 6.0%, preferably from 0.1% to 3.0%. In said emulsion, if the softener comprises a mixture of a fatty acid, or a derivative thereof, and a wax, the ratio between said fatty acid, or a derivative thereof, and said wax is in the range between 1:1 and 10:1, preferably, between 2:1 and 6:1.

Said rheology modifying agent preferably comprises a melted mixture of 10% to 90% glycerin monostearate, 10% to 90% microcrystalline wax, and 0.1% to 5% BHT; more preferably 15% to 85% glycerin monostearate, 15% to 85% microcrystalline wax; and 0.1 to 1% BHT.

The present invention also comprehends the SBR rubber product, mixture or composition having differentiated rheological properties and a Mooney viscosity varying from 30 to 45, which comprises the butadiene-styrene copolymer, prepared in accordance with the present invention, thoroughly mixed with a rheology
modifying agent prior to coagulation and then, coagulated. Preferably, said rheology modifying agent comprises the one prepared in accordance with the present invention. Said SBR rubber composition has a solid SBR rubber content of from 70% to 90% and a rheology modifying agent content of from 10% to 30%, preferably from 75% to 88% rubber and 12% to 25% modifying agent.

The present invention also refers to a gum base comprising (a) about 1 to 50% weight percent of SBR rubber composition having a Mooney viscosity of 30 to 45, prepared in accordance with the present invention, (b) about 10 to 50 weight percent glycerol ester of rosin, (c) about 0 to 50 weight percent of synthetic or natural rubber or elastomer, (d) about 1 to 45 weight percent plasticizer, (e) about 0 to 65% filler, (f) about 0.1 to 5% antioxidant.

The present invention further relates to a chewing gum and a bubble gum, which may comprise, in addition to the gum base as defined above, other components essential for their composition. Said gums of the present invention consist of (a) about 5 to 40% of gum base as defined above, (b) about 0 to 25% plasticizer, (c) about 0 to 10% stabilizer, (d) about 50 to 80% sweetener, (e) about 0.01 to 5% flavoring, and (f) about 0 to 10% acidulant.

Examples given below are non-limitative as they intend to be merely illustrative of the preferred embodiment of the invention.

Examples;

Comparative Example

I- Preparation of the copolymer
In this experiment, SBR copolymer has been synthesized by using a conventional emulsion polymerization technique. To a 20-liter reactor, under vacuum (about 11 mmHg), 6,000 g water, 2,000 g potassium oleate, 2,600 g of styrene, 2,200 g butadiene and 15 g n-dodecylmercaptan were added. The reaction mixture was heated to a temperature of about 50°C, and maintained under stirring. Three hundred and twenty grams of 5% potassium persulfate solution were added. The polymerization reaction was maintained at a constant temperature of 50°C for about 10 hours, until 28-29% of total solids content in the latex were obtained. Thereafter, 350 g of 5% aqueous sodium sulfide solution were added.

The latex was coagulated by using a conventional technique, and immediately dried at 65°C for 18 hours. The SBR copolymer was analyzed and rendered 46% of combined styrene, having a Mooney viscosity of 60.

**II- Preparation of the gum base**

**Step 1 - Pre-base preparation**

In a Sigma-type open mixer, previously heated at 85°C, 250 g of SBR rubber having a Mooney viscosity of 60 and prepared in accordance with Comparative Example were added. The elastomer was subjected to mastication for 60 minutes. Subsequently, 550 grams of esterified rosin were gradually incorporated into the plasticized elastomer. The addition of said rosin was carried out in 60 minutes. The total amount of said rosin was added in five portions. After the complete incorporation of said rosin the material was maintained under mastication for a period of time of
over 3 hours, under heating, at a temperature of about 85°C. After completion of the mastication step of the material, 200 g of microcrystalline wax were added. The total amount of microcrystalline wax was also added in five portions, wherein each portion was only added after complete incorporation of the previous portion, thus amounting to a total period of time of 60 minutes.

The total time spent in preparing said pre-base, including its discharge, was 6 hours.

**Step 2 - Gum base preparation**

In a Sigma-type open mixer, previously heated at 85°C, 400 g of said pre-base prepared in accordance with the conventional process disclosed in step 1 above were added. Said pre-base was subjected to mastication for 15 minutes until a texture suitable for beginning the addition of the remaining ingredients was achieved. One hundred grams of polyvinyl acetate were added. After complete homogenization, 20 g of triacetine were added. The mixture was maintained under mastication for a further 30 minutes. Subsequently 340 g of sodium carbonate were added in five portions. After addition of carbonate and its complete homogenization, 20 g of soy lecithin and 40 g of glycerin monostearate were sequentially added in a balanced manner, at intervals of about 5 minutes. After complete homogenization, 20 g of hydrogenated soybean oil divided in five portions were added within 25 minutes. The total time spent in adding and homogenizing said components was approximately 2 hours. After homogenization
was complete, 20 g of drinking water were added. The mixture was maintained heated at a temperature of 85°C for about 30 minutes. The time required for preparing said gum base in the second step was 3 hours, at a residual humidity of 1.5%.

The total time spent in preparing said gum base was 9 hours.

Step 3 - Chewing Gum Preparation

In a Sigma-type mixer, previously heated at 55°C, 200 g of glucose syrup were added and maintained at a temperature of 55°C. Next, 200 g of the previously melted gum base, prepared in accordance with the process of step 2 above, were added. After homogenization of the gum base and glucose, 600 g of sugar and 7 g of Tutti Frutty flavoring were added. Components of the mixture were stirred until a homogeneous mass having a texture characteristic of bubble chewing gum type was obtained.

An analysis of the resulting chewing gum has shown that the product exhibited texture and ability suitable for producing bubbles by mouth blowing technique.

Typical Examples of the Present Invention

Example 1

I- Preparation of the SBR copolymer

In this experiment, the SBR copolymer was synthesized through the emulsion polymerization process of the present invention. In a 20 L reactor, under vacuum (about 11 mmHg), 6,150 g water, 2,085 g potassium oleate, 2,635 g styrene, 2,225 g butadiene and 9 g n-dodecyl mercaptan were added. The reaction mixture was heated at a temperature of about 50°C and maintained under stirring. Next, 320
g of a 5% aqueous potassium persulfate solution were added. The polymerization reaction was maintained at a constant temperature of 50°C for about 10 hours until a 29-30% total solids content of latex was obtained when 350 g of a 5% aqueous sodium sulfide solution were added. A latex sample was coagulated by using a conventional method and dried, thereby rendering 48% of combined styrene having a Mooney viscosity of 95.

II- Preparation of the rheology control agent emulsion

In a 1,000 mL container, 70 g glycerin monostearate and 50 g microcrystalline wax were added. The system was heated until the material was entirely melted. Under mechanical stirring, 1.2 g oleic acid, 0.4 g of 50% aqueous potassium hydroxide solution, 1.6 g butyl hydroxy toluene (BHT) and 80 g water were added.

III - Coagulation of SBR latex by means of rheology control agent emulsion

In order to obtain an elastomer having differentiated rheological properties, the SBR latex having a Mooney viscosity of 95, as prepared in step I above, was coagulated. One hundred grams of rheology control agent emulsion, as prepared in step II above, were added to 2,000 g copolymer latex. Next the rubber was coagulated and dried at 65°C for 18 hours. The obtained dried SBR rubber showed a Mooney viscosity of 37.

Example 2

I- Preparation of the melted rheology modifying agent

In a 1,000 mL container, 130 g glycerin monostearate, 120 g microcrystalline wax and 4 g butyl hydroxytoluene (BHT) were
added. Under mechanical stirring, said materials were heated at 85°C until completely melted.

II- Coagulation of the SBR latex by using the melted rheology modifying agent

In order to obtain an elastomer having differentiated rheological properties, SBR latex having a Mooney viscosity of 95 of Example 1 - step I was coagulated. Two hundred thirty grams of the melted mixture of Example 2- step I, comprising rheology control agents were added to 2,450 g of said latex. Next the rubber was coagulated and dried at 65°C for 18 hours.

Using the same mass of SBR latex, a new coagulation was performed, where the amount of rheology modifying agent was increased to 243 g. The dried SBR rubber showed a Mooney viscosity of 32.

Example 3

I - Gum base preparation

Step 1 - Pre-base preparation

As formerly described, use of the SBR rubber composition having differentiated rheological properties, which is prepared through the process for preparing a gum base in accordance with the present invention, eliminates the pre-base preparation step.

Step 2 - Gum base preparation

In a Sigma-type open mixer, previously heated at 85°C, 150 g of said SBR composition having a Mooney viscosity prepared in accordance with Example 2 were added. Said rubber was subjected to mastication for 5 minutes until a texture suitable for beginning
addition of the remaining ingredients was obtained. Three hundred grams of rosin ester resin are added in five portions, during a total mastication time of 10 minutes. After homogenization was complete 100 g of polyvinyl acetate were added. After mastication for 15 minutes so that homogenization was complete, 10 g triacetine were added. The mixture was maintained under mastication. Next, 220 g calcium carbonate, divided in five portions, was added within about 25 minutes. When the addition of carbonate was concluded and its homogenization complete, 20 g soy lecithin, 40 g glycerin monostearate and 60 g hydrogenated soybean oil were sequentially added in a balanced manner. After homogenization was complete, 100 g of drinking water were added. The mixture was maintained heated at a temperature of 85°C for 30 minutes.

The total time spent in preparing the gum base was 2 hours, at a residual humidity of 1.5%.

**Step 3 - Chewing gum**

In a Sigma-type mixer previously heated at 55°C, 200 g glucose syrup were added and maintained at a temperature of 55°C. Next, 200 g of the previously melted gum base, prepared in accordance with step 2 above, were added. After homogenization of the gum base and glucose, 600 sugar and 7 g of Tutti Frutti flavoring were added. Components of the mixture were stirred until a homogeneous mass having texture characteristic of a bubble chewing gum was obtained.
Analysis of the chewing gum has shown that the product exhibits a texture and ability suitable for producing bubbles by mouth blowing technique.

Upon evaluating the results of the Comparative and Inventive Examples, one may observe that both techniques produce chewing gum and bubble gum having properties that meet gum users' requirements. Nevertheless, the use of the new technique shows obvious advantages when the SBR rubber composition having differentiated rheological properties, more particularly having a Mooney viscosity of 30-45, prepared in accordance with the process of the present invention, is used.

The utilization of said compositions is more efficient and more effective than the SBR copolymers produced and used in the conventional technique of manufacturing gum base. The time of incorporation of additives to the rubber has shown an enormous reduction, higher than 2/3 of the total time, since a reduction of 7 hours (from 9 hours to 2 hours of operation) has been observed, thus resulting in reduction of operational and production costs as well as the size of equipments employed in the manufacture of bubble gum.
1. Process for obtaining butadiene-styrene copolymers by hot aqueous emulsion polymerization, characterized in that it comprises controlling the molecular weight of the resulting copolymer, more particularly, the Mooney viscosity of the latex, which, during said hot aqueous emulsion polymerization process carried out at temperatures ranging from 40°C to 65°C, must be maintained in the range between 80 and 120; keeping a total solids content in the range between 20 and 40%; and, prior to the coagulation step, adding a rheology modifying agent for copolymer to the latex, wherein after said coagulation step, the solid rubber exhibits a Mooney viscosity in the range of 30 to 45.

2. Process, in accordance with Claim 1, characterized in that polymerization preferably takes place at a temperature in the range between 45 and 60°C.

3. Process, in accordance with Claim 1, characterized in that Mooney viscosity of the copolymer in the latex is preferably maintained between 85 and 110.

4. Process, in accordance with Claim 1, characterized in that said solids content is preferably maintained between 22 and 30%.

5. Process, in accordance with Claim 1, characterized in that the rheology modifying agent of the copolymer can be added directly to the tank containing said latex or to the stream flowing towards the coagulation tank.
6. Process, in accordance with Claim 5, characterized in that the addition of said rheology modifying agent is effected directly in the tank containing the referred latex.

7. Process, in accordance with Claim 5, characterized in that the addition of said rheology modifying agent to the stream flowing towards the coagulation tank is carried out at a flow rate of 150 to 500 kg/h.

8. Rheology modifying agent for butadiene-styrene copolymer characterized in that it comprises 0.1 to 50% by weight in relation to the dry rubber of a softener compound and 0.1 to 5% by weight in relation to the dry rubber of an antioxidant.

9. Modifying agent, in accordance with Claim 8, characterized in that said softener compound is selected from synthetic waxes, such as, for example, polyethylene wax; natural waxes such as, for example, candellila, carnauba, rice bran waxes and mixtures thereof; and those waxes derived from petroleum such as microcrystalline and paraffin waxes and mixtures thereof; hydrogenated or partially hydrogenated vegetable oils; glycerin monostearate, glycerin triacetate; lecithin; mono-, di- and triglycerides; fatty acids such as, for example, stearic, palmitic, oleic, linoleic acids; and mixtures thereof.

10. Modifying agent, in accordance with Claim 8, characterized in that said softener compound comprises preferably from 0.1 to 50% glycerin monostearate and from 0.1 to 50% of a wax.
11. Modifying agent, in accordance with Claim 8, characterized in that said antioxidants are selected from beta-carotenes, acidulants such as, for example, Vitamin C, tocopherol (Vitamin E), propyl gallate, butyl hydroxyanisole (BHA), and butyl hydroxytoluene (BHT).

12. Modifying agent, in accordance with Claim 11, characterized in that the preferred antioxidant is butyl hydroxytoluene (BHT).

13. Modifying agent, in accordance with Claims 8, 9, 10, 11, or 12, characterized in that it comprises an emulsion or a melted mixture.

14. Modifying agent, in accordance with Claim 13, characterized in that said agent comprises a mixture melted at temperatures in the range of 60°C to 100°C.

15. Modifying agent, in accordance with Claim 14, characterized in that said agent comprises a mixture preferably melted at a temperature in the range of 80°C to 90°C.

16. Modifying agent, in accordance with Claim 14 or 15, characterized in that the referred melted mixture preferably has 10 to 90% glycerin monostearate, 10 to 90% microcrystalline wax, and 0.1 to 5% BHT.

17. Modifying agent, in accordance with Claim 16, characterized in that said melted mixture preferably comprises 15 to 85% glycerin monostearate, 15 to 85% microcrystalline wax and 0.1 to 1% BHT.
18. Modifying agent, in accordance with Claim 13, characterized in that it comprises an emulsion that is obtained by mixing 5 to 70 weight percent softener compound with the antioxidant compound, followed by adding 0.05 to 6 weight percent emulsifying agent.

19. Modifying agent, in accordance with Claim 18, characterized in that the concentration of said emulsifying agent in the emulsion preferably varies from 0.1 to 3 weight percent.

20. Modifying agent, in accordance with Claim 18, characterized in that the concentration of said softener compound in the emulsion preferably varies from 10 to 50 weight percent.

21. Process for obtaining butadiene-styrene copolymers by hot aqueous emulsion polymerization, the process being characterized in that it comprises the following steps:

1- purging the reactor with nitrogen gas to completely remove oxygen from the medium, which would inhibit initiation of said process and the reaction progress;

2- adding an emulsifier preheated at temperatures in the range of 40°C-60°C;

3- adding monomers (butadiene and styrene) and chain transfer agent;

4- adding a previously prepared free radical initiator solution;

5- polymerizing at temperatures in the range of 40°C to 65°C until formation of SBR copolymer latex, the Mooney viscosity of
which is controlled to be within the range of 80-120 and the total solids content is maintained in the range of 20-40%;

6- stopping polymerization after a 60%-80% conversion of monomers;

7- removing unreacted butadiene and styrene monomers;

8- treating the resulting SBR copolymer latex with the rheology modifying agent prepared in accordance with any of Claims 8 to 20;

9- coagulating said latex by adding coagulants, such as aqueous solutions of inorganic salts, to a coagulation container; and

10- washing and drying said SBR copolymer, the Mooney viscosity of which ranges from 30-45.

22. Process, in accordance with Claim 1 or 21, characterized in that the styrene content in the SBR rubber is 1 to 50 weight percent.

23. Process, in accordance with Claim 22, characterized in that the styrene content in the SBR rubber is about 1 to 30%, preferably 20 to 25%.

24. SBR rubber composition having differentiated rheological properties characterized in that it consists essentially of 70 to 90 weight percent of a butadiene-styrene copolymer having a Mooney viscosity between 30 and 45.

25. Rubber composition, in accordance with Claim 24, characterized in that it additionally comprises 10 to 30% rubber of a rheology modifying agent.
26. Rubber composition, in accordance with Claim 24, characterized in that said composition preferably comprises 75 to 88% rubber and 12 to 25% of a rheology modifying agent.

27. Rubber composition, in accordance with Claims 24, 25 or 26, characterized in that said rheology modifying agent comprises 0.1 to 50 weight percent of a softener compound and 0.1 to 5 weight percent of an antioxidant.

28. Rubber composition, in accordance with Claim 27, characterized in that said softener compound is selected from synthetic waxes, such as, for example, polyethylene wax; natural waxes such as candellila, carnauba, rice bran waxes and mixtures thereof; and those waxes derived from petroleum such as microcrystalline and paraffin waxes and mixtures thereof; hydrogenated or partially hydrogenated vegetable oils; glycerin monostearate; glycerin triacetate; lecithin; mono-, di- and triglycerides; fatty acids such as, for example, stearic, palmitic, oleic, linoleic acids; and mixtures thereof.

29. Rubber composition, in accordance with Claim 27 or 28, characterized in that said softener compound comprises preferably from 0.1 to 50% glycerin monostearate and from 0.1 to 50% wax.

30. Rubber composition, in accordance with Claim 27, characterized in that said antioxidants are selected from beta-carotenes, acidulants such as, for example, Vitamin C, tocopherol (Vitamin E), propyl gallate, butyl hydroxyanisole (BHA), and butyl hydroxy toluene (BHT).
31. Rubber composition, in accordance with Claim 30, characterized in that the preferably used antioxidant is butyl hydroxytoluene (BHT).

32. Gum base characterized in that it is prepared from a rubber composition having differentiated rheological properties and a Mooney viscosity between 30 and 45.

33. Gum base, in accordance with Claim 32, characterized in that it comprises:
   (a) about 1 to 50% weight percent of the butadiene-styrene rubber composition having a Mooney viscosity of 30 to 45, (b) about 10 to 50% of glycerol ester of rosin, (c) about 0 to 50 weight percent of another synthetic or natural rubber or elastomer, (d) about 1 to 45 weight percent plasticizer, (e) about 0 to 65% filler; (f) about 0.1 to 5% stabilizer and (g) about 0 to 0.5% antioxidant.

34. Gum base characterized in that it comprises:
   (a) about 5 to 40% of the gum base as defined in Claims 32 and 33; (b) about 0 to 25% plasticizer, (c) about 0 to 10% stabilizer, (d) about 50 to 80% sweetener, (e) about 0.01 to 5% flavoring and (f) about 0 to 10% acidulant.

35. Bubble gum characterized in that it comprises:
   (a) about 5 to 4% of a gum base as defined in Claims 32 and 33; (b) about 0 to 25% plasticizer; (c) about 0 to 10% stabilizer; (d) about 50 to 80% sweetener; (e) about 0.01 to 5% flavoring; and (f) about 0 to 10% acidulant.
INTERNATIONAL APPLICATION N o
PCT/BR2007/000209

INTERNATIONAL SEARCH REPORT

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

B FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F  C08L

Other 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 practical, search terms used)

EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 6 369 158 B1 (SENYEK MICHAEL LESLIE [US] ET AL) 9 April 2002 (2002-04-09) examples 2,3; tables 1,2</td>
<td>1-31</td>
</tr>
<tr>
<td>X</td>
<td>US 6 469 104 B1 (COLVIN HOWARD ALLEN [US] ET AL) 22 October 2002 (2002-10-22) column 12, lines 14-25; claims 1,5,11,90,93,112,115; examples 4-6 column 16, lines 33-67 column 1, line 65 - column 2, line 39</td>
<td>1-31</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C

See patent family annex

Date of the actual completion of the international search

21 December 2007

Date of mailing of the international search report

07/01/2008

Name and mailing address of the ISA/ International Search Authority

European Patent Office P B 5818 Patentlaan 2 NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx 31651 epo nl
Fax (+31-70) 340-3016

Authorized officer

Adams, Flori an
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>WO 02/069729 A (LA DREYFUS CO [US]; GMUNDER CHARLEAN [US]; KANCA KENNETH M [US]; LWF) 12 September 2002 (2002-09-12) page 20, lines 19-24; examples 2,4</td>
<td>8-20, 24-35</td>
</tr>
<tr>
<td>X</td>
<td>EP 0 054 911 A (ASAHI CHEMICAL IND [JP]) 30 June 1982 (1982-06-30) page 4, lines 20-26; examples 9-11; tables 2,8,9</td>
<td>8-20, 24-31</td>
</tr>
<tr>
<td>X</td>
<td>US 5 200 213 A (ORFAN CHARLES P [US] ET AL) 6 April 1993 (1993-04-06) col umn 4, line 27 - column 7, line 2; example 1</td>
<td>8-20</td>
</tr>
<tr>
<td>X</td>
<td>EP 0 942 043 A (GOODYEAR TIRE &amp; RUBBER [US]) 15 September 1999 (1999-09-15) claims 1-3; examples 1,2; table 1</td>
<td>8-20</td>
</tr>
<tr>
<td>A</td>
<td>US 4 415 704 A (WEINSTEIN ARTHUR H [US]) 15 November 1983 (1983-11-15) col umn 5, lines 28-51; examples 3,4; tables 4,6,7</td>
<td>1</td>
</tr>
<tr>
<td>Patent document cited in search report</td>
<td>Publication date</td>
<td>Patent family member(s)</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>-----------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>US 6369158</td>
<td>B1</td>
<td></td>
</tr>
<tr>
<td>US 6469104</td>
<td>B1</td>
<td></td>
</tr>
<tr>
<td>WO 02071860</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>WO 02069729</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>US 4186214</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>US 4489099</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>EP 0054911</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>US 5200213</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>EP 0942043</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>US 4415704</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>WO 9803075</td>
<td>A</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td>US 6369158</td>
<td>B1</td>
<td></td>
<td>09-04-2002</td>
</tr>
<tr>
<td>US 6469104</td>
<td>B1</td>
<td></td>
<td>22-10-2002</td>
</tr>
<tr>
<td>WO 02071860</td>
<td>A</td>
<td></td>
<td>19-09-2002</td>
</tr>
<tr>
<td>WO 02069729</td>
<td>A</td>
<td></td>
<td>12-09-2002</td>
</tr>
<tr>
<td>US 4186214</td>
<td>A</td>
<td></td>
<td>29-01-1980</td>
</tr>
<tr>
<td>US 4489099</td>
<td>A</td>
<td></td>
<td>18-12-1984</td>
</tr>
<tr>
<td>EP 0054911</td>
<td>A</td>
<td></td>
<td>30-06-1982</td>
</tr>
<tr>
<td>US 5200213</td>
<td>A</td>
<td></td>
<td>06-04-1993</td>
</tr>
<tr>
<td>EP 0942043</td>
<td>A</td>
<td></td>
<td>15-09-1999</td>
</tr>
<tr>
<td>US 4415704</td>
<td>A</td>
<td></td>
<td>15-11-1983</td>
</tr>
<tr>
<td>WO 9803075</td>
<td>A</td>
<td></td>
<td>29-01-1998</td>
</tr>
</tbody>
</table>