Title: ELASTOSOLS, PREPARATION, USE AND PRODUCTS THEREOF

Abstract

An elastosol is provided comprising: (a) a finely powdered, linear or branched block copolymer having a particle size of 800 micron or less, comprising at least one polymer block (A) derived predominantly from a monovinyl aromatic compound and at least one, optionally hydrogenated, polymer block (B) derived predominantly from a conjugated diene, wherein the content of monovinyl aromatic compound is at least 40 % by weight based on the weight of the block copolymer, and (b) a rubber compatible liquid plasticizer, the weight ratio (a)/(b) being in the range of from 0.1 to 10. Furthermore, there is provided a process for the preparation of an elastosol as well as a process for the preparation of a homogeneous rubbery product derived from said elastosol.
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ELASTOSOLS, PREPARATION FOR
USE AND PRODUCTS THEREOF

The present invention relates to elastosols, to a process for
the preparation of such elastosols, to a process for use of these
elastosols and to products derived from them.

With the term "elastosols" as used throughout this
specification is meant dispersions of very fine elastomeric block
copolymer particles in liquid organic media, or more specifically,
in rubber compatible liquid plasticizers.

At present polyvinylchloride plastisols, i.e. dispersions of
very fine PVC particles in liquid organic media, are widely used
for a variety of applications, such as in the preparation of bottle
cap seals, conveyor belts, carpet backing and wall- and
floor-coverings. In other applications PVC plastisols are processed
by means of dipping, such as in the case of industrial gloves,
surgical gloves, shoes, boots and coated wire products. The shaping
of products by means of roto-casting or moulding, which is the
reverse of dipping, is also a widely used technique. The latter
method is particularly suited for the production of hollow goods,
such as certain toys (balls, dolls and the like). Since there is an
increasing demand for environmental friendly products, PVC
containing compositions are the subject of many discussions due to
the presence of the environmentally charging element chlorine in
PVC. It will be appreciated that upon disposal of PVC containing
products, e.g. by incineration, toxic compounds containing chlorine
may be released into the environment. Therefore, extensive research
effort is put in by industry to find halogen-free alternatives for
PVC. However, a significant problem is to find such alternatives,
which provide at least the same processing and product
characteristics as the presently applied PVC plastisols. One of the
main advantages of using PVC plastisols namely, is their ability to be processed by the above mentioned inexpensive processing techniques, such as spreading, moulding or roto-casting and dipping, followed by zero-shear fusion of the plastisol to form the desired product. These techniques are much more flexible and provide higher production speeds than the conventional thermoplastics processing techniques like extrusion and injection moulding. Up to now not any satisfactory halogen-free alternative for PVC plastisols has been found, which can be prepared and processed according to said advantageous plastisol processing techniques. Moreover, as in the present situation these techniques are widely used in the PVC-plastisol industry, it is by far preferred to develop halogen-free alternatives which can be processed (and prepared) using the existing equipment in order to keep the investment costs as low as possible.

It will be appreciated that it is a main object of the present invention to provide a halogen-free PVC alternative in the form of a dispersion and more particularly in the form of an elastosol, which can be processed by means of the presently applied plastisol techniques.

From Canadian Patent No. 1,132,283 a composition is known containing a highly oil extended conjugated diene/vinyl aromatic radial teleblock copolymer. Said composition is prepared by dissolving the block copolymer in the oil under shear conditions, e.g. by stirring, and at an elevated temperature of 120 °C to 205 °C. The radial block copolymer contains 50-95% by weight of the conjugated diene and 5-50% by weight of the monovinyl aromatic compound. Due to the relatively higher content of conjugated diene in comparison with the monovinyl aromatic compound, the radial block copolymer is highly elastic. The oil to be used preferably is a naphtenic oil as the bleeding-out of oil is most likely to occur if paraffinic oil is used. The weight ratio of polymer to oil may vary from 0.5 to 0.1, which implies that oil is always present in larger amounts than the polymer. As a result, the composition is rather soft and the complete absence of bleeding-out of oil is
difficult to realize. Moreover, during the preparation of the composition, the radial teleblock copolymer must be dissolved at an elevated temperature in order to obtain a homogeneous blend eventually. The processing of such compositions prepared by this melt technique is rather difficult, as shaped articles or homogeneous films can only be prepared starting from a hot mixture. It will be appreciated that storage of the homogeneous blend is in fact impossible as homogeneity is only reached at elevated temperatures and after cooling the resulting product is too stiff to be processed any further. So after its preparation, the homogeneous blend immediately must be processed.

Hence, it would be advantageous to provide an elastosol, which is stable at room temperature and which consequently can be prepared, handled and stored at relatively low temperatures.

Heating the elastosol is carried out only after the elastosol has been brought in its desired end shape.

It is therefore another object of the present invention to provide a process for the preparation of an elastosol, which process can be carried out at relatively low temperature, in order to obtain an elastosol which is stable at room temperature.

A further object of the present invention is to provide a process for the preparation of a product obtainable from said elastosol via a phase inversion process.

Accordingly, the invention relates to an elastosol comprising:

(a) a finely powdered, linear or branched block copolymer having a particle size of 800 micron or less, comprising at least one polymer block A derived predominantly from a monovinyl aromatic compound and at least one, optionally hydrogenated, polymer block B derived predominantly from a conjugated diene, wherein the content of monovinyl aromatic compound is at least 40% by weight based on the weight of the block copolymer, and

(b) a rubber compatible liquid plasticizer, the weight ratio (a)/(b) being in the range of from 0.1 to 10.

With the terms "derived predominantly from a monovinyl aromatic compound" and "derived predominantly from a conjugated..."
diene" as used throughout the present specification in connection
with the composition of the polymer blocks of the block copolymer,
are meant that respectively the monovinyl aromatic compound and the
conjugated diene are present in the polymer block under
consideration in an amount of at least 80% by weight based on said
polymer block. The remaining 20% by weight or essentially less
consists of conjugated diene monomer in the case of a monovinyl
aromatic polymer block and of monovinyl aromatic monomer in the
case of a conjugated diene polymer block. Preferably, these
(co)monomers are similar to those actually incorporated in the
poly(conjugated diene) and poly(monovinyl aromatic) blocks.

From British Patent Specification No. 1,125,499 a closure for
containers is known comprising a shell adapted for mechanical
engagement with the container and a liner in said shell for
engaging and sealing the container. This liner is transparent and
comprises a triblock copolymer of general configuration A-B-A with
A being a poly(monovinyl aromatic) block and B an optionally
hydrogenated poly(conjugated diene) block and per 100 parts by
weight of said block copolymer 20 to 100 parts by weight of a
mineral oil extender. The composition must be soft and elastic in
order to be able to actually engage and seal a container and
therefore the content of monovinyl aromatic compound can not be too
high. Furthermore, the composition is prepared by mixing the block
copolymer and the oil, followed by extrusion of the resulting
mixture. Hence, a shear requiring technique, such as extrusion,
must be applied for processing the block copolymer/oil blend
according to said British patent specification. Such techniques are
undesired because of the relatively expensive equipment necessary.
According to the present invention this disadvantage is overcome by
using an elastosol, as a result of which processing can take place
via plastisol techniques which do not require shear.

From U.S. patent no. 4,331,581 a process for the preparation
of an elastosol paste is known using three different organic
solvents, such as cyclohexane and toluene (first solvent), methyl
ethyl ketone (second solvent) and isopropyl alcohol (third
solvent). In the final step of the disclosed process, the elastosol paste precipitates from the last added, i.e. third, solvent. Consequently, the precipitated elastosol paste still contains a substantial amount of solvent, which requires an extra process step for removing solvent, e.g. by evaporation. Such a method requiring the use of organic solvent is undesired for environmental reasons and moreover, in the presently applied plastisol techniques organic solvents are not used at all, thereby avoiding said extra solvent removal step. Therefore, the present invention provides processes for preparing elastosols and pastes derived therefrom without using any organic solvents.

It will be appreciated that the size of the block copolymer particles is very important. Small particles are necessary for obtaining a stable dispersion in the plasticizer. Moreover, if the block copolymer particles are too large, it is not possible to transfer the dispersion of block copolymer particles in the rubber compatible plasticizer into a homogeneous product. In general, a particle size of 800 micron or less will suffice, whereas a particle size of 200 micron or less is preferred. A particle size of 100 micron or less is most preferred. The lower limit of the particle size preferably is as close to zero as possible and is determined by the technique used for obtaining the small block copolymer particles. In general, a lower limit of 1 micron, more suitably 10 micron, will suffice for the purpose of the present invention.

In a preferred embodiment of the present invention, the monovinyl aromatic content is in the range of from 50 to 95% by weight, whereas linear block copolymers comprising two poly(monovinyl aromatic) endblocks A and one poly(conjugated diene) block B are also preferred. The polymer blocks B may be either unhydrogenated or hydrogenated to any desired extent.

The poly(monovinyl aromatic) block A can be derived from styrene, α-methylstyrene, o-methylstyrene, p-methylstyrene, p-tert-butylstyrene, 1,3-dimethylstyrene or mixtures thereof, of which styrene is the preferred monomer. The apparent molecular
weight of block A, as determined by gel permeation chromatography using polystyrene standards, can vary within wide ranges. In general, block A may have any apparent molecular weight in the range of from 5,000 to 150,000 and preferably between 8,000 and 70,000.

The poly(conjugated diene) block B can be derived from 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene or mixtures thereof, of which 1,3-butadiene and isoprene are the most preferred monomers. The number average molecular weight of the rubbery block B is primarily determined by the amount of plasticizer to be absorbed during phase-inversion from elastosol to final product. In general, any number average molecular weight within the range of from 5,000 to 300,000 may be suitable, whereas a number average molecular weight in the range of from 10,000 to 150,000 is preferred.

Basically, the rubber compatible liquid plasticizer has two functions. Firstly, it embodies a liquid medium which enables the block copolymer particles to disperse, thus forming the elastosol according to the invention. This elastosol consists of three separate phases: a first phase formed by the "hard" poly(monovinyl aromatic) domains in the block copolymer particles, a second phase formed by the "soft" poly(conjugated diene) domains of said block copolymer particles and a third phase formed by the rubber compatible liquid plasticizer.

The second function of the plasticizer is that upon heating to a temperature above the glass transition temperature of the poly(monovinyl aromatic) domains it extends the rubber phase, i.e. the poly(conjugated diene) domains. After the plasticizer has been absorbed completely by the rubber phase, this rubber phase will have swollen to such an extent that it will now form the continuous phase. At temperatures above the glass transition temperature of the poly(monovinyl aromatic) domains, said domains will completely soften and upon cooling rearrange into new, interconnecting poly(monovinyl aromatic) domains. Hence, a phase inversion has
occurred, as the original 2+1 phase-situation has been transformed into a 2 phase-situation: one phase consisting of the newly formed poly(monomethyl aromatic) domains and one phase formed by the plasticizer extended rubber phase. This 2 phase-situation is a homogeneous extended rubber, which remains stable after cooling down to e.g. room temperature.

The weight ratio between the block copolymer and the plasticizer is also very important. If this ratio is too high, i.e. higher than 10, the viscosity of the obtained elastosol will be too high. However, a too low ratio, i.e. lower than 0.1, will result in an extended rubber being very weak at room temperature, because the plasticizer will not be completely absorbed by the rubber phase. As a result, bleeding out of the plasticizer is likely to occur. In a preferred embodiment said weight ratio lies within the range of from 0.4 to 3.

The plasticizer to be used may be any known rubber compatible liquid plasticizer, such as a naphthenic oil, a paraffinic oil, an aromatic oil or a mixture thereof, as well as a low molecular weight polyisobutylene or polybutylene. A paraffinic oil, however, is preferred.

The elastosol according to the invention can be prepared by any suitable process for preparing dispersions with the proviso that the finally formed block copolymer particles are small enough to be dispersed in an oil. The block copolymer may be produced by any well known block polymerization or copolymerization process including the well known sequential addition of monomer techniques, incremental addition of monomer technique or coupling technique as illustrated in, for example, U.S. patent specifications nos. 3,251,905; 3,390,207; 3,598,887 and 4,219,627. In order to obtain the block copolymer in a powdered form in which the individual particles all have about the same, small size, any of the presently known techniques may be applied. Examples of such techniques are dispersing under high shear and subsequent precipitation, precipitation of a true solution into a non-solvent under high-speed mixing, cryogenic milling and spray drying. Cryogenic
milling and spray drying are preferred, but since the minimum
obtainable particle size via cryogenic milling is about 150 micron,
whereas spray drying may result in particle sizes of less than 50
micron, the technique of spray drying the block copolymer after its
preparation is most preferred. Hence, the elastosol according to
the invention can be prepared by a process comprising the steps of:
(a) preparing the block copolymer using conventional techniques;
(b) turning the block copolymer into particles having a particle
size of less than 800 micron; and
(c) dispersing the thus obtained, finely powdered block copolymer
in a rubber compatible liquid plasticizer at room temperature.

The present invention also offers a process for the
preparation of a homogeneous, extended rubbery product from said
elastosol, which process comprises the steps of:
(a) heating the elastosol under zero-shear conditions to a
temperature higher than the glass transition temperature of
the polymer blocks A; and
(b) cooling the resulting homogeneous mass.

This process can be successfully applied for the preparation of
films or in the manufacture of any other shaped article, such as
gloves, boots and toys. The elastosol first is spreaded in the case
of films or brought into its desired shape in the case of shaped
articles, after which the above described process for fusion of the
elastosol takes place. Consequently, the homogeneous films and
shaped articles made from said elastosol are also embraced by the
present invention.

The invention is further illustrated by the following examples
without restricting the scope of the invention to these
embodiments.

Example 1

10 parts of a finely powdered styrene-butadiene-styrene block
copolymer having a particle size of about 500 micron, were
dispersed in 4 parts of the paraffinic oil Primol 352 (Primol is a
trade mark) at room temperature. This dispersion was spreaded as a
thin layer on siliconized paper. Upon heating the elastosol in an
oven for 10 minutes at 200 °C followed by cooling to room temperature, a homogeneous film was obtained.

**Example 2**

K-Resin 04 (K-Resin is a trade mark), an asymmetric, branched block copolymer of formula \((S-B)_nX\), with \(S\) representing a polystyrene block, \(B\) a polybutadiene block and \(X\) a polyepoxy resin and with \(n\) varying from 4 to 10, said block copolymer having a styrene content of about 70\% by weight based on the total block copolymer, was spray dried. The resulting median particle size of the block copolymer particles was 16 micron.

The polymer particles were dispersed in a paraffinic oil (Primol 352) by stirring, the weight ratio polymer to oil being 1:1. The dispersion was spreaded as a thin layer on siliconized paper and subsequently heated in an oven for 10 minutes at 180 °C. After cooling to room temperature a homogeneous film was obtained.
CLAIMS

1. An elastosol comprising:
   (a) a finely powdered, linear or branched block copolymer having a
   particle size of 800 micron or less, comprising at least one
   polymer block A derived predominantly from a monovinyl
   aromatic compound and at least one, optionally hydrogenated,
   polymer block B derived predominantly from a conjugated diene,
   wherein the content of monovinyl aromatic compound is at least
   40% by weight based on the weight of the block copolymer, and
   (b) a rubber compatible liquid plasticizer,
   the weight ratio (a)/(b) being in the range of from 0.1 to 10.

2. An elastosol according to claim 1, characterized in that the
   block copolymer has a particle size of 200 micron or less.

3. An elastosol according to claim 2, characterized in that the
   block copolymer has a particle size of 100 micron or less.

4. An elastosol according to any one of the claims 1 to 3,
   characterized in that the content of monovinyl aromatic compound in
   component (a) is in the range of from 50 to 95% by weight.

5. An elastosol according to any one of the preceding claims,
   characterized in that component (a) is a linear block copolymer
   comprising two endblocks A and one midblock B.

6. An elastosol according to any one of the preceding claims,
   characterized in that the monovinyl aromatic compound is styrene
   and the conjugated diene is 1,3-butadiene.

7. An elastosol according to one or more of the claims 1 to 6,
   characterized in that component (b) is a paraffinic oil.

8. An elastosol according to one or more of the claims 1 to 7,
   characterized in that the weight ratio (a)/(b) is in the range of
   from 0.4 to 3.

9. A process for the preparation of an elastosol according to one
   or more of the claims 1 to 8 comprising the steps of:
   (a) preparing the block copolymer using conventional techniques;
(b) turning the block copolymer into particles having a particle size of less than 800 micron; and
(c) dispersing the thus obtained, finely powdered block copolymer in an oil at room temperature.

10. A process according to claim 9, wherein step (b) is carried out by cryogenic milling or spray drying the block copolymer obtained from step (a).

11. A process according to claim 10, wherein step (b) is carried out by spray drying the block copolymer.

12. A process for the preparation of a homogeneous rubbery product from the elastosol according to one or more of the claims 1 to 8, comprising the steps of:
(a) heating the elastosol under zero-shear conditions to a temperature higher than the glass transition temperature of the polymer blocks A; and
(b) cooling the resulting homogeneous mass.

13. A homogeneous film obtained by the process according to claim 12.

14. Shaped articles prepared according to the process of claim 12.
INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 93/01408

I. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both National Classification and IPC

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II. FIELDS SEARCHED

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Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched

III. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>X</td>
<td>WO.A,9 105 014 (RAYCHEM LIMITED) 18 April 1991 see claims 1-2,4</td>
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<td>US.A,4 143 185 (ROBERT D. LUNDBERG) 6 March 1979 see examples 1-3 see claim 1</td>
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* 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 document 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 cannot be considered to involve an inventive step
- "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.
- "Z" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 20 AUGUST 1993

Date of Mailing of this International Search Report 0 1. 09. 93

International Searching Authority EUROPEAN PATENT OFFICE

Signature of Authorized Officer SIEMENS T.

Form PCT/ISA/310 (second sheet) (January 1985)
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| X        | CA,A,1 132 283 (PHILLIPS PETROLEUM COMPANY)  
21 September 1982  
cited in the application  
see example 1  
see claims 1,4 | 1,6-8 |
ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. EP 9301408 SA 74844

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on the European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 20/08/93

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For more details about this annex: see Official Journal of the European Patent Office, No. 12/82