

598012

FORM 1

SPRUSON & FERGUSON

APPLICATION ACCEPTED AND AMENDMENTS
ALLOWED 27.3.90

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

LODGED AT SUB-OFFICE

13 AUG 1987

Sydney

Huls Aktiengesellschaft, incorporated in the Federal Republic of Germany, of D-4370 Marl 1, FEDERAL REPUBLIC OF GERMANY, hereby apply for the grant of a standard patent for an invention entitled:

ABC Block copolymers based on butadiene and isoprene,
process for their preparation and their use

which is described in the accompanying complete specification.

Details of basic application(s):-

Basic Applic. No: Country:

Application Date:

P 36 27 675.8

FEDERAL REPUBLIC OF GERMANY

14 August 1986

P 36 31 706.3

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18 September 1986

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26 March 1987

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DATED this THIRTEENTH day of AUGUST 1987

Huls Aktiengesellschaft

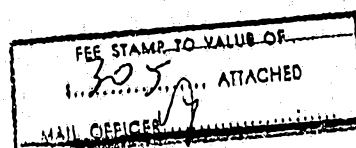
By:

M. J. Anderson

Registered Patent Attorney

TO: THE COMMISSIONER OF PATENTS
OUR REF: 28380
S&F CODE: 52640

5845/2



PATENT OFFICE



PATENT OFFICE



FIVE DOLLARS

SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application made for a patent for an invention entitled:

ABC Block copolymers based on butadiene and isoprene, process for their preparation and their use

X/We, WOLFGANG STICHERLING and JOACHIM BERGMANN
[full name of declarant(s)]

care of HULS AKTIENGESSELLSCHAFT, Kreis Recklinghausen, and
[full address of declarant(s) - not post office box]

Paul-Baumann-Str. 1, D-4370 Marl, Federal Republic of Germany, respectively

do solemnly and sincerely declare as follows:-

1. ~~XXX~~/We are authorised by Huls Aktiengesellschaft, the applicant for the patent to make this declaration on its behalf.

2. The basic applications as defined by Section 141 of the Act were made in Federal Republic of Germany on 14 August, 1986; on 18 September, 1986 and on 26 March, 1987 all by Huls Aktiengesellschaft.

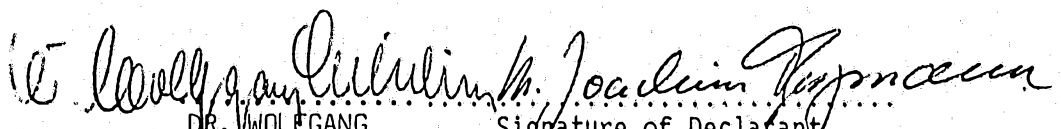
3. WALTER HELLERMANN, CHRISTOPH HERRMANN, HANS-BERND FUCHS, KARL-HEINZ NORDSIEK, JURGEN WOLPERS and HANS-EBERHARD VON PORTATIUS, of Waldstrasse 16, 4270 Dorsten 21; Siedlungsstrasse 3, 4370 Marl; Leverkusener Strasse 12, 4370 Marl; Neumarkstrasse 4, 4370 Marl; Hetfeld 15 c, 4358 Haltern, and Am Gecksbach 40, 4270 Dorsten 11, all in the Federal Republic of Germany [respectively], are the actual inventors of the invention and the facts upon which the applicant is entitled to make the application are as follows:

Huls Aktiengesellschaft is entitled by Contract of Employment between the inventors as employees and Huls Aktiengesellschaft as employer, as a person who would be entitled to have the patent assigned to it if a patent were granted upon an application made by the inventors.

4. The basic applications referred to in paragraph 2 of this Declaration were the first applications made in a Convention country in respect of the inventions the subject of the application.

DECLARED at D-4370 Marl this

day of November 19 87


DR. WOLFGANG STICHERLING Signature of Declarant
DR. JOCHACHIM BERGMANN

TO: THE COMMISSIONER OF PATENTS
AUSTRALIA
SBR/JS/0082W

(12) PATENT ABRIDGMENT (11) Document No. AU-B-76835/87
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 598012

(54) Title
ABC BLOCK COPOLYMERS BASED ON BUTADIENE AND ISOPRENE, PROCESS FOR THEIR PREPARATION AND THEIR USE

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(56) Prior Art Documents
US 4413098
GB 2090840

(57) Claim

1. Unsaturated, elastomeric ABC block copolymers on the basis of
40 to 80% butadiene-1,3,
5 to 40% isoprene and
0 to 30% styrene, comprising
40 to 75% of a block A containing exclusively butadiene
units with a content of uniformly distributed vinyl groups
of less than 15%,
up to 25% of a block B which contains
 - either butadiene and isoprene units with a vinyl
content of less than 15%,
 - or butadiene units having a vinyl content of more

than 75%, and

20 to 55% of a block C, which comprises butadiene and isoprene units having a vinyl content of more than 75%.

6. Process for the manufacture of ABC block copolymers according to claim 1 by anionic polymerisation of the monomers in an inert organic solvent in the presence of a Li-organic compound and a cocatalyst, characterised in that
- a) first a block A is produced by polymerising butadiene,
 - b) thereafter a block B is produced by polymerising a mixture of butadiene and isoprene,
- or
- polymerising butadiene in the presence of a cocatalyst, and
 - c) a block C is produced by polymerising a mixture of butadiene and isoprene in the presence of a cocatalyst.

13. Process according to any one of claims 6 to 12, characterised in that the polymers obtained after complete polymerisation are converted with a coupling agent.

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FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

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Complete Specification Lodged:
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Related Art:

This document contains the
amendments made under
Section 49 and is correct for
printing.

Name and Address
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Complete Specification for the invention entitled:

ABC Block copolymers based on butadiene and isoprene,
process for their preparation and their use

The following statement is a full description of this invention, including the
best method of performing it known to me/us

Abstract:

1. ABC block copolymers on the basis of butadiene and isoprene, process for their manufacture and their use.

2.1 The AB and ABC block copolymers according to the state of the art exhibit a tan delta curve having a comparatively narrow damping region. In order to obtain tyre treads of optimum performance, these known block copolymers must be blended with other caoutchoucs of specific glass transition points. This is considered disadvantageous in practice.

2.2 The block copolymers according to the invention, comprise

40 to 75% of a block A based on butadiene (uniformly distributed vinyl group content less than 15%)

up to 25% of a block B based on butadiene and isoprene (vinyl content less than 15%) or based on butadiene

(vinyl content more than 75%)

20 to 55% of a block C based on butadiene and isoprene (vinyl content more than 75%)

2.3 Use of the ABC block copolymers for the manufacture of tyre treads.

ABC Block copolymers based on butadiene and isoprene, process for their preparation and their use

The present invention relates to unsaturated elastomeric ABC block copolymers based on butadiene, isoprene and optionally styrene, their manufacture and their use for the manufacture of tyre treads.

It is generally accepted that caoutchoucs which are to be employed in tyre making must satisfy the following requirements:

- cold creep must be as little as possible.
- The caoutchoucs must be readily processable in subsequent blending processes.
- The caoutchoucs must be flowable during the moulding processes.
- The caoutchoucs must be readily vulcanisable.

In addition, special requirements have to be complied with which arise from their particular application in tyre making. It is well known that in recent times increased demands are being made on the properties of tyre treads:

- a) They are required to remain highly resilient even at low temperatures.

- b) They must exhibit good anti-skid properties in wet conditions.
- c) They are required to have high abrasion resistance to provide a correspondingly long life expectancy.
- d) When subjected to dynamic loads they should generate as little heat as possible. Their rolling resistance is to be as low as possible in order to keep the fuel consumption of the vehicle as low as possible.

It is known that caoutchoucs, when subjected to torsional vibration tests exhibit a temperature dependency of the logarithmic decrement of mechanical damping and derived therefrom a temperature dependency of the mechanical loss factor $\tan \delta$ which when expressed as a graph, yields a graph configuration which is characteristic for the particular caoutchouc. The desired requirements for tyre treads are met in particular if the $\tan \delta$ curve comprises a vibration damping range which is as wide as possible (cf. K. H. Nordsiek. Kautschuk und Gummi, Kunststoffe 38, 178 (1985) and 39, 599 (1986)).

It is also known that these partly contradictory properties of tyre threads are determined to a substantial extent by the nature and composition of the caoutchoucs employed for this purpose.

Homopolymers based on the conventionally employed monomeric raw materials such as butadiene, isoprene and styrene do not meet these requirements satisfactorily (cf. EP-OS 0 054 204 and JP-OS 82/87 406).

Blends of caoutchouc types are in practice subject to the disadvantage that the above stated spectrum of properties is not attained and the desired tyre-technological qualities are not reproduced reliably. Accordingly, there exists a need for caoutchoucs which substantially satisfy the aforesaid desired properties. In principle it should be possible to attain this object with caoutchoucs composed of polymers comprising a variety of blocks.

For purposes of this invention, the meaning of blocks of a polymer is not restricted only to chain segments composed of different monomeric building elements, but also includes those segments which - dictated by the extraneous process parameters - vary in their nature of interlinking of the monomeric building elements or in the proportion in which they are inserted in a chain segment.

20 Although the butadiene-isoprene copolymer described in EP-OS 0 054 204 comprises in its initial and terminal portion a different content of isoprene as a result of the lower tendency

of isoprene to polymerise as compared with butadiene, it is not to be considered a block copolymer within the meaning just explained.

Even if during the copolymerisation of dienes and styrene the styrene proportion is changed (cf. DE-OS 31 08 583) no block copolymers are attained, but merely a gradual transition. The desired improvement of tyre technological properties is still inadequate, even in that case. Single phase caoutchouc systems are described in DE-OS 31 08 583 comprising a damping maximum created by a glass transition point in a very narrow temperature range.

An improvement is attained only by virtue of a copolymer being produced comprising two different blocks A and B which differ in their structure and/or composition.

A statistical styrene-butadiene block copolymer is thus described for example in DE-OS 31 51 139. The blocks differ in their butadiene contents and their contents of vinyl bonds. They are so intermixed that they are rendered compatible and that instead of two separate damping maxima only a single such maximum is created.

In DE-OS 35 30 438 caoutchouc compositions are claimed which

comprise at least 20% of a styrene-butadiene block copolymer. The blocks differ in respect of their styrene contents, their vinyl bond contents and - as a result thereof - in their glass transition temperatures. In that case as well, the tan delta curve exhibits only a narrow temperature range of maximum damping.

Branched caoutchoucs have been described which may be obtained by the conversion e.g. of a metallic tetrahalogen compound, such as SnCl_4 with block copolymers comprising a polyisoprene and a polybutadiene block. Thus each of the two blocks is present as a homopolymer. The star-shaped caoutchouc which is attained after conversion with the metallic coupling agent forms a single phase caoutchouc system having a glass transition point.

GB-PS 2 090 840 describes block copolymers which are attained by the polymerisation of dienes or the copolymerisation of diene mixtures and the blocks of which differ in respect of their contents of 1,2 and/or 3,4 structural units by 20 to 50 mol %. The preparation of such block copolymers takes place in the presence of different amounts of co-catalyst or at different temperatures.



Tyre treads are described in EP-OS 0 173 791, the caoutchouc component of which may be composed to 30 to 100% of block copolymers based on butadiene, isoprene and optionally styrene and/or piperylene. The block copolymers are produced in the presence of cocatalysts by increasing the temperature and may comprise AB or ABC structures. The polymers always contain a terminal block based on butadiene which is formed at rising temperature and which accordingly comprises a comparatively high content of 1,2 structural units and an uneven distribution of the vinyl groups. Even those block copolymers do not yield tan delta curve having an adequately wide plateau in order to comply optimally with all required tyre properties (see comparative example A). Accordingly, even that specification proposes to blend the block copolymers so obtained with other caoutchouc components (see claim 1 and example 2).

All aforementioned block copolymers are subject to at least one of the following shortcomings:

1. The block copolymers do not satisfy adequately the abovementioned requirements with a view to their use as tyre materials.
2. Compatability problems of the two blocks are experienced.
3. The tan delta curve exhibits only a narrow damping maximum.

4. Large amounts of comparatively expensive isoprene are required.

It has been an object of the present invention to develop ABC block copolymers based on isoprene and butadiene which provide a tan delta curve of a vibration damping region so broad that an admixture of further caoutchouc components for broadening the vibration damping range is no longer required. Preferably this vibration damping region is to be between -90°C and $+30^{\circ}\text{C}$.

According to a first embodiment of this invention there is provided unsaturated, elastomeric ABC block copolymers on the basis of

40 to 80% butadiene-1,3,

5 to 40% isoprene and

0 to 30% styrene, comprising

40 to 75% of a block A containing exclusively butadiene units with a content of uniformly distributed vinyl groups of less than 15%, up to 25% of a block B which contains

- either butadiene and isoprene units with a vinyl content of less than 15%,
- or butadiene units having a vinyl content of more than 75%, and 20 to 55% of a block C, which comprises butadiene and isoprene units having a vinyl content of more than 75%.

Preferably the content of isoprene units in block B does not exceed 33%. Preferably the content of butadiene units in block C is 5 to 40%.

Block B and/or block C may comprise styrene in amounts of up to 40%. The ABC block copolymers may be linear as well as branched. Such branching may be attained during the polymerisation by means of a branching agent or with the aid of a coupling agent towards the end of the polymerisation.

According to a second embodiment of this invention there is provided a process for the manufacture of ABC block copolymers according to the



first embodiment by anionic polymerisation of the monomers in an inert organic solvent in the presence of a Li-organic compound and a cocatalyst, characterised in that (a) first a block A is produced by polymerising butadiene, (b) thereafter block B is produced by polymerising a mixture of butadiene and isoprene, or polymerising butadiene in the presence of a cocatalyst, and (c) a block C is produced by polymerising a mixture of butadiene and isoprene in the presence of a cocatalyst.

In principle it is possible to introduce into the reaction vessel at the commencement of the polymerisation of each block the amounts of monomers which are required for the preparation of each block. However, it is also possible to introduce even at the commencement of the polymerisation of block A the total amount of butadiene and to commence the preparation of block B by the addition of the cocatalyst or of isoprene. The same considerations apply to the introduction of the isoprene. The combined use of styrene as a comonomer for blocks B and/or C is preferred.

Preferably a monofunctional Li-organic compound is employed in the process of the invention. Typically the cocatalysts used in the process of the invention are glycol ethers of the formula $R_1(O-CH_2-CH_2)_n-O-R_2$, wherein $n = 1$ or 2 and R_1 and R_2 each represent an alkyl moiety having 1 to 4 C atoms. Preferably $n = 1$ and the alkyl moieties R_1 and R_2 of the glycol ether have different numbers of C atoms.

Generally in the process of the invention the polymers obtained after complete polymerisation are converted with a coupling agent. Typically at least one of the process steps of the polymerisation is carried out in the presence of divinylbenzene.

According to a third embodiment of this invention there is provided Use of the ABC block copolymers according to the first embodiment of the invention for the manufacture of tyre treads.



In the following the process is to be described in detail.

An inert organic solvent is employed as the reaction medium.

Hydrocarbons having 6 to 12 C atoms such as pentane, hexane, heptane, octane and decane and their cyclic analogues are particularly suitable. Aromatic solvents, e.g. benzene, toluene, xylene and others are also suitable. It stands to reasons that mixtures of the aforementioned solvents may also be employed.

Alkyl lithium compounds which can readily be obtained by the



conversion of lithium with the corresponding alkylhalogenides are employed as catalysts. The alkyl moieties comprise 1 to 10 C atoms. Individual hydrogen atoms may be substituted by phenyl moieties. The following alkyl lithium compounds are particularly suitable: methyllithium, ethyllithium, pentyllithium, n-butyllithium being particularly preferred.

In order to improve the cold creep properties, at least one polymerisation stage is preferably carried out in the presence of small amounts of a branching agent, e.g. divinylbenzene (DVB). Not more than 0,5 parts DVB based on 100 parts monomer are employed. Such addition is dispensed with if after the polymerisation a coupling reaction is provided for.

The nature and amount of catalyst and branching agent are generally so selected that the block copolymer obtained has the following properties:

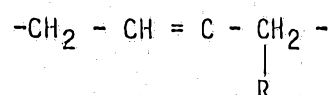
Mooney viscosity (ML_{1-4} , 100°C DIN 53 523): 35 to 120;

Non-uniformity $U = (M_w/M_n) - 1$, determined by gel permeation chromatographic analysis (GPC analysis): 0,6 to 3,0;

Defo elasticity (80°C, DIN 53 514): ≥ 20 ;

In the present process individual blocks are prepared in the absence of the cocatalyst whilst others are prepared in the presence of a cocatalyst.

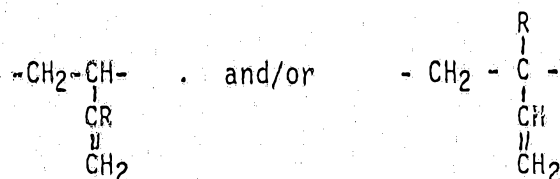
In the former case, i.e. when the cocatalyst is absent, the process is carried out at temperatures of 20 to 120°C, preferably of 20 to 80°C, and in the case of the dienes, polymers are obtained comprising more than 85% 1,4 structural units of the general formula



R = H (butadiene)

R = CH₃ (isoprene)

In the second case the object is to obtain polymers with as high as possible a content of 1,2 and/or 3,4 structural units.



R = H (Butadiene)

R = CH₃ (Isoprene)

Thus the cocatalysts are selected in accordance with their ability to control the microstructure, i.e. the manner in which the polymerisation proceeds in respect of directing it towards as complete as possible a formation of 1,2 and/or 3,4 structural units.

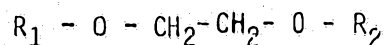
The cocatalyst is generally selected from the group of

- ethers,
- tertiary amines or
- tertiary amines containing ether groups

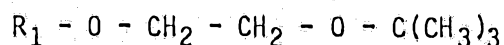
Suitable ethers comprise in particular

- dialkyl ethers of ethyleneglycol and diethylene glycol, their alkyl groups each comprising up to 4 C atoms.

Ethers of the general formula

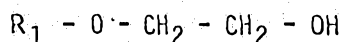


are preferred in particular for the manufacture of branched block copolymers, R_1 and R_2 representing alkyl moieties having different numbers of C atoms selected from the group of methyl, ethyl, n- and iso-propyl as well as n-, iso-, sec.- and tert. butyl. Preferably the sum of the C atoms of the two moieties R_1 and R_2 is from 5 to 7, more particularly 6. A particularly suitable ethyleneglycol ether is the compound wherein R_1 = ethyl and R_2 = tert. butyl. The glycol ethers are for example obtainable in accordance with the principles of the Williamson synthesis from a sodium alcoholate and an alkyl halogenide. The ethers of the formula



may be produced in a simple manner by converting the

corresponding alcohol



with isobutene in the presence of an acid ion exchanger.

Suitable tertiary amines are for example N,N,N',N'-tetramethylethylene diamine, N,N,N',N'-tetraethylethylene diamine and triethylene diamine.

Suitable amines containing ether groups are N-methylmorpholine and N-ethylmorpholine.

10 The cocatalyst is employed in a ratio of 2:1 to 30:1, in particular 2:1 to 50:1 based on the mol number of the catalyst. At higher temperatures larger quantities of cocatalyst are generally required in order to attain the desired microstructure control. Reaction temperatures of 100°C should not be exceeded. The polymerisation is advantageously carried out at constant temperature. It is possible, however, to operate at rising or falling temperatures; in that case, however, care must be taken that the microstructure does not suffer fundamental change.

20 In the production of the blocks B and/or C styrene may be added as a comonomer. Care must be taken by suitable expedients to ensure that the content of polystyrene blocks in the ABC block copolymer does not exceed 2% by mass. (A process for determining

the content of polystyrene blocks is described in the textbook Houben-Weyl "Methoden der Organischen Chemie", Vol. 14/1 (1061), page 698.) It is also possible to add part of the styrene to block C towards the end of the polymerisation.

It is known that certain compounds proposed as cocatalysts have the property of suppressing the formation of polystyrene blocks. The same property is present in compounds which are known as randomisers and which are usually potassium salts of alcoholates as well as organic carboxylic and sulphonic acids.

10 In accordance with a particular embodiment of the process, the "live polymers" present at the end of the polymerisation can be converted into branched or star-shaped block copolymers with a coupling agent.

Suitable coupling agents are polyepoxides such as epoxidised linseed oil, polyisocyanates, polyketones such as 1,3,6-hexanetrione, polyanhydrides, for example the dianhydride of pyromellithic acid and dicarboxylic acid esters such as adipic acid diethylester. Particularly suitable are

- the tetrahalogenides of the elements Si, Ge, Sn and Pb, in particular SiCl_4 ,
- organic compounds of the general formula $\text{R}_n[\text{SiHal}_3]_n$, wherein $n = 1$ to 6, in particular $n = 1$ and 2. In this context R is an organic moiety having a valency of n, for

example an aliphatic, cycloaliphatic or aromatic moiety.

1,2,4-Tris(2-trichlorosilylethyl)-cyclohexane,

1,8-bis(trichlorosilyl)-octane and 1-(trichlorosilyl)-octane may serve as examples.

- Organic compounds which contain at least once the moiety >SiHal_2 , e.g. dimethylsilylchloride.
- Halogen hydrosilanes of the general formula $\text{Si(H)}_m(\text{Hal})_{4-m}$ wherein m is from 3 to 1
- di- and trivinylbenzenes, e.g. 1,4-divinylbenzene.

10 In the context of coupling two cases are to be distinguished. If the block C is formed exclusively from butadiene and isoprene, any one of the abovementioned coupling agents will be suitable. If the block C also includes styrene units as part of the structure, it was found advantageous to employ divinyl benzene as the coupling agent.

The process may be conducted discontinuously as well as continuously.

The person skilled in the art will be able by means of the tan delta curve to produce block copolymers by varying the reaction
20 conditions which can be processed into tyre treads having the desired combinations of properties.

The amorphous polymers obtained will be mixed with active reinforcing fillers, a vulcanising agent and conventional additives if they are to be converted into vulcanisation products. Generally speaking, it is necessary to carry out such mixing in the presence of shear force effects.

Compositions which are intended for the manufacture of tyre threads are generally formed as camelbacks. During the homogenisation and moulding which may for example take place in an extruder the conditions of temperature and time are so selected that no vulcanisation takes place.

The caoutchouc component in the vulcanisable compositions may for example comprise 70 to 100 mass % of a block copolymer according to the invention and 0 to 30 mass % of a caoutchouc selected from the group of known amorphous general purpose caoutchoucs, e.g. styrene-butadiene caoutchouc, 1,4-cis-polybutadiene, 1,4-cis-polyisoprene and natural rubber.

Active, reinforcing fillers are for example tyre tread carbon black compositions of various activities, optionally treated with silane bonding agents, highly dispersed silicic acids and mixtures thereof.

Conventional vulcanising agents contain e.g. sulphur in

combination with accelerators. The amount of vulcanising agents depends on the remaining components in the vulcanisable composition and can be determined by simple preliminary tests.

Plasticiser oils as conventionally used in caoutchouc technology, preferably aromatic, aliphatic and naphthenic hydrocarbons and conventional auxiliaries, for example zinc oxide, stearic acid, resin acids, ageing protective agents and ozone protective waxes may serve as additives, added in conventional quantities.

- 10 The block copolymers according to the invention, are suitable for the manufacture of tyre treads for automobile tyres and truck tyres, not only for the manufacture of new tyres, but also for the retreading of old tyres.

The tyre treads are characterised in particular by the following advantageous properties:

- high-skid resistance under wet conditions
- high abrasion resistance
- low rolling resistance and thus low fuel consumption
- high wear resistance
- all-weather suitability

20 A hydrocarbon mixture was employed as the solvent, comprising

about 50% hexane. Additional components of this hydrogenated C₆ fraction were in particular pentane, heptane and octane and their isomers. The solvent was dried over a molecular sieve of pore size 0,4 nm, such that the water content was lowered below 10 ppm, followed by N₂ stripping.

The organic lithium compound was n-butyllithium which, unless stated otherwise, was employed in the form of a 20 mass % solution in hexane.

The monomers isoprene and styrene were boiled under reflux over calcium hydride for 24 hours prior to use, distilled off and titrated to the end point with n-butyllithium in the presence of o-phenanthroline.

The glycol ethers were distilled over calciumhydride and subsequently titrated to the end point with n-butyllithium in the presence of O-phenanthroline.

The divinyl benzene (DVB) was present as a mixture of m- and p-divinylbenzene and was employed in the form of a 64% solution in hexane. The extent of conversion was determined by determining the solids content after evaporating off the solvent and the monomers.

The tan delta curves were determined with a dynamic viscoelastometer (Type Rheovibron supplied by Toyo Measuring Instruments Co. Ltd., Japan) at a vibration frequency of 1 Hz (cf. D. J. Massa J. Appl. Physics 44, 2595 (1973)).

The coupling yield is considered to be the percentage of caoutchouc which after the conversion with a coupling agent comprises a star-shaped structure and is characterised as compared with the non-coupled caoutchouc by a considerably higher molecular mass. This is determined by GPC analysis, tetrahydrofurane being used as solvent and polystyrene as the column material. The polymers are characterised by means of a light scattering detector. For that purpose samples are taken from the reactor prior to the addition of the coupling agent and also towards the end of the reaction.

Parts are given in terms of parts by mass, percentages (%) are expressed in terms of mass %.

Example 1

20 225 parts hexane (technical C₆ fraction), 46,5 parts butadiene and 0,20 parts DVB were introduced into a first V2A stainless steel agitating autoclave, rinsed with dry nitrogen. The polymerisation was started at 50°C by the addition of 0,54 parts n-butyllithium. In spite of cooling, the temperature rose

briefly to a maximum of 58°C. After 75 minutes, once the 1,3-butadiene input had been virtually completely converted, an IR sample was taken.

Immediately thereafter, in a matter of 3 minutes, the contents of a second V2A stainless steel agitator autoclave (50°C) were added. The latter contained a solution titrated with *n*-butyllithium, of 20,2 parts 1,3-butadiene and 33,3 parts isoprene in 80 parts hexane. 10 minutes later two samples were taken. The first sample showed that 60% of all the monomers introduced had been converted. The second sample served for the IR-analysis.

Immediately thereafter 0,85 parts diethyleneglycol dimethyl ether were added. The temperature was kept constant. 3 hours after the start the polymerisation was stopped by the addition of a solution of 0,5 parts 2,2'-methylene-bis-(4-methyl-6-tertiarybutylphenol) in 2 parts moist toluene. The solvents and non-converted isoprene were distilled off with steam, and the polymerisation products was dried for 24 hours at 70°C in a circulating air drying cabinet.

20 Example 2

A titrated solution of 284 parts hexane, 65 parts 1,3-butadiene

and 0,054 parts DVB was introduced into a first agitating autoclave. The polymerisation was started at 40°C by the addition of 0,056 parts n-butyllithium. The temperature was held in the range of 40 to 42°C by cooling. After 26 minutes, after 90% of the 1,3-butadiene introduced had been converted, 0,7 parts glycol diethyl ether were added. After a further 30 minutes and after the 1,3-butadiene had been converted almost completely, an IR-sample was taken.

Immediately thereafter, the contents of a second agitator autoclave (50°C) were added in a matter of 2 minutes. The latter contained a solution titrated with butyllithium of 2 parts 1,3-butadiene and 25 parts isoprene in 200 parts hexane. The temperature was held in the range of 45 to 48°C. After the monomers had been converted virtually completely (approximately 2,5 hours) the polymerisation was stopped and the polymerisation product was processed.

Example 3

A titrated solution of 270 parts hexane, 70 parts 1,3-butadiene and 0,054 parts DVB was introduced into a first agitating autoclave. The polymerisation was started at 40°C by the addition of 0,056 parts n-butyllithium. The temperature was maintained in the range of 40 to 44°C by cooling. After 25 minutes, after 67% of the 1,3-butadiene introduced had been

converted, 0,7 parts glycol diethyl ether were added. After a further 30 minutes, after the 1,3-butadiene had been converted virtually completely, an IR sample was taken.

Immediately thereafter the contents of a second agitating autoclave (50°C) were added in a matter of 1,5 minutes. The latter contained a solution titrated with butyllithium of 3 parts 1,3-butadiene, 16 parts isoprene and 11 parts styrene in 146 parts hexane. The temperature was maintained in the range of 47 to 50°C. After the monomers had been converted virtually completely (about 115 minutes) the polymerisation was stopped and the polymerisation product was processed.

Example 4

335 parts hexane, 60 parts 1,3-butadiene and 0,035 parts DVB were introduced into a V2A stainless steel agitating autoclave. The polymerisation was started at 50°C by the addition of 0,055 parts n-butyllithium, and the reaction temperature was maintained between 50 and 52°C by cooling. After the 1,3-butadiene introduced had been converted virtually completely (after 174 minutes) an IR sample was taken.

20 Immediately thereafter, within 75 seconds, the contents of a second V2A agitating autoclave were added. The latter contained

a solution titrated with butyllithium of 10 parts 1,3-butadiene, 15 parts isoprene and 15 parts styrene in 187 parts hexane at a temperature of 50°C. 4 minutes thereafter two samples were taken. The first sample showed that 68% of the total introduced monomer had been converted. The second sample served for IR analysis.

10 Immediately thereafter one part glycol diethyl ether were added and the temperature maintained at 50°C. 4 hours after the commencement of the polymerisation a solution of 0,5 parts 2,2'-methylene-bis-(4-methyl-6-tertiarybutylphenol) in two parts moist toluene were added. Subsequently the solvent was distilled off with the aid of steam and the polymerisation product was dried for 24 hours at 70°C in a circulating air drying cabinet.

Comparative example A

The block copolymer 1 according to EP-OS 0 173 791 was produced as described there on pages 16, 19 and 20.

20 Fig. 1 shows the tan delta curve of vulcanised test bodies (produced in analogy to the prescribed procedure for SBR in accordance with ISO 2322-1985 (E) Series A) with ABC block copolymers according to Examples 1, 3 and 4 and comparative Example A. It is clearly apparent that the tan delta curve of Examples 1, 3 and 4 in accordance with the invention is wider

than the tan delta curve according to the comparative example
(Example 1 of EP-OS 0 173 791).

Percentage proportions of the structural elements obtained by the polymerisation of the following monomers

	Butadiene			Isoprene		Styrene
	1,4-trans	1,4-cis	1,2-	1,4-	3,4-	
Ex.1						
Block A	53	38	9	-	-	-
Block AB	52	36	8	3	1	-
Block ABC	30	20	23 ¹⁾	1	26	-
Ex.2						
Block AB	43	33	24	-	-	-
Block ABC	30	21	25	2	22	-
Ex.3						
Block AB	38	28	34	-	-	-
Block ABC ²⁾	29	21	29 ¹⁾	1	11	10
Ex.4						
Block A	51	37	12	-	-	-
Block AB	51	36	10	2	1	0,5
Block ABC	33	23	15	2	10	17
Ex. A						
Block A	54	35	11			
Block B	22	31	47 ¹⁾			

1) Including isoprene-1,2

2) The content of polystyrene blocks amounts to 0,3% based on the block copolymer

	Parts by mass of blocks A, B and C in the ABC block copolymer in % ¹⁾			Proportion of 1,2 butadiene and 3,4-isoprene units in block C in %
	Block A	Block B	Block C	
Ex.1	46	14	40	90%
Ex.2	59	6	35	90%
Ex.3	47	23	30	90%
Ex.4	60	8	32	90%

¹⁾ determined by evaluation of the IR spectrum

Table: Characterisation of the ABC block copolymers

Example	Mooney-Viscosity	Defo Elasticity of ABC Block copolymers	non-uniformity U
Ex. 1	87	42	4,6
Ex. 2	51	38	1,6
Ex. 3	48	30	1,4
Ex. 4	54	23	1,3
A	76	27	1,3

Comparative example B (according to GB-PS 2 090 840)

550 parts hexane, 100 parts butadiene and 0,1 parts DVB are introduced into an agitating autoclave. The polymerisation was started at 50°C with 0,068 parts n-butyllithium, the temperature reaching at the most 54°C. After 25 minutes, after a conversion of 45% had been attained, an IR sample was taken.

Immediately thereafter 0,67 parts diethyleneglycol dimethyl ether were added and the polymerisation was continued, the temperature reaching a maximum of 56°C. After the conversion had been completed (approximately after 60 minutes) the reaction mixture was processed in the usual manner.

The AB block copolymer at the glass transition temperature of -67°C exhibited a narrow damping maximum.

Example 5

654 parts hexane and 67 parts 1,3-butadiene were introduced into a V2A stainless steel autoclave rinsed with dry nitrogen. Heating then took place to 50°C and titration with thermal electric control was done with a 5% solution of n-butyllithium in hexane. The polymerisation was started at 50°C by the addition of 0,069 parts n-butyllithium. The temperature was kept constant by cooling. After 70% of the butadiene feed had been converted an IR sample was taken and processed in the same manner as the final product.

Immediately thereafter 33 parts isoprene were added at 50°C, two samples being taken 10 minutes later. The first sample showed that 75% of the total butadiene feed had been converted. The second sample was used for IR analysis.

Immediately thereafter 0,5 parts ethyleneglycol diethyl ether were added. After 80 minutes a further sample was taken for GPC analysis.

Thereafter 0,7 parts DVB were added at 50°C. After 2 hours at 50°C the charge was cooled to room temperature and 0,5 parts 2,2'-methylene-bis(-4-methyl-6-tert.-butylphenol) were added. The caoutchouc so obtained was precipitated with 4000 ml of a mixture of isopropanol and methanol in a volume ratio of 80:20

and dried for 24 hours at 70°C in a circulating air drying cabinet.

The evaluation of the IR analysis revealed that the block C comprised 90% structural units obtained by 1,2-polymerisation of 1,3-butadiene and isoprene and by 3,4-polymerisation of isoprene.

Example 6

734 parts hexane and 75 parts 1,3-butadiene were heated to 50°C in an agitating autoclave and titrated with a 5% n-butyllithium solution. The polymerisation was started at 50°C by the addition of 0,074 parts n-butyllithium. The temperature was kept constant by cooling. After 65% of the butadiene had been converted, 0,56 parts ethyleneglycol diethyl ether were added. After 85% of the 1,3-butadiene had been converted an IR-sample was taken.

Immediately thereafter 25 parts isoprene were added at 50°C. After 80 minutes a further sample was taken for GPC-analysis.

Thereafter 1,53 parts DVB were added. After 2 hours at 50°C the polymerisation was stopped and the polymerisation product was processed. The evaluation of the IR-analysis revealed that the block C comprised 90% structural units obtained by 1,2-polymerisation of 1,3-butadiene and isoprene and by

3,4-polymerisation of isoprene.

Example 7

643 parts hexane and 72 parts 1,3-butadiene were heated to 50 °C in an agitating autoclave and titrated with a 5% n-butyllithium solution.

The polymerisation was started at 50 °C by the addition of 0,068 parts n-butyllithium. The temperature was kept constant by cooling. After 65% of the butadiene had been converted, 0,56 parts ethyleneglycol diethyl ether were added. After 95% of the 1,3-butadiene had been converted an IR-sample was taken.

Immediately thereafter, 16,5 parts isoprene and 11,5 parts styrene were added at 50 °C. After 80 minutes a further sample was taken for GPC analysis.

Thereafter 1,38 parts DVB were added. After 2 hours at 50 °C the polymerisation was stopped and the polymerisation product was processed.

The evaluation of the IR analyses revealed that the block C comprised 90% of structural units obtained by 1,2-polymerisation of 1,3-butadiene and isoprene, by 3,4-polymerisation of isoprene and by polymerisation of styrene.

Example 8

654 parts hexane and 67 parts 1,3-butadiene were introduced into a V2A stainless steel agitating autoclave rinsed with dry nitrogen. This was followed by heating to 50°C and titration with a 5% solution of n-butyllithium in hexane using thermal electric control.

The polymerisation was initiated at 50°C by the addition of 0,074 parts n-butyllithium. The temperature was kept constant by cooling. After 55% of the butadiene had been converted, an IR-sample was taken and the final product was processed.

Immediately thereafter, 33 parts isoprene were added at 50°C; 10 minutes thereafter two samples were taken. The first sample revealed that 58% of the overall input of butadiene had been converted. The second sample served for IR-analysis.

Immediately thereafter, 0,76 parts 1-ethoxy-2 tert. butoxy-ethane were added. After 80 minutes a further sample was taken for GPC analysis.

Thereafter 1,51 parts DVB were added at 50°C. After 2 hours at 50°C cooling to room temperature took place and 0,5 parts 2,2'-methylene-bis-(4-methyl-6-tert.-butylphenol) were added.

The caoutchouc so obtained was precipitated with 4000 ml of a mixture of isopropanol and methanol in a volume ratio of 80:20 and dried for 24 hours at 70°C in a circulating air drying cabinet.

The evaluation of the IR-analysis revealed that the block C comprised 90% structural units obtained by 1,2-polymerisation of 1,3-butadiene and isoprene and by 3,4-polymerisation of isoprene.

Table: Characterisation of the star-shaped ABC block copolymers in accordance with Examples 5, 6, 7 and 8 and comparative Example A

No.	Mooney-Viscosity	Defo Elasticity	Macrostructure		
			U	Z ¹⁾	K % ²⁾
5	63	33	1,9	5	80
6	58	30	2,1	8	80
7	58	26	2,45	9	80
8	60	35	2,0	9	85

1) Z = numerity = number of arms

2) K = coupling yield

Table: Percentage proportion of the structural elements obtained by polymerisation of the following monomers

	Butadiene			Isoprene		Styrene
	1,4-trans	1,4-cis	1,2-	1,4-	3,4-	
Ex.5						
Block A	54	38	8	-	-	-
Block AB	51	33	10	5	1	-
Block ABC	32	23	14 ¹⁾	4	27	-
Ex.6						
Block AB	42	30	28	-	-	-
Block ABC	33	22	24 ¹⁾	1	20	-
Ex.7						
Block AB	41	29	30	-	-	-
Block ABC	29	21	26 ¹⁾	3	10	11
Ex.8						
Block A	56	36	8	-	-	-
Block AB	54	33	8	4	1	-
Block ABC	30	20	20	4	26	-

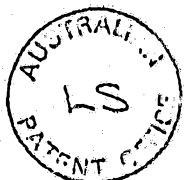
1) including isoprene-1,2

Fig. 2 shows the tan delta curve of vulcanised test bodies (produced in analogy to the instruction for SBR in ISO 2322-1985 (E) Series A) with the ABC block copolymers of Examples 5 and 7.

The claims defining the invention are as follows:

~~Patent claims:~~

1. Unsaturated, elastomeric ABC block copolymers on the basis of
40 to 80% butadiene-1,3,
5 to 40% isoprene and
0 to 30% styrene, comprising
40 to 75% of a block A containing exclusively butadiene
units with a content of uniformly distributed vinyl groups
of less than 15%,
up to 25% of a block B which contains
 - either butadiene and isoprene units with a vinyl
content of less than 15%,
 - or butadiene units having a vinyl content of more
than 75%, and20 to 55% of a block C, which comprises butadiene and
isoprene units having a vinyl content of more than 75%.
2. ABC block copolymers according to claim 1, characterised in
that the number of isoprene units in block B amounts to 0 to
33%.
3. ABC block copolymers according to claim 1, characterised in
that the proportion of butadiene units in block C amounts to
5 to 40%.
4. ABC block copolymers according to ^{any one of} claims 1 to 3,



characterised in that block B and/or block C contains styrene in amounts of up to 40%.

5. ABC block copolymers according to ^{any one of} claims 1 to 4, characterised in that the block copolymers have been subjected to branching by means of branching or coupling agents.
6. Process for the manufacture of ABC block copolymers according to claim 1 by anionic polymerisation of the monomers in an inert organic solvent in the presence of a Li-organic compound and a cocatalyst, characterised in that
- a) first a block A is produced by polymerising butadiene,
 - b) thereafter a block B is produced by polymerising a mixture of butadiene and isoprene,
- or
- polymerising butadiene in the presence of a cocatalyst, and
- c) a block C is produced by polymerising a mixture of butadiene and isoprene in the presence of a cocatalyst.
7. Process according to claim 6, characterised in that
- even at the start of the polymerisation the entire butadiene feed is introduced and step b) - without addition of butadiene - is carried out with an at least 50% conversion



of the monomeric butadiene.

8. Process according to claim 6^{or} and 7,

characterised in that

according to the first modification the entire amount of isoprene is already introduced in process step b) and the polymerisation of block C is carried out after at least 45% conversion of monomeric butadiene and isoprene has been attained.

9. Process according to^{any one of} claims 6 to 8,

characterised in that

in process steps b) and/or c) styrene is added as a comonomer.

10. Process according to^{any one of} claims 6 to 9,

characterised in that

a monofunctional Li-organic compound is employed.

11. Process according to^{any one of} claims 6 to 10,

characterised in that

glycol ethers of the formula $R_1(O-CH_2-CH_2)_n-O-R_2$ are employed as cocatalysts, wherein $n = 1$ or 2 and R_1 ^{and R_2} each represent an alkyl moiety having 1 to 4 C atoms.



12. Process according to claim 11, characterised in that $n = 1$ and the alkyl moieties R_1 and R_2 of the glycol ether have different numbers of C atoms.

13. Process according to any one of claims 6 to 12, characterised in that the polymers obtained after complete polymerisation are converted with a coupling agent.

14. Process according to any one of claims 6 to 13, characterised in that at least one of the process steps of the polymerisation is carried out in the presence of divinylbenzene.

15. Use of the ABC block copolymers according to any one of claims 1 to 5 for the manufacture of tyre treads.

16. Unsaturated, elastomeric ABC block copolymers on the basis of 40 to 80% butadiene-1,3, 5 to 40% isoprene and 0-30% styrene, substantially as herein described with reference to any one of Examples 1 to 8.

17. Process for the manufacture of unsaturated, elastomeric ABC block copolymers by anionic polymerisation of the monomers in an inert organic solvent in the presence of a Li-organic compound and a cocatalyst, substantially as herein described with reference to any one of Examples 1 to 8.

18. An unsaturated, elastomeric ABC block copolymer whenever prepared by the process of claim 17.

DATED this SECOND day of MARCH 1990

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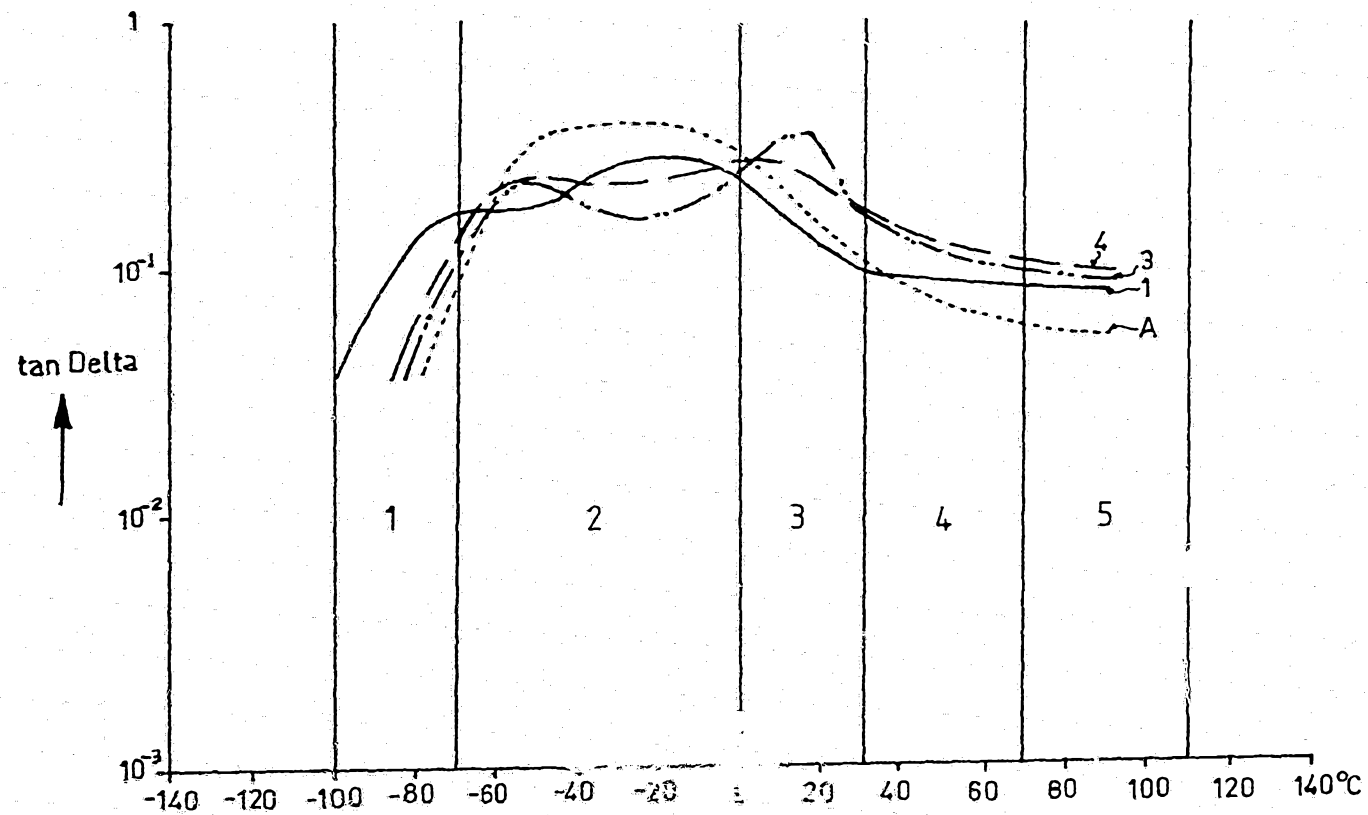


FIG. 1

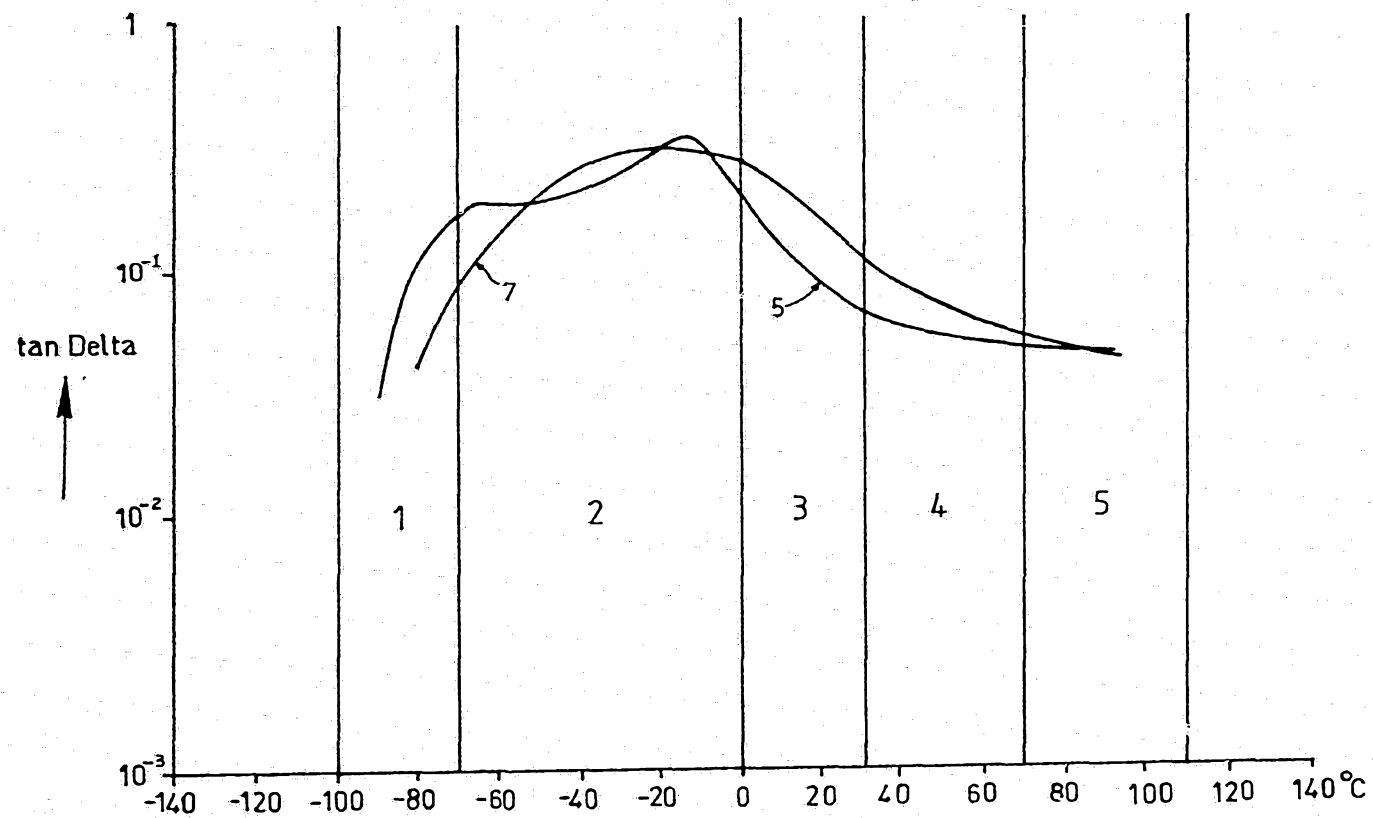


FIG. 2