

AUSTRALIA
PATENTS ACT 1952

B

APPLICATION
BY ASSIGNEE
OF INVENTOR

DECLARATION IN SUPPORT OF AN APPLICATION
FOR A PATENT

NAME OF
APPLICANT

In support of an application made by:
RAYCHEM LIMITED

TITLE

for a patent for an invention entitled:
"GELS COMPRISING BLOCK COPOLYMERS"

FULL NAME AND
ADDRESS OF
SIGNATORY

I, ROBERT LEONARD HALL
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do solemnly and sincerely declare as follows:

1. I am authorised by the above mentioned applicant for the patent to make this declaration on its behalf.

2. The name and address of each actual inventor of the invention is as follows:

JANE VALERIE FRANCIS of St. Mary's, Fouracre Close, Ashton Keynes, Nr. Swindon, Wiltshire SN6 6PJ, England; NOEL MARCEL MICHIEL OVERBERGH of Corbielaan 20, B-3060 Bertem, Belgium; and JAN LODEWIJK M.F.G. VANSANF of Minneveld 2, B-3040 Leuven, Belgium

SEE NOTES OVER

3. The facts upon which the applicant is entitled to make this application are as follows:

The Applicant is the assignee of the actual inventor

DELETE PARAGRAPHS
3 AND 4 FOR
NON-CONVENTION
APPLICATION

4. The basic application(s) as defined by Section 141 of the Act was (were) made as follows:

Country GREAT BRITAIN on 18 July 1986

in the name(s) RAYCHEM LIMITED

and in on

in the name(s)

PLACE AND DATE OF
SIGNING

5. The basic application(s) referred to in the preceding paragraph was (were) the first application(s) made in a Convention country in respect of the invention the subject of this application.

Declared at Swindon, Wiltshire, England

this 7th day of March 1990

Signed

ROBERT LEONARD HALL

Position AUTHORISED SIGNATORY

GRIFFITH HACK & CO

PATENT AND TRADE MARK ATTORNEYS

MELBOURNE · SYDNEY · PERTH

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(56) Prior Art Documents
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US 4361508

(57) Claim

1. A gel or gelloid liquid-extended polymer composition having (i) an ASTM D217 cone penetration value within the range from 100 to 400 (10^{-1} millimetres), (ii) an ASTM D412 ultimate elongation greater than 100% with substantially elastic deformation to an elongation of at least 100%, (iii) an ASTM D412 ultimate tensile strength of less than 1 MegaPascal, and (iv) a dynamic storage modulus at 23°C of less than 50000 Pascals; the composition comprising an intimate mixture of

(a) more than 50% (based on the total polymer) of a block copolymer containing relatively hard blocks and relatively elastomeric blocks;

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(b) additional polymer or copolymer material having at least partial compatibility with, and a higher glass transition, softening or melting temperature than, the hard blocks of the said block copolymer; and

(c) at least 500 parts by weight of extender liquid per 100 parts by weight of the said block copolymer, which liquid extends and softens the elastomeric blocks of the said block copolymer.

16. A method of manufacturing a gel composition according to claim 1, comprising mixing the extender liquid with a blend of the said block copolymer and the said additional polymer or copolymer material at a temperature not less than the glass transition temperature of the hard blocks of the said block copolymer in the blend.

PCT

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(54) Title: GELS COMPRISING BLOCK COPOLYMERS

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

(57) Abstract

A gel or gelloid liquid-extended polymer composition having (i) an ASTM D217 cone penetration value within the range from 100 to 400 (10⁻¹ millimetres), (ii) an ASTM D412 ultimate elongation greater than 100 % with substantially elastic deformation to an elongation of at least 100 %, (iii) an ASTM D412 ultimate tensile strength of less than 1 MegaPascal, and (iv) a dynamic storage modulus at 23°C of less than 50000 Pascals; the composition comprising an intimate mixture of a) mainly a block copolymer containing relatively hard blocks and relatively elastomeric blocks; b) additional polymer or copolymer material having at least partial compatibility with, and a higher glass transition, softening or melting temperature than, the hard blocks of the said block copolymer; and c) at least 500 parts by weight of extender liquid per 100 parts by weight of the said block copolymer, which liquid extends and softens the elastomeric blocks of the said block copolymer. SEBS triblock copolymers with polyphenylene ether 'alloys' as the added material are preferred, the extender liquid preferably being an oil of substantially zero aromatic content.

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GELS COMPRISING BLOCK COPOLYMERS

This invention relates to a gel or gelloid composition, by which is meant a liquid-extended polymer composition having a cone penetration value (measured by a modified version of ASTM D217, as described below) within the range from 100 to 400, (preferably 100 to 350), (10^{-1} millimetres); an ultimate elongation (measured by ASTM D412 as described below) greater than 100%, with substantially elastic deformation to an elongation of at least 100%; ultimate tensile strength (ASTM D412) less than 1 MegaPascal; and dynamic storage modulus (as hereinafter described) less than 50000 Pascals. The composition may either contain a three-dimensional network of cross-linked molecular chains (gels) or may merely behave as if it contained such a network (gelloids).

The invention is more particularly concerned with gel or gelloid compositions mainly (more than 50%, preferably more than 90%, especially more than 95%, of the total polymer) comprising a block copolymer having relatively hard blocks and relatively elastomeric blocks (e.g. hydrogenated rubber blocks) examples of such copolymers including styrene-diene block copolymers (linear or radial) for example styrene-butadiene or styrene-isoprene diblock or triblock copolymers, or styrene-ethylene-butylene-styrene triblock copolymers.

Oil-extended compositions of block copolymers are known, for example from U.S. Patents 3676387 (Lindlof), 3827999 (Crossland), 4176240 (Sabia), and 4369284 (Chen), and it has previously been found necessary to subject
5 copolymer-oil adhesive compositions to radiation cross-linking in order to modify their physical and adhesive properties, as described for example in European Published Patent Application 0224389 (Raychem, Gamarra), U.S. Patents 3845787 (Haefele) and 4151057 (St. Clair), and in "Radiation Curing of PSA's Based on Thermoplastic Rubbers" by D.J. St. Clair, in Adhesives Age, March 1980, pages 30 to 36.

The present invention improves the characteristics of gel or gelloid compositions comprising block copolymers having the aforementioned hard blocks and elastomeric blocks without the need for cross-linking.
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The invention accordingly provides a gel or gelloid liquid-extended polymer composition having (i) an ASTM D217 cone penetration value within the range from 100 to 400 (10^{-1} millimetres), (ii) an ASTM D412 ultimate elongation greater than 100% with substantially elastic deformation to an elongation of at least 100%, (iii) an ASTM D412 ultimate tensile strength of less than 1 MegaPascal, and (iv) a dynamic storage modulus at 23°C of less than 50000 Pascals; the composition comprising an intimate mixture of

25 (a) more than 50% (based on the total polymer) of a block copolymer containing relatively hard blocks and relatively elastomeric blocks;



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(b) additional polymer or copolymer material having at least partial compatibility with, and a higher glass transition, softening or melting temperature than, the hard blocks of the said block copolymer; and

(c) at least 500 parts by weight of extender liquid per 100 parts by weight of the said block copolymer, which liquid extends and softens the elastomeric blocks of the said block copolymer.

Mixtures comprising 200 parts or less of the extender liquid, e.g. as in the hot melt adhesives described in U.S. Patents 4141876 and 4104323, per 100 parts of block copolymer, generally do not behave as gel or gelloid compositions. Such mixtures tend to be too hard and to have too high an ultimate tensile strength and dynamic storage modulus, especially when tackifying resins are added.

Preferred gel or gelloid compositions according to the present invention have a cone penetration value within the range from 100 to 300 (10^{-1} millimetres), and comprise preferably at least 1000, and preferably not more than 5000 parts by weight of the extender liquid per 100 parts by weight of the said block copolymer.

Despite such high levels of extender liquid, the compositions of this invention remain surprisingly stable, homogeneous, and free from phase separation and exudation of extender, and various properties are improved by the additional material while maintaining an adequate balance of other properties.

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The extender liquid preferably has a boiling point higher than the softening or melting temperature of the mixture of the said block copolymer and the said additional polymer or copolymer, and the extender liquid is preferably mixed with the said block copolymer and the said additional polymer or copolymer at a temperature not less than the melting or softening temperature of the mixture of the said block copolymer and the said additional polymer or copolymer. Mastication or other mixing techniques at lower temperatures, perhaps with the aid of volatile solvents, may however be used if the resulting composition is acceptable for the intended end use.

An especially interesting class of block copolymer for the purposes of this invention are those wherein the hard blocks comprise polystyrene. The weight ratio of the hard blocks to the elastomeric blocks in those (and other) copolymers is preferably within the range from 0.25:1 to 0.75:1.

A preferred kind of additional polymers for styrene block copolymers are polyphenylene ethers (PPO), for example poly(2,6-dimethyl-1,4-phenylene) ether, which have substantially complete compatibility with the polystyrene blocks. Substantially complete compatibility of the additional polymer or copolymer material with the hard blocks of the block copolymer is preferable in all cases, and can usually be recognised by a substantial increase in the glass transition temperature of the hard blocks.

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The requirement for the additional material to be at least partly compatible with the hard blocks does not, however, exclude cases where the additional polymer or copolymer material comprises a significant proportion of a polymer or copolymer which is not itself significantly compatible with the hard blocks of the said block copolymer, blended with at least one compatibilising material which renders the additional polymer material at least partially compatible with the said hard blocks. Preferred examples are blends or "alloys" of PPO with other polymers - for example polystyrene, which also has substantially complete compatibility with the hard blocks, although blends of PPO with other materials not substantially complete compatibility with hard block e.g., polyamides are also useful.

The additional polymer or copolymer material is preferably present in an amount sufficient to increase significantly, for example by at least 5°C, or even 10°C, the softening or melting temperature of the composition over that of the same composition without the said additional polymer or copolymer. It has been found useful to include 0.15 to 3, preferably 0.15 to 1.5, more preferably 0.15 to 1.2, parts by weight of the said additional polymer or copolymer material per part by weight of the hard blocks in the said block copolymer.

Although the present invention avoids the need for cross-linking, cross-linking of the composition may still be effected if desired, and may produce

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further improvements in properties. Cross-linking, however, tends to increase the hardness of the composition at room temperature, whereas the use of the additional polymer according to the present invention improves temperature performance without significantly increasing the hardness.

Within the specified range of properties for the gels and gelloids according to this invention, those having an ultimate elongation of at least 200% are preferred. Substantially elastic deformation up to an elongation of at least 200% is also preferred.

Among the block copolymers useful in the present invention are the hydrogenated styrene-diene block copolymers in which the styrene blocks have a molecular weight within the range from 2000 to 50000 and the diene blocks have a molecular weight within the range from 20000 to 300000. Preferred are those having at least two styrene end-blocks and at least one diene mid-block, the styrene end blocks comprising up to 55% by weight of the block copolymer. Examples include poly(styrene-ethylene-butylene-styrene) triblock copolymers, generally referred to as SEBS triblock copolymers. These copolymers have styrene end blocks and ethylene and butylene center blocks and are characterised by the ratio of styrene blocks to the combined ethylene-butylene blocks. Blends of two different SEBS triblock copolymers e.g. as described in European Published Patent Application 0224389 (Gamarra), the disclosure of which is incorporated herein by reference, provide oil extended elastomers according

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to this invention having certain desired cone penetration, elongation and tensile strength properties.

The extender liquids useful in the compositions of this invention comprising the block copolymer and additional polymer or copolymer as aforesaid may be selected from oils conventionally used to extend elastomeric materials. The oil may be a hydrocarbon oil such as paraffinic or naphthenic oils, synthetic oils such as polybutene or polypropene oils, and mixtures thereof. The preferred oils are mixtures of non-aromatic paraffins and naphthenic hydrocarbon oils. The oils should have a minimum boiling point higher than the softening point of the mixture of the block copolymer(s) and the additional polymer or copolymer. The ratio of polymer mixture to the oil will generally range from 2 to 30 parts polymer mixture to 70 to 98 parts oil. In general, it is preferred to use 3 to 10 parts of the block copolymer with 97 to 90 parts oil and most preferred for many applications to use from 4 to 8 parts of the block copolymer, with 96 to 92 parts oil.

The compositions of this invention are preferably prepared by mixing the oil with a blend of the block copolymer(s) and the additional polymer or copolymer material at a temperature not less than the glass transition temperature of the hard blocks of the said block copolymer in the blend, the glass transition temperature of the hard blocks having been raised by the blending. In order to achieve adequate mixing and for the polymers to melt fully and disperse

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in the oil, sufficiently high temperatures and sufficient mixing shear are preferably used. The mixing at the elevated temperature should be continued until the mixture is uniform and all of the polymers are evenly dispersed or blended in the oil. After sufficient mixing, the composition is then poured into the desired moulds or shapes and allowed to cool. The resulting elastomeric composition can be re-melted and again cooled without any significant change in physical properties.

The compositions of this invention can be made having a wide range of physical properties, such as cone penetration, ultimate elongation, and tear strength, desirable for particular end use applications. The preferred compositions having a cone penetration from about 100 to about 300 or 350 (10^{-1} mm) (ASTM D217-82) and an ultimate elongation of at least 200% (ASTM D412) are particularly useful as sealing materials.

The styrene-diene block copolymers useful in the compositions of this invention include the SEBS triblock copolymers discussed above, poly(styrene-butadiene-styrene) block copolymers (SBS), poly(styrene-isoprene-styrene) block copolymers (SIS) and similar styrene-diene block copolymers known in the art. The SEBS block copolymers are preferred in some applications.

The oils useful in the radiation cross-linked versions of the composition of this invention can, for example, be the same oils as defined above.

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The cross-linking agents useful in the electron beam radiation cross-linking of the block copolymer-oil composition, the amount of cross-linking agent, and the electron beam radiation dosage will depend on the composition, its configuration and the degree of cross-linking desired, and may be selected by the usual criteria, for example along the lines disclosed in the aforementioned European Published Patent Application 0224389.

It will be useful to use various additives for various purposes in any of the compositions of this invention. Such additives may be stabilisers, antioxidants, flame retardants, tackifiers, corrosion inhibitors and the like. It is useful to use antioxidants in all the compositions of this invention.

The compositions of this invention have numerous uses as elastomeric materials and in particular may be used as sealing materials, for example as illustrated in published European Patent applications 0108518 and 0191609, although the compositions of this invention will have many and varied uses depending on the properties desired and the temperatures to be encountered.

Gel or gelloid compositions within the scope of this invention are preferably defined by the following criteria (1) to (8) derived from Tests I to V described subsequently, of which preferably not more than one criterion (not(1) or (2)) will be outside the specified ranges.

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I. Cone Penetration.

- (1) Cone Penetration value in the range 100-400 (1/10 mm).

II. Tensile Testing.

- (2) Ultimate Elongation greater than 100%.
- (3) Ultimate Tensile Strength less than 1MPa.

III. Dynamic Viscoelastic Properties (23°C).

- (4) Dynamic Storage Modulus, G' , less than 50000 Pa at 1Hz, preferably less than 5000 Pa, more preferably less than 1000 Pa at 1Hz.
- (5) Dynamic Mechanical Damping, Tan Delta, less than 1.00 at frequencies less than 5Hz.

IV. Dynamic Viscoelastic Properties (80°C).

- (6) Dynamic Storage Modulus, G' , greater than 10 Pa at 1Hz.
- (7) Dynamic Mechanical Damping, Tan Delta, less than 1.00 at frequencies less than 5Hz.

V. Stress Relaxation.

- (8) Relaxation Time greater than 900 seconds.

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Test I: Cone Penetration

Test method ASTM D217, for testing cone penetration in greases, is applied to the gel or gelloid compositions of the present invention (hereafter referred to as gels for simplicity), using a standard full-scale cone, to determine the penetration at 23°C by releasing the cone assembly from a penetrometer and allowing the cone to drop freely into the gel for 5 seconds.

The gel sample is contained in a straight-sided circular cylindrical container which is filled to the brim with the gel. The height of the beaker is 72 mm and its internal diameter is 74 mm. The surface of the sample should be level and free from defects where possible. Air bubbles, especially close to the surface of the sample, should be avoided, and the surface should be protected from dust prior to testing.

Each measurement should be made close to the centre of the sample but not directly in the same place each time. Surface damage caused by the cone is generally clearly visible and must be avoided when making a subsequent measurement.

Test II: Tensile Testing

The method for the tensile testing of gels is a modified version of ASTM D412 in which tensile strength and ultimate elongation are measured at 23°C on dumbbell shaped gel specimens that have not been

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prestressed. Ultimate elongation is measured by 'jaw separation' and tensile strength is based on the original cross sectional area of a uniform section of the specimen.

Tensile tests are performed on a power driven machine equipped to produce a uniform rate of grip separation of 50 mm/min for a distance of at least 1000 mm. The equipment should be capable of measuring the applied force to within 2% and of recording the resultant stress strain curve on a chart recorder. In the current work tensile stress strain measurements of the gel samples were made using an Instron floor model, TT-BM, fitted with a load cell capable of measuring to a lower limit full-scale deflection of 0.4 Newton. The load was indicated on a variable speed chart recorder to an accuracy of 0.5%.

Samples for tensile testing are cut from sheets of gel of uniform thickness between 1 and 6 mm using a Type 1 BS 2782/ISO 37 or a Type 3ASTM D412 dumbbell cutter.

The gel specimens once cut may be difficult to handle. This may be improved by wrapping the ends of each specimen in lint-free tissue up to the distance where the sample will protrude from the machine jaws, (see below). This has also been observed to have the additional beneficial effect of restricting the flow of gel from within the grips themselves when the sample is tested, thereby improving the accuracy of the elongation measurement.

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The tensile machine should first be calibrated in the normal way. Conventional air-grips may be used at an operating air pressure of approximately 20psi. The dumbbell sample is placed in the jaws of the air-grips such that the jaws will hold predominantly onto the tissue covering the ends of the specimen rather than the gel itself. Some exudation of the gel from the far ends of the grips may be observed on closing the jaws. This will not prove to be a problem provided that exudation into the restricted section of the sample, between the two grips is minimal. The tissue wrap will help to minimise this in the case of very soft gels.

The sample is then tested to failure, which should ideally occur in the restricted section, at a cross-head speed of 50 mm/min and the stress-strain curve recorded on a chart recorder. A chart speed of 20 mm/min was found to be adequate for most samples.

The Ultimate Elongation of the sample may be obtained by calculating the cross-head movement from the chart recorder, (knowing the speeds of both). The elongation as a percentage of the original gauge length may then be determined.

For elongations less than the ultimate elongation, the sample will preferably undergo elastic deformation up to at least 100% (preferably at least 200%) as aforesaid, by which is meant that the stretched sample will "snap back" substantially to its original unstressed state if released substantially immediately from the elongating tension.

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Tests III, IV and V: Dynamic Viscoelastic Properties
& Stress Relaxation

Characterisation of the intrinsic viscoelastic properties of gel materials may be preformed using a dynamic spectrometer.

Dynamic mechanical behaviour, in oscillating shear stress and strain conditions, makes it possible to calculate a storage modulus, G' , (or $G(T)$, the relaxation torque modulus in the case of stress relaxation), and a quantity responsible for the dissipation of energy as heat, G'' . The complex dynamic viscosity, Eta^* , may also be used to describe the 'viscous' characteristics of the mechanical behaviour when viscoelastic materials such as gels are deformed; part of the energy being stored as potential energy and part being dissipated as heat. The ratio of energy lost to energy stored in the system manifests itself as mechanical damping, Tan Delta . Such behaviour will vary over a time, temperature and frequency spectrum but may be used to predict the overall performance of a gel, especially with regard to structural effects resulting from molecular transitions, crystallisation, crosslinking, phase separation etc.

The storage and loss moduli, G' and G'' respectively, together with the complex dynamic viscosity, Eta^* , and mechanical damping, Tan Delta , are measured at 23 and 80°C on 25 mm diameter disc specimens as a function of frequency. Similar specimens

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are used in the measurement of the elastic torque modulus, $G(T)$, as a function of time at 23°C in stress relaxation.

Dynamic mechanical measurements on gels are performed on a suitable dynamic spectrometer such as a Rheometrics machine. In the current work a Rheometrics RDS-7700 has been used. The RDS-7700 is primarily a dynamic mechanical instrument for characterising the viscous and elastic behaviour of fluids and solids over an angular frequency of 0.1 to 100 rad/sec. and a temperature range of -150 to 400C. The main operating mode of the RDS is sinusoidal shear oscillation over four decades of amplitude. Steady shear rheological measurement over a shear rate range of 0.01 to 10,000 reciprocal seconds may also be performed. The viscoelastic response of materials to deformation is monitored by a precision air-bearing transducer enabling maximum torque sensitivity coupled with high stability and resonant frequency. Instrument control, data acquisition and analysis are performed by a DEC 11/23 Minc computer system.

Samples for dynamic mechanical testing are cut from sheets of gel of uniform thickness between 1 and 5 mm using a 25 mm diameter circular razor cutter. The samples are cleaned with lint-free wipes before testing in order to remove any unwanted surface deposits and surplus extender.

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Procedure

a) Frequency Sweeps.

The dynamic mechanical properties of gels are measured using the oscillatory parallel plate mode at 23 and 80°C over an angular frequency range of 0.1 to 100 reciprocal seconds. Dynamic strain is generally maintained at 0.05 except for measurements at low rates and high temperatures in which cases larger deformations may be necessary to improve instrument signal resolution.

b) Stress Relaxation.

Stress relaxation experiments are performed using the transient parallel plate mode, allowing the input of a preselected step strain level up to 100%. The decay of the resultant torque modulus and normal stress are measured as a function of time at constant temperature.

Specific examples of the preparation of compositions according to this invention will now be described.

Solution blends of the two polymers, Kraton G1651 (Shell) and poly (2,6-dimethyl-1,4-phenylene) ether (PPO) from Aldrich Chemical Co. were made by the following method. The required amount of each polymer was dissolved in chloroform, at approximately 5% w/v concentration, mixing the solutions and precipitating

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the blend by pouring with stirring into a tenfold excess of methanol. The precipitated blends were filtered and dried overnight at 60°C under vacuum.

Gels were made from the above blends. The components were weighed into a reaction vessel fitted with a mechanical stirrer, a thermometer and a nitrogen bleed. The mixing was carried out under nitrogen to minimise any risk of oxidation of the polymer but would not be necessary with higher shear mixing at lower temperatures. The components were heated with stirring to between 150-200°C, depending on the polymer blend used, until homogenous. The gel could then be poured into suitable receptacles where, it solidified on cooling, and was subjected to the tests indicated below, G' and Tan Delta being determined at 23°C, 1Hz. All samples had cone penetration and ultimate elongation within the acceptable ranges mentioned above. Softening points were determined by Thermomechanical Analysis (TMA) using the point of intersection of a line extrapolated from the pre-softening part of the graph with a line extrapolated from the softening slope part of the graph.

All gels contained:

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	parts
Kraton G1651	100
White mineral oil*	2000
Antioxidant (Irganox 1010)	20

*From Fisons Laboratory Supplies (substantially zero aromatics)

while the PPO content varied:

<u>Gel</u>	<u>Parts PPO</u>
<u>Example</u>	
1 (control)	0
2	10
3	20
4	40
5	80

Results

<u>Example</u>	1	2	3	4	5
TMA softening pt. °C	98	101	117	126	114
G' at 23°C, 1Hz (kPa)	0.68	0.52	0.56	0.50	0.61
tan Delta at 23°C, 1Hz	0.18	0.14	0.19	0.24	0.21

Similarly, a second series of gels were made and tested each containing:

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	parts
Kraton G1651	100
Edelex 45*	2000
Antioxidant	20

* Shell process oil (5% aromatics)

and varying the PPO content:

<u>Gel</u>	<u>parts PPO</u>
<u>Example</u>	
6 (control)	0
7	20
8	40
9	60
10	80

Results

<u>Example</u>	6	7	8	9	10
TMA softening pt. °C	68	102	109	115	116
G' at 23°C, 1Hz (kPa)	1.28	0.98	1.2	1.2	1.26
tan Delta at 23°C, 1Hz	0.19	0.25	0.24	0.2	0.23

Further examples were prepared by procedures similar to those described above, using in each case 100 parts by weight of the Kraton G1651 block copolymer and 2000 parts by weight of FINA A400 B extender oil which is a pharmaceutical grade white mineral oil substantially free from aromatic components, and the

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same antioxidant as described for the preceding examples.

Different PPO molecular weights are illustrated as follows:

	parts
Kraton G1651	100
FINA A400 B	2000
Antioxidant	20

<u>Gel</u> <u>Example</u>	<u>Parts PPO</u>	<u>PPO Mw</u>
11	0	-
12	20	18,000
13	20	35,000
14	20	44,000
15	20	47,000
16	20	56,000
17	20	59,000
18	20	81,000

Results

<u>Example</u>	11	12	13	14	15	16	17	18
TMA softening pt. °C	103	109	117	118	113	107	111	113
G' at 23°C, 1Hz (kPa)	1.09	1.03	0.84	0.77	0.78	0.78	0.54	0.68
Tensile strength (kPa)	71	16	5	5	5	5	3	5
Elongation (%)	988	466	401	459	342	451	306	375

Low levels of PPO (M.W. 18000) are illustrated as follows:

	parts
Kraton G1651	100
FINA A400 B	2000
Antioxidant	2

Gel Parts PPO
Example

19	1
20	2
21	4
22	6
23	8
24	10

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Results

<u>Example</u>	19	20	21	22	23	24
TMA softening pt. °C	105	105	108	113	112	113
G' at 23°C, 1Hz (kPa)	0.96	0.96	0.88	0.86	0.84	0.96
Tensile strength (kPa)	15	21	24	15	13	10
Elongation (%)	619	583	667	536	501	390

Different additives are illustrated as follows, using various polymer "alloys" as the said additional polymer or copolymer material:-

	parts
Kraton G1651	100
FINA A400 B	2000
Additive	20
Antioxidant	2

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<u>Gel</u>	<u>Additive (* Trade Mark)</u>	
<u>Example</u>		
25	Noryl* 110	- PPO/Polystyrene "alloy" from G.E.
26	Noryl* 731	- PPO/Polystyrene "alloy" from G.E.
27	Noryl* EN 130	- PPO/Polystyrene "alloy" from G.E.
28	Prevex* BJA	- PPO/Polystyrene "alloy" from Borg-Warner
29	Prevex* VQA	- PPO/Polystyrene "alloy" from Borg-Warner
30	Luranyl* KR 2401	- PPO/High Impact Poly styrene "alloy" from BASF
31	Dylark*	- Styrene/Maleic anhydride copolymer from BASF

Results

<u>Example</u>	25	26	27	28	29	30	31
TMA softening pt. °C	113	112	110	112	113	112	107
G' at 23°C, 1Hz (kPa)	0.83	0.84	0.88	0.81	0.77	0.79	0.87
Tensile strength (kPa)	-	-	-	-	-	8	20
Elongation (%)	-	-	-	-	-	447	672

The addition of the said polymer or copolymer material comprising Noryl 110 "alloy" in various amounts is illustrated as follows:

	parts
Kraton G1651	100
FINA A400 B	2000
Antioxidant	20

Gel Parts Noryl 110
Example

32	1
33	2
34	4
35	6
36	8
37	10
38	20
39	40
40	60
41	80
42	100

Results

<u>Example</u>	32	33	34	35	36	37	38	39	40	41	42
TMA softening pt. °C	101	110	108	110	107	112	113	112	112	115	113
G' at 23°C, 1Hz (kPa)	0.96	0.85	0.92	0.97	0.96	0.91	0.83	0.79	0.86	0.87	1.04
Tensile strength (kPa)	49	19	20	13	12						
Elongation (%)	914	558	651	596	567						

From the preceding examples it can be seen that the additional polymer or copolymer material can be

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used to restore the softening temperature of gels wherein the extender liquid includes aromatic components, which tend to soften the hard blocks. (Examples 6 to 10). When the extender liquid has less than 5%, preferably less than 2%, and especially when it is substantially free from, aromatic components, the additional polymer, copolymer or polymer alloy material can still contribute useful improvement in softening temperature which may enable a gel to meet performance requirements which would require cross-linking in the absence of the additional material. The additional material may also improve the resistance to compression set in the presence of aromatic extender liquid components, and tends to reduce the storage modulus.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A gel or gelloid liquid-extended polymer composition having (i) an ASTM D217 cone penetration value
5 within the range from 100 to 400 (10^{-1} millimetres), (ii) an ASTM D412 ultimate elongation greater than 100% with substantially elastic deformation to an elongation of at least 100%, (iii) an ASTM D412 ultimate tensile strength of less than 1 MegaPascal, and (iv) a dynamic storage modulus at 23°C of less than 50000 Pascals; the composition comprising an intimate mixture of

(a) more than 50% (based on the total polymer) of a block copolymer containing relatively hard blocks and relatively elastomeric blocks;

15 (b) additional polymer or copolymer material having at least partial compatibility with, and a higher glass transition, softening or melting temperature than, the hard blocks of the said block copolymer; and

(c) at least 500 parts by weight of extender liquid
20 per 100 parts by weight of the said block copolymer, which liquid extends and softens the elastomeric blocks of the said block copolymer.

2. A composition according to claim 1 having an ASTM D217 cone penetration value within the range from 100
25 to 300 (10^{-1} millimetre).

3. A composition according to claim 1 or 2, wherein the said additional polymer or copolymer material has



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substantially complete compatibility with the hard blocks.

4. A composition according to any of the preceding claims, wherein the boiling point of the extender liquid is higher than the softening or melting temperature of a mixture of the said block copolymer and the said additional polymer or copolymer material.

5. A composition according to claim 4, wherein the extender liquid has been mixed with the said block copolymer and the said additional polymer or copolymer material at a temperature not less than the melting or softening temperature of the mixture of the said block copolymer and the said additional polymer or copolymer material.

6. A composition according to claim 5, wherein the block copolymer and the additional polymer or copolymer material have been blended together before mixing with the extender liquid.

7. A composition according to any of the preceding claims, wherein the elastomeric blocks of the said block copolymer comprise hydrogenated rubber.

8. A composition according to any of the preceding claims, wherein the hard blocks of the said block copolymer comprise polystyrene.

9. A composition according to any of the preceding claims, wherein the said additional polymer material comprises a polyphenylene ether.

10. A composition according to any of the preceding claims, wherein the additional polymer or copolymer material comprises a significant proportion of a polymer or copolymer which is not itself significantly compatible with the hard blocks of the said block copolymer, together with at least one compatibilising material which renders the additional polymer material at least partially compatible with the said hard blocks.

11. A composition according to any of the preceding claims, wherein the weight ratio of the hard blocks to the elastomeric blocks in the said block copolymer is within the range from 0.25:1 to 0.75:1.

12. A composition according to any of the preceding claims, wherein the amount of the said additional polymer or copolymer material is sufficient to increase significantly the softening or melting temperature of the composition over that of the same composition without the said additional polymer or copolymer material.

13. A composition according to claim 12, comprising from 0.15 to 3, preferably 0.15 to 1.2, parts by weight of the said additional polymer or copolymer material per part by weight of the hard blocks in the said block copolymer.

14. A composition according to any of the preceding claims, having an ultimate elongation of at least 200%.

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15. A composition according to any of the preceding claims, wherein the extender liquid has less than 2%, preferably substantially zero, aromatics content.


16. A method of manufacturing a gel composition according to claim 1, comprising mixing the extender liquid with a blend of the said block copolymer and the said additional polymer or copolymer material at a temperature not less than the glass transition temperature of the hard blocks of the said block copolymer in the blend.

* * * * *

INTERNATIONAL SEARCH REPORT

International Application No **PCT/GB 87/00506**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ : C 08 L 53/02; C 08 L 71/04; //(C 08 L 53/02, 71:04, 91:00)		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁴	C 08 L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US, A, 3639508 (ROGER P. KAMBOUR) 1 February 1972 see column 9, lines 39-46; claims	1-16
X	US, A, 4361508 (LARRY G. BOURLAND) 30 November 1982 see example 1; claims	1-16
P,X	Patent Abstracts of Japan, volume 10, no. 296 (C-377)(2352), 8 October 1986, & JP, A, 61111354 (ASAHI CHEM IND CO LTD) 29 May 1986 see the whole abstract	1-16

<p>⁹ Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"Δ" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 18th December 1987	Date of Mailing of this International Search Report 20 JAN 1988	
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer  P. C. G. VAN DER PUTTEN	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 8700506
SA 17940.

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 07/01/88. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3639508	01-02-72	NL-A- 6919433	07-07-70
		DE-A, B, C 2000118	16-07-70
		FR-A- 2027757	02-10-70
		GB-A- 1274050	10-05-72

US-A- 4361508	30-11-82	None	
