(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 231 402 A1**

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **85309062.9**

(22) Date of filing: **12.12.85**

(51) Int. Cl.⁴: **H01B 3/22** , H01B 7/28

(43) Date of publication of application:
12.08.87 Bulletin 87/33

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

(71) Applicant: **SHELL OIL COMPANY**
900, Louisiana
Houston Texas 77001(US)
Applicant: **MITSUI PETROCHEMICAL INDUSTRIES, LTD.**
2-5, Kasumigaseki 3-chome Chiyoda-ku
Tokyo 100(JP)

(72) Inventor: **Handlin, Dale L.**
12233 Waldemar Drive
Houston Texas 77077(US)
Inventor: **Lutz, Robert G.**
8322 Twining Oaks
Houston Texas 77379(US)
Inventor: **Korcz, William H.**
11201 Olympia Drive 2708
Houston Texas 77042(US)

(74) Representative: **Myerscough, Philip Boyd et al**
J.A.Kemp & Co. 14, South Square Gray's Inn
London, WC1R 5EU(GB)

(54) **Gel-forming compound for use in filling cables.**

(57) A slow forming, thermally reversible gel for filling cables at or below the polybutylene use temperature, which comprises a butene-1 polymer which may contain C_2-C_5 comonomer, optionally a styrene-ethylene-butylene-styrene block copolymer, and a naphthenic or paraffinic oil with an aromatic content up to 25% by weight.

EP 0 231 402 A1

"GEL-FORMING COMPOUND FOR USE IN FILLING CABLES"

Cables for power, electronic (telephone) transmission, hydrophone cables for oil exploration at sea and other uses have been filled with various substances in order to protect against water intrusion since 1970. Intrusion occurs when water penetrates into a localized opening in a cable sheath and is free to channel as far as physical processes for water spread and transport allow, often hundreds of meters. Not only does this upset the capacitance balance of a transmission cable line but it introduces potential corrosion sites in proportion to the length of wire that is wetted. The useful life of water-soaked wires is obviously shorter than that of dry wires.

The solution that has been widely adopted is to fill the voids in the cable with a water insoluble filling material that simply encapsulates the cable components to prevent water intrusion. However, although this physical function of the cable filling material is straight-forward, the choice of the material is not. Among the many considerations that are important for the materials to be used in this application are the hydrophobic nature of the material, low temperature properties, flow characteristics at elevated temperatures, the highest temperature at which it may be used ("upper service temperature"), processing characteristics, handling characteristics, dielectric properties, toxicity and cost.

Materials that satisfy most of these criteria and which have been widely used are described in US-A-3607487 and US-A-3717716. These materials are essentially a petroleum jelly, mixed with a polymer, usually polyethylene, to impart consistency and prevent flowing at warm temperatures below the upper service temperature.

Similar hydrophobic encapsulants have been proposed for filling splice closures. For example, US-A-3879575 describes a mixture of a low viscosity oil gelled by a styrene-isoprene-styrene copolymer, again with polyethylene added to impart consistency and reduce slump.

US-A-4259540 discloses the use of a styrene-ethylene-butylene-styrene block copolymer, polyethylene, and a paraffinic or napthenic oil, where the oil has a maximum of 5% aromatic oils, in order to enable the cable encapsulant to meet the functional requirements of the cable and to provide good handling characteristics that a petroleum jelly material does not possess.

However, all of these above described encapsulants must be heated during the filling process to a temperature above the "upper service temperature" of the encapsulant. The upper service temperature of the material is the temperature above which the material cannot be used in the cable. Thus, filling of most materials requires a time consuming step in order to heat the encapsulant to a pumpable consistency for filling. There has been long felt need for an encapsulant which meets other filling material requirements but which could be processed into the cable well below the "upper service temperature" of the encapsulant. Previously used encapsulants required that they and the cable be heated to a temperature well above the melting point of the encapsulant (i.e. the upper service temperature) in order to significantly reduce the viscosity of the encapsulant to allow filling of the cable. This heating is energy intensive and may be damaging to some of the electrical components of a cable. It also precludes the use of desirable cable component materials that may be advantageous, but which cannot tolerate high filling temperatures.

In addition, an encapsulant which is thermally reversible has long been sought. This means that the encapsulant may be removed and replaced during maintenance time and time again at a temperature below the temperature that would damage the cables. An encapsulant which is thermally reversible can be heated to a liquid and then cooled to a gel over and over again without damage to the nature of the filling material, or cable components. This is especially true in hydrophone cables that are generally not permanently installed but towed at sea where such utility is paramount.

This invention relates to a slow forming, thermally reversible gel which may be heated to a liquid and cooled to a gel over and over again at a temperature below a temperature that will damage a cable so that the gel may be removed and replaced during maintenance. The gel is slow forming, as the viscosity of a clear liquid formed upon heating rises over a period of several hours to several days to form the gel. It is this length of time that one has to fill the cables before the gel material becomes to viscous to flow, or remove the gel during maintenance.

According to the invention there is provided a gel-forming compound which comprises (a) from 2 to 8 percent by weight of a butene-1 polymer containing from 0 to 10 percent by weight of a C_2-C_5 comonomer, (b) from 0 to 10 percent by weight of a styrene-ethylene-butylene-styrene block copolymer, and (c) from 82 to 98 percent by weight of a naphthenic or paraffinic oil having an aromatic content of from 0 to 25 percent by weight.

The gel-forming compound is based on light hydrocarbon process oils and isotactic butene-1 polymers (both homopolymers and copolymers) and is suitable for use in encapsulating water sensitive cable components, wires in particular. Preferred compounds comprise (a) from 4 to 7 percent by weight of a butene-1 polymer containing from 3 to 8 percent by weight of said C_2-C_5 comonomer, - (b) from 4 to 6 percent by weight of said styrene-ethylene-butylene-styrene block copolymer, and - (c) from 87 to 92 percent by weight of a naphthenic or paraffinic oil having an aromatic content of from 5 to 25 percent by weight. A particularly preferred compound comprises (a) about 6 percent by weight of a butene-1 polymer containing about 6 percent by weight of said C_2-C_5 comonomer, (b) about 5 percent by weight of said styrene-ethylene-butylene-styrene block copolymer, and (c) about 89 percent by weight of a naphthenic or paraffinic oil having an aromatic content of about 15 percent by weight. The C_2-C_5 comonomer is preferably an ethylenic comonomer.

This invention also provides a cable or other conduit requiring water protection which contains the gel-forming compound of the invention. Such a cable typically comprises a wire within a cable body with the wire being protected against water intrusion by the gel-forming compound of the invention.

FIG. 1 is a graph which compares the polybutylene gel upper service temperature and the temperatures at which previously described encapsulants such as waxes or rubbers ("KRATON" G -Registered Trade Mark) had to be filled, as well as the temperature at which the encapsulating gel compound of the present invention may be filled.

The encapsulating compound or gel-forming compound of the present invention has the following properties:

1) Above the gel temperature the material is a clear, low viscosity fluid;

2) after cooling to room temperature the viscosity rises over a period of several hours to several days to form a gel, rendering the material too viscous to flow.

3) As the gel forms it becomes translucent.

4) The gel is thermally reversible at a temperature below the temperature that will damage the cables so that the gel may be removed and replaced during maintenance.

5) The melting temperature, forming temperature and forming time of the gel can be controlled by the choice and concentration of the butylene polymeric component in the base polymer (homopolymer or copolymer).

6) The gel is hydrophobic and protects the cable from water leakage.

The gel is based on light hydrocarbon process oils and isotactic butene-1 polymer. Because of their compatibility with the oils and crystallinity, the isotactic butene-1 polymers dissolve in the oils above the polymers' melting temperature. Once dissolved, these polymers exhibit <u>very</u> <u>slow</u> recrystallization and gel network formation from solution as the temperature is lowered allowing the material to remain fluid at temperatures much below the gel's melting temperature for a period of approximately 24 to 48 hours. Eventually, the crystallites form and become connected in a network forming a translucent gel.

We have found that the presence of ethylene comonomer in the butylene polymer decreases both the gel's melting temperature and rate of polymer crystallization.

EXAMPLE 1

An isotactic butene-1 homopolymer was dissolved in HVI 100 N oil at 120°C so that the solution contained 6 weight percent isotactic butene-1 homopolymer. As the solution temperature was lowered the viscosity began to rise sharply at about 40°C (taken as the minimum filling temperature) and continued to rise to form a firm gel within <u>one</u> <u>hour</u> of reaching room temperature. The gel formed had a melting point of about 80°C.

EXAMPLE 2

Six weight percent DP 8010 isotactic butene-1 copolymer containing 5.7 percent by weight ethylene comonomer was dissolved in HVI 100 N oil. The solution was cooled from 120°C, the temperature necessary for the dissolving, and the viscosity began to rise at about 30°C. The solution material formed into a viscous, usable gel within 24-48 hours after the initiation of the cooling process. The resulting gel had a melting point of 55-60°C.

EXAMPLE 3

The ethylenic comonomer containing polybutene-1 gel of Example 2 was filled into a suitable cable within 24-48 hours after initial cooling from the solution. The cable was ready for use within approximately 12 hours after such filling.

It is apparent that the presence of a C_2-C_5 comonomer, preferably ethylene, and in the range of 2 to 8 weight percent, but preferably about 6 weight percent comonomer, has a dramatic effect on the properties of the gel. In addition, it is thought that many hydrocarbon fluids above a molecular weight of 150 will be gelled by isotactic butene-1 homopolymers and copolymers. For example, HVI 100 N oil has been used which has a 16 percent aromatic content. "Shellflex" 131 - (Registered Trade Mark), which may be obtained from Shell Oil Company, Houston, Texas may also be used as a suitable oil and contains about 24 weight percent aromatic content as well as "Sunpar" 120 LW (Registered Trade Mark) available from Sun Oil Co. which contains less then 5 weight percent aromatic content.

It is also noted that blends of polybutylene with microcrystalline waxes such as Shellmax 500, available from Shell Oil Company, Houston, Texas produced a firmer, more opaque gel which forms somewhat more rapidly than that gel claimed by applicants.

In addition, the addition of from 0 percent by weight to 10 percent by weight of "KRATON" G thermoplastic rubbers, available from Shell Oil Company, Houston, Texas increases the strength and clarity of the gels, with a slight decrease in gel formation time.

In reference FIG. 1, it may be seen that the encapsulating compound or gel-forming compound of the invention can be used to fill a cable at 55 to 60°C --well below the polybutene-1 use temperature of 80°C. The firm gel-forming temperature is at 30°C and the filling range is thus a 50°C range between 80°C and 30°C. If a filling material of waxes or rubbers were used, such filling material would have to be filled, as indicated in FIG. 1, at a point <u>above</u> the 80°C use temperature of the polybutene-1. This would necessitate, of course, a time consuming and cost inefficient additional heating step prior to filling, as well as a reheating every time it became necessary to refill the cable because of leaks or other problems. The use of such materials would also preclude the use of cable components sensitive to temperatures above 80°C.

The invention encompasses a gel-forming material which is not only slow forming to allow plenty of time to fill a cable without an additional heating step, but is also thermally reversible so that if the cable is later punctured and the gel-forming material must be released and/or refilled into the cable, it may be heated to form a liquid and cooled to the filling temperature over and over again without any loss of the gel-forming materials' desirable filling characteristics.

Claims

1. A gel-forming compound which comprises - (a) from 2 to 8 percent by weight of a butene-1 polymer containing from 0 to 10 percent by weight of a C_2-C_5 comonomer, (b) from 0 to 10 percent by weight of a styrene-ethylene-butylene-styrene block copolymer, and (c) from 82 to 98 percent by weight of a naphthenic or paraffinic oil having an aromatic content of from 0 to 25 percent by weight.

2. A compound according to claim 1, which comprises (a) from 4 to 7 percent by weight of a butene-1 polymer containing from 3 to 8 percent by weight of said C_2-C_5 comonomer, (b) from 4 to 6 percent by weight of said styrene-ethylene-butylene-styrene block copolymer, and (c) from 87 to 92 percent by weight of a naphthenic or paraffinic oil having an aromatic content of from 5 to 25 percent by weight.

3. A compound according to claim 1 or 2 which comprises (a) about 6 percent by weight of a butene-1 polymer containing about 6 percent by weight of said C_2-C_5 comonomer, (b) about 5 percent by weight of said styrene-ethylene-butylene-styrene block copolymer, and (c) about 89 percent by weight of a naphthenic or paraffinic oil having an aromatic content of about 15 percent by weight.

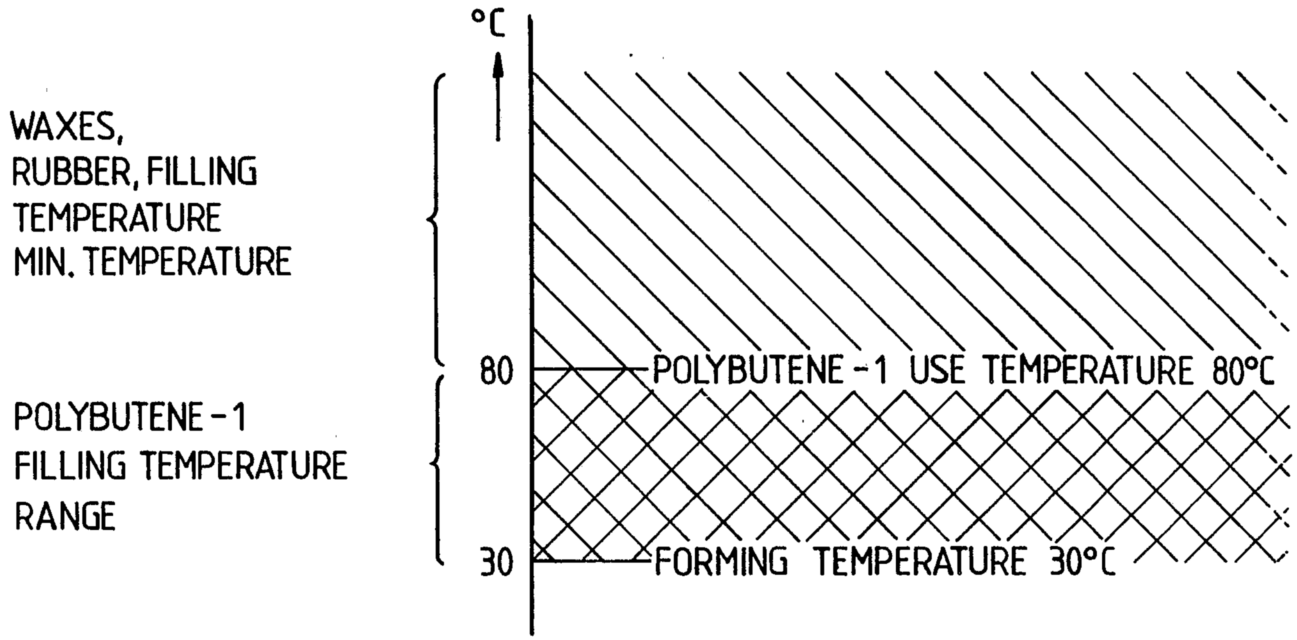
4. A compound according to claim 1, 2 or 3 wherein the C_2-C_5 comonomer is ethylene.

5. Use of a gel-forming compound as claimed in any one of claims 1 to 4 as a filling material for cables.

6. A cable which comprises a wire within a cable body, the wire being protected against water intrusion by, as slow forming, thermally reversible encapsulating compound, a gel-forming compound as claimed in any one of claims 1 to 4.

Fig.1.

TEMPERATURE FILLING RANGES AND USE TEMPERATURES FOR POLYBUTENE-1, WAXES, AND RUBBER,



European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 85 30 9062

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-3 573 209 (R. DE DRYVER et al.) * Column 2, lines 18-29,53-54; claims *	1	H 01 B 3/22 H 01 B 7/28
A	US-A-4 324 453 (N.I. PATEL)		
A	DE-A-2 320 254 (SIEMENS)		
D,A	US-A-4 259 540 (R.A. SABIA)		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			H 01 B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22-08-1986	STIENON P.M.E.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document
T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document