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(54)	Thermally responsive frangible bulb Wärmeempfindliche zerbrechbare Ampulle Ampoule frangible thermosensible	
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(30) (43) (73) (72) •	Priority: 03.10.1996 GB 9620598 Date of publication of application: 29.04.1998 Bulletin 1998/18 Proprietor: TYCO FIRE PRODUCTS MANUFACTURING LIMITED Stockport, SK4 2JW (GB) Inventors: Pepi, Jerome Stefansson Foxboro, Massachusetts 02035 (US) Nettleship, Stephen James Knutsford, Cheshire, WA16 9QJ (GB)	 (74) Representative: Ajello, Michael John Urquhart-Dykes & Lord Greg's Buildings 1 Booth Street Manchester M2 4DU (GB) (56) References cited: WO-A-88/06046 WO-A-97/26945 US-A- 5 392 993 H.H.FAHRENKROG ET AL: "Untersuchung der Einflußgrößen beim Bersten von Sprinklerampullen" SPRECHSAAL, vol. 121, no. 9, 1988, pages 781-787, XP002105149

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Description

[0001] THIS INVENTION relates to a thermally responsive frangible bulb of the type used to automatically release quick response, fire protection sprinklers (nozzles) or, other types of thermally actuated devices.

- 5 [0002] Automatic fire sprinklers (nozzles) have a frame with an outlet at one end, an orifice which is usually just upstream of the outlet, and an inlet which is connectable to a source of fire retarding fluid under pressure. The outlet is secured in the normally closed or sealed position by a cap, the cap being held in place by a thermally responsive element which is releasable when its temperature is increased from a normal ambient condition to a value within a prescribed operating range, by the heat from a fire. Upon release of the thermally responsive element, a stream of fire 10 retarding fluid rushes from the outlet towards a deflector, which is mounted on the frame at the opposite end from the
- outlet, and is distributed over the area to be protected by the sprinkler (nozzle) from fire. [0003] The two primary types of thermally responsive elements used to automatically release fire sprinklers are fusible solder links and frangible glass bulbs. Automatic fire sprinklers were first commercially introduced in the 1870's with various types of fusible solder links. Although ultimately satisfactory, a great deal of effort went into the development
- 15 of the fusible solder links to ensure, among other requirements, that they would: not creep apart, over time, at the normally expected ambient temperature conditions; not be deteriorated or corroded by the normally expected environmental conditions; release with a sharp, positive action; be thrown free of the sprinkler upon activation, so as to not interfere with the distribution of the fire retarding fluid; and, respond promptly to fire conditions.
- [0004] The search for improvements to fusible solder links, which would achieve these requirements, ultimately led 20 to the invention of frangible glass bulb elements, for use in automatic fire sprinklers, as exemplified and discussed in U.S. Patent 654188, U.S. Patent 842725 and U.S. Patent 1639911. With general improvements in material, glass forming, as well as metal casting technology, it has been possible, within the last 20 years or so, to reduce the size of the frangible glass elements and the frames of automatic fire sprinklers, as initially typified by U.S. Patent 4121665 and U.S. Patent 4167974. However, the principles concerning the method of operation of frangible glass bulbs as well
- 25 as the advantages of their use, in automatic fire sprinkler applications, have remained essentially the same. The inherent nature of frangible glass bulb elements not only addressed the above mentioned performance requirements for fusible solder links, and indeed for automatic fire sprinklers in general, at a low manufacturing cost for the thermally responsive element, they have also ultimately provided a ready means for automating the assembly of automatic fire sprinklers.
- 30 [0005] The successful use of frangible glass bulbs, as thermally responsive elements for automatic fire sprinklers, has comprised; particular strength, thermophysical, shape and dimensional requirements for the glass shell which forms the exterior of the bulbs; the need to have certain thermophysical properties for the liquid used to fill the glass shell; and the necessity for precise control over the extent to which the glass shell is filled with liquid prior to sealing. Some discussion of the required combinations of attributes are presented in U.S. Patents 1290602, 1290762 and Re.
- 35 16132. Although it has been found that sodium borosilicate glass is more preferable to quartz material for use in forming the shell of the bulbs, and other liquids have been found to be more preferable to the carbon tetrachloride initially used for filling the bulbs, the basic description of the operating cycle of frangible glass bulbs has remained substantially the same, as stated in the Third Edition of the Grinnell Company Inc. pamphlet Grinnell Quarts Bulb Sprinkler dated May 1929. that is -
- 40 [0006] "The bulb is initially filled with a liquid, the remaining space being largely a bubble. The liquid used has been chosen because of its low freezing point, large co-efficient of (thermal) expansion, slight compressibility, low specific heat and the reluctance with which it retains air in solution. When the head (fire sprinkler) is exposed to rising temperature, the liquid expands and gradually the bubble decreases in size, the air being forced into solution because of the increasing pressure and in spite of the elevated temperature. Finally, all of the air becomes dissolved and the entire
- 45 bulb is filled with the expanding liquid. When this occurs, an almost irresistible internal force is brought to bear on the walls of the bulb and fracture soon occurs. At the instant of rupture the pressure is suddenly decreased so that the air which has been held in solution is free to escape with a mildly explosive action which is sufficient to completely shatter the bulb even in spite of heavy loadings (due to the sprinkler assembly)."
- [0007] In the publication "Sprechsaal", Volume 121, No. 9, 1988, criteria for selecting liquids for use in frangible bulbs 50 for sprinklers are discussed in a paper entitled "Untersuchung der Einflußgrößen beim Bersten von Sprinklerampullen". Characteristics of a wide range of substances are set out in a list on page 786. The list in effect does no more than present values for pressure gradients of various liquids derived by calculation from published data, and a limited number of such values derived experimentally. The conclusion is reached that "only glycerine, ethylene glycol and polyethylene glycol can be considered" because of problems encountered with working with aniline, bromoform and di-iodine methane.
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[0008] Starting in the early 1970's, research into the requirements for making further improvements in the safety to life benefits provided by automatic fire sprinkler systems demonstrated that safety to life could be substantially enhanced through the use of so-called "quick response" or "fast response" thermally responsive elements for the auto-

matic fire sprinklers. Further research in the 1980's showed that property protection could also be enhanced by the use of the quick response elements. Up until the mid to late 1980's, fusible solder links had an advantage over frangible glass bulbs in that they could readily achieve the desired thermal sensitivity for quick response sprinklers through utilising links constructed of thin wall, high thermal conductivity metals joined by a thin bond of fusible solder. However,

- 5 improvements in glass bulb formation machinery along with inventions concerning alternate formations for the shell of frangible glass bulbs, as described in U.S. Patent 4796710 and U.S. Patent 4993496 have provided the means for achieving the structural attributes needed for them to be able to provide quick response operating characteristics. In addition, when combined with the use of more thermophysically responsive liquids, frangible glass bulbs have been able to be produced with the thermal sensitivity requirements for quick response sprinklers, as described below.
- 10 [0009] Since the invention of the frangible glass bulb sprinkler, various types of liquids have been used for filling the bulbs, such as: mercury, carbon tectrachloride, alcohol, tetrachloroethane, acetone, amyl acetate, triethylene glycol, glycol diacetate, ethylene glycol, glycerol, and other dielectric fluids commonly used for heat transfer applications. However, these types of fluids do not offer the combination of properties needed to achieve quick response operating characteristics as well as low Hazard Ratings in cost effective frangible glass bulbs having a nominal operating tem-15 perature rating of at least up to 93°C and, preferably at least up to 141°C.
- [0010] Initially, trichloromethane was used for the filling of quick response, frangible glass bulbs, but more recently liquids such as tetrachloroethylene (perchloroethylene) as described in U.S. Patent 4938294 have been used to fill bulbs having a nominal operating temperature rating of up to 93°C. Because the boiling point of the tetrachloroethylene liquid is about 121°C, it is not generally suitable for use in filling the subsequently developed quick response, frangible
- 20 glass bulbs having a nominal operating temperature rating of up to 93°C. Because of the boiling point of the tetrachloroethylene liquid is about 121°C, it is not generally suitable for use in filling the subsequently developed quick response, frangible glass bulbs having a nominal operating temperature rating of 141°C and other liquids have been used exclusively for filling high temperature bulbs.

[0011] It is an object of the invention to provide an improved thermally responsive frangible bulb.

- 25 [0012] According to the invention, there is provided a thermally responsive frangible bulb comprising a shell defining a closed interior space containing a liquid which expands to fill the space and fracture the bulb when heated to within a pre-determined temperature range, wherein the liquid comprises at least one member from either of the chemical groups consisting of derivatives of aromatic hydrocarbons containing two or more halogen substituents and aliphatic amides.
- 30 [0013] Although the technical choice of suitable liquids for fast response sprinkler bulbs has been based on consideration of thermophysical properties such as compressibility, thermal expansivity and thermal conductivity, for example as described in U.S. patent 4938294, the data available for candidate liquids is sparse, often dubious and rarely in the pressure/temperature regime of a sprinkler bulb at operation. It is not possible to accurately predict performance as a bulb filling liquid based on incomplete or contentious literature values. Practically no independent empirical measures
- 35 exist of important liquid properties such as the dP/dT ratio which defines the relationship between bulb operating temperature and sensitivity. The choice of the most suitable liquid depends on an extensive empirical testing programme where the thermophysical factors outlined above will indicate, but not exclude candidate substances. Examples of liquids assessed by this approach are shown in Table 1. In addition, consideration should be made of factors such as melting and boiling points, long term stability, flammability, toxicity and cost and availability of liquids.
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Substance	Boiling	Density (g/	Heat	Thermal	Thermal	dP/dT
	Point (°C)	cm)	Capacity (J/°K/cm ³)	Conductivity (W/m/°K)	Expansion (cm/°K)	(measured) (Bar/°K)
1,2 Dibromobenzene	224	1.956	1.54			12.51
1,3 Dichlorobenzene	173	1.28	1.4	0.13	0.00094	11.20
1,3 Dioxolane	74	1.06				13.11
1 Bromo 3 Chlorobenzene	196	1.63	1.47			11.79
Cyclohexane	81	0.779	1.4	012	0.0018	9.17

Formamide

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1.134

15.22

Substance	Boiling Point (°C)	Density (g/ cm)	Heat Capacity (J/°K/cm³)	Thermal Conductivity (W/m/°K)	Thermal Expansion (cm/°K)	dP/dT (measured) (Bar/°K)
N,N Dimethylformamide	153	0.944	1.9		0.00104	13.82
Propanone (Acetone)	56	0.791	1.69	0.16	0.00149	
Tetrachloroethylene	121	1.61	1.38	0.11	0.00102	11.22

Table 1. (continued)

[0014] By means of detailed experimental analysis the desirable properties for performance can be correlated with the chemical structure in terms of specific combinations of functional groups, and identification of a suitable liquid can be narrowed down to members of chemical structure classes. A preferred filling liquid comprises a member of the group of halogenated aromatic hydrocarbons containing two or more halogen substituents, or of the group of aliphatic amides.

20 **[0015]** Preferably, the halogenated aromatic hydrocarbon is benzene for which two or more hydrogens are substituted by a halogen, such as 1,3 dibromobenzene illustrated below.

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1,3 dibromobenzene

[0016] The above is an example of a Hückel aromatic hydrocarbon, containing 2n+2π electrons, with two halogen groups bound directly to the aromatic ring. The halogen may be selected from bromine, chlorine or fluorine, for example, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,2-dibromobenzene, 1-bromo-2-chlorobenzene, 1-bromo-2-fluorobenzene, 1-bromo-4-fluorobenzene, 1-chloro-4-fluorobenzene, 1,2,4-dichlorobenzene, 1-bromo-2,4,5-trifluorobenzene, 1,3-dichloro-2,5-difluorobenzene or a mixture of any two or more of the above halogen derivatives.

[0017] Compounds containing the amide group such as formamide, N,N dimethylformamide, N,N-dimethylacetamide and N-methylformamide possess relevant functionality for use in liquids for trigger elements N,N-dimethylacetamide is illustrated below and is an example of the aliphatic amide group, containing the amide linkage (-C(O)N-).

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N,N-dimethylacetamide

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[0018] In combination with satisfying sensitivity requirements to fast response standard, the present invention bestows a number of advantageous properties. These include benefits to the manufacturer of low scrap wastage due to

high values of dP/dT ratio, greater predictability of properties and performance across an extended range of temperature ratings and more efficient manufacturing processes and hazard analysis for manufacturers and end users and use in sub-zero environments where temperatures approach -50°C or less for extended periods. The liquids contained in the glass bulbs are readily available and represent a reduced level of toxicity in comparison with previously used substances, some of which, such as carbon tetrachloride and trichloroethane, have at this date been banned for many

applications.

[0019] An embodiment of the invention will now be described, by way of example, with reference to the accompanying drawings, in which:-

10 Fig. 1 is a partial sectional view of an automatic fire sprinkler showing a preferred embodiment of the quick response, frangible glass bulb, thermally responsive element of this invention;

and Fig. 2 is an enlarged, axial, cross-sectional view of the quick response, frangible glass bulb of this invention taken along the line A-A of Fig. 1.

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[0020] With reference to Fig. 1, automatic fire sprinklers (nozzles) of this invention have a frame 1 with an outlet 2 at one end, an orifice 3 which is usually just upstream of the outlet 2, and an inlet 4 which is connectable to a source of fire retarding fluid under pressure. The outlet 2 is secured in the normally closed or sealed position by a cap 5, the cap 5 being held in place by a thermally responsive element 6 which is secured in position by bulb assembly screw 7

- 20 and releasable when its temperature is increased from a normal ambient condition to a value within a prescribed operating range, by the heat from a fire. Upon release of the thermally responsive element 6, a stream of fire retarding fluid rushes from the outlet towards a deflector 8, which is connected to the frame 1 at the opposite end from the outlet 2, and is distributed over the area to be protected by the sprinkler (nozzle) from fire.
- [0021] With reference to Figs. 1 and 2, the thermally responsive element 6 of this invention is comprised of a frangible 25 glass bulb being itself comprises of a shell 9 and a liquid 10 which, in the room temperature state, nearly completely fills the interior space 11 of the shell 9, except for a relatively small gas pocket 12. With further reference to Fig. 2, the shell 9 of the frangible glass bulb of this invention consists of a central region R₁ which has a uniform outer diameter D₁, a spherical end region R₂, and a stem end region R₃, the spherical end region having a seat of diameter D₂ and the stem end region having a seat of diameter D₃, the distance between the spherical end seat and the stem end seat 30
- being length L.

[0022] In the preferred embodiment of this invention, the frangible glass bulb 6 is of the quick response type with a diameter D_1 of from about 2mm to about 3mm, a diameter D_2 of up to about 2.5mm, a diameter D_3 of up to about 2.2mm, and a length L of from about 12mm to about 24mm, the diameters D_2 and D_3 being in proportion to diameter D₁. The liquid 9 which nearly completely fills the shell 8 of the frangible glass bulb 6 is 1,3-dichlorobenzene.

- 35 [0023] The frangible glass bulb described above has been found to have the combination of thermophysical properties needed to meet all known prescribed operating temperature range, functionality, and maximum RTI requirements for automatic fire sprinklers, as well as, provide a boiling point well above that necessary to fill at least up to 141°C nominal operating temperature rating frangible glass bulbs, in addition to, providing a desirable reduction in Health Hazard and Contact Hazard Ratings.
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Claims

- 1. A thermally responsive frangible bulb comprising a shell defining a closed interior space containing a liquid which expands to fill the space and fracture the bulb when heated to within a predetermined temperature range, wherein the liquid is selected from the group comprising at least one halogen derivative of an aromatic hydrocarbon containing two or more halogen substituents, an aliphatic amide, and a mixture thereof.
- 2. A frangible bulb according to Claim 1, wherein the liquid is benzene in which two hydrogens are substituted with halogens, for example 1,3-dichlorobenzene.
- 3. A frangible bulb according to Claim 1, wherein the liquid is benzene in which three hydrogens are substituted with halogens, for example 1,2,4-dichlorobenzene.
- 55 4. A frangible bulb according to Claim 1, wherein the liquid is benzene in which four hydrogens are substituted with halogens, for example 1 -bromo-2,4,5-trifluorobenzene.
 - 5. A frangible bulb according to Claim 1, wherein the liquid is an aliphatic amide, for example N,N-dimethylformamide,

N,N-dimethylacetamide, N-methylformamide formamide.

- 6. A frangible bulb according to Claim 1, wherein the liquid is a mixture of any two or more of the compounds according to Claims 2 to 5.
- 7. An automatic fire sprinkler having an inlet which in use is connected to a source of fire retarding fluid under pressure, and an outlet which is secured in a normally closed or sealed condition by a thermally responsive frangible bulb according to any one of the preceding claims.
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Patentansprüche

- 1. Ein thermisch ansprechender, zerbrechlicher Kolben, beinhaltend eine Hülle, die einen geschlossenen Innenraum definiert, und die eine Flüssigkeit enthält, die sich ausdehnt, um den Raum auszufüllen und den Kolben zu zerbrechen, wenn sie bis in einen vorgegebenen Temperaturbereich erhitzt wird, wobei die Flüssigkeit aus einer Gruppe ausgewählt ist, die mindestens ein Halogenderivat eines aromatischen Kohlenwasserstoffs mit zwei oder mehr Halogensubstituenten, ein aliphatisches Amid und eine Mischung davon enthält.
- 2. Ein zerbrechlicher Kolben nach Anspruch 1, wobei die Flüssigkeit Benzol ist, bei dem zwei Wasserstoffatome durch Halogene, beispielsweise 1,3-Dichlorbenzol, ersetzt sind.
 - **3.** Ein zerbrechlicher Kolben nach Anspruch 1, wobei die Flüssigkeit Benzol ist, bei dem drei Wasserstoffatome durch Halogene, beispielsweise 1,2,4-Dichlorbenzol, ersetzt sind.
- **4.** Ein zerbrechlicher Kolben nach Anspruch 1, wobei die Flüssigkeit Benzol ist, bei dem vier Wasserstoffatome durch Halogene, beispielsweise 1-Brom-2,4,5-Trifluorbenzol, ersetzt sind.
 - 5. Ein zerbrechlicher Kolben nach Anspruch 1, wobei die Flüssigkeit ein aliphatisches Amid ist, beispielsweise N, N-Dimethylformamid, N,N-Dimethylacetamid, N-Methylformamid Formamid.
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- 6. Bin zerbrechlicher Kolben nach Anspruch 1, wobei die Flüssigkeit eine Mischung von zwei oder mehr Verbindungen entsprechend der Ansprüche 2 bis 5.
- Eine automatische Feuer-Sprinkleranlage mit einem Einlass, der im Betrieb mit einem Vorrat einer unter Druck stehenden, feuerhemmenden Flüssigkeit verbunden ist, und mit einem Auslass, welcher durch einen thermisch ansprechenden, zerbrechlichen Kolben entsprechend einem der vorangehenden Ansprüche in einem üblicherweise verschlossenen oder abgedichteten Zustand gesichert ist.

40 Revendications

- 1. Une ampoule fragile réagissant à la chaleur comprenant une enveloppe délimitant un espace interne enclos contenant un liquide qui se dilate pour remplir l'espace et briser l'ampoule lorsqu'elle est chauffée à une gamme de température prédéterminée, dans laquelle le liquide est sélectionné parmi un groupe comprenant au moins un dérivé halogène d'un hydrocarbure aromatique contenant deux ou plus substituants halogènes, un amide aliphatique et un mélange des précédents.
- 2. Une ampoule fragile selon la Revendication 1, dans laquelle le liquide est du benzène et dans lequel deux hydrogènes sont substitués par des halogènes, par exemple 1,3-dichlorobenzène.
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- **3.** Une ampoule fragile selon la Revendication 1, dans laquelle le liquide est du benzène dans lequel trois hydrogènes sont substitués par des halogènes, par exemple 1,2,4-dichlorobenzène.
- 4. Une ampoule fragile selon la Revendication 1, dans laquelle le liquide est du benzène dans lequel quatre hydrogènes sont substitués par des halogènes, par exemple, 1-bromo-2,4,5-trifluorobenzène.
- **5.** Une ampoule fragile selon la Revendication 1, dans laquelle le liquide est un amide aliphatique, par exemple N, N-diméthylformamide, N,N-diméthylacétamide, N-méthylformamide formamide.

- 6. Une ampoule fragile selon la Revendication 1, dans laquelle le liquide est un mélange de deux ou plus des composés selon les Revendications 2 à 5.
- 7. Un diffuseur anti-incendie automatique ayant un orifice d'admission qui lors de son utilisation est relié à une source d'un fluide ignifuge sous pression, et un orifice de sortie qui est assujetti dans un état normalement fermé ou scellé au moyen d'une ampoule fragile réagissant à la chaleur selon n'importe laquelle des revendications précédentes.



Fig. 1



Fig. 2