

United States Patent

Krause

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[54] **ZERO TEMPERATURE COEFFICIENT
ULTRASONIC TRANSMISSION
MEDIUM HAVING TEMPORAL
STABILITY**

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[51] Int. Cl. **H03f 3/68**, C03c 3/04, C03c 3/10

[58] Field of Search 106/53; 333/30

[56] **References Cited**

UNITED STATES PATENTS

3,154,425 10/1964 Hoover et al. 106/53

FOREIGN PATENTS OR APPLICATIONS

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1,383,962 11/1963 France 106/53

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[57]

ABSTRACT

An ultrasonic delay line, having as the delay medium a glass of the nominal composition in mole per cent 17 per cent lead oxide, 95 per cent barium oxide and 73.5 per cent silicon dioxide, exhibits an average temperature coefficient of delay time of not more than about ± 5 parts per million per degrees centigrade over the range 0° to 100° C., a thermal after-effect of not more than about 10 p.p.m., and an aging of delay time of not more than -10 parts per million per decade (decade is an order of magnitude of time in days).

3 Claims, 2 Drawing Figures

FIG. 1

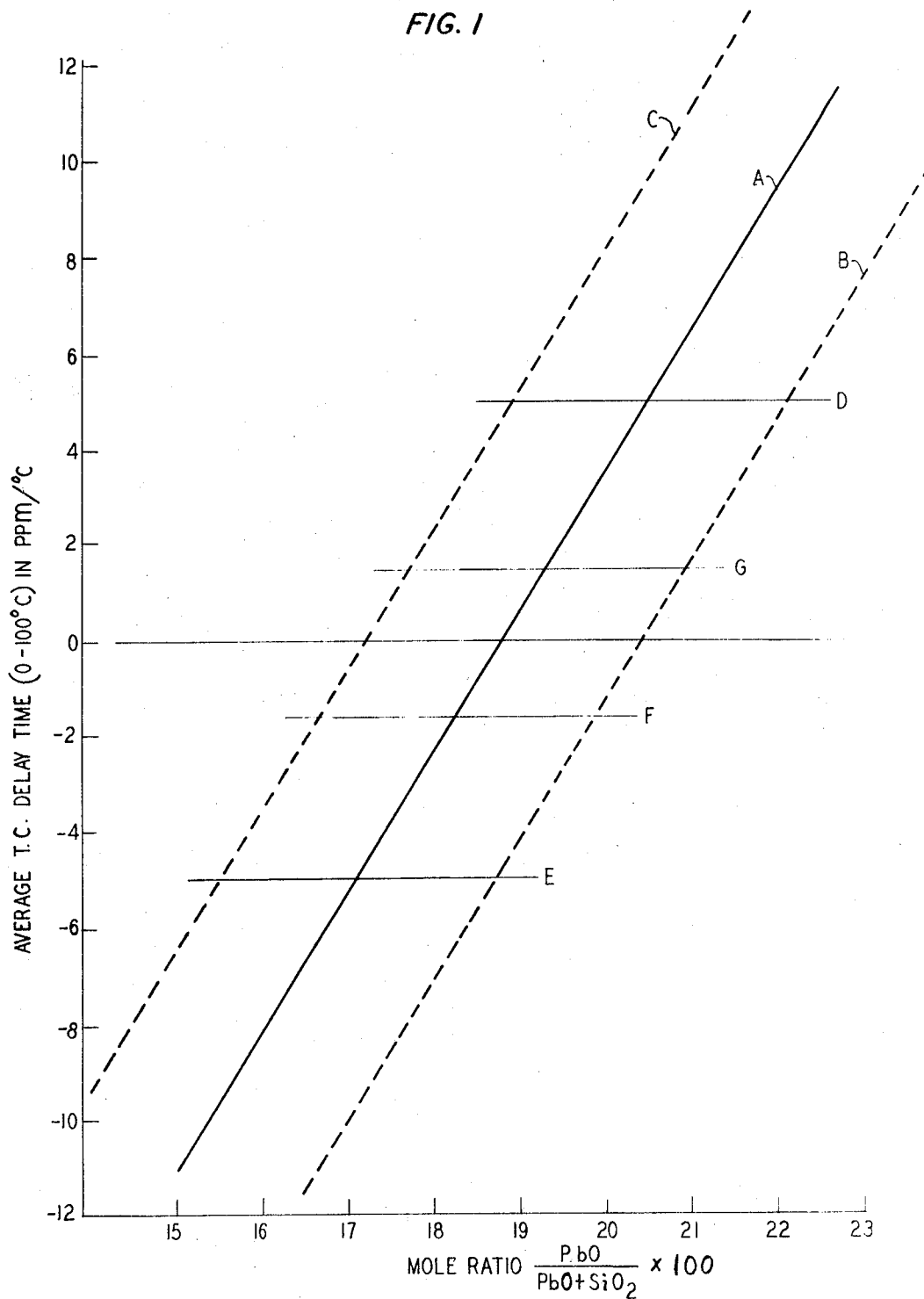
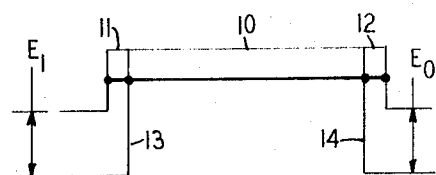


FIG. 2



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ZERO TEMPERATURE COEFFICIENT ULTRASONIC TRANSMISSION MEDIUM HAVING TEMPORAL STABILITY

FIELD OF THE INVENTION

This invention relates to a glass ultrasonic transmission medium having both high temporal stability and temperature stability of delay time, and to ultrasonic devices utilizing same.

PRIOR ART

Many applications being considered for ultrasonic delay lines require a unit delay time which is stable with time over the normally encountered temperature range. Various glass delay media are known which have near zero temperature coefficients of delay time falling within the temperature range of normal use (0° to 100° C.). Among these are the alkali-lead-silicate glasses described in U.S. Pat. No. 3,154,425 issued to H. L. Hoover and M. E. Nordberg on Oct. 27, 1964, and having average temperature coefficients of delay time of up to 8 parts per million per degrees centigrade.

However, when changes in delay time from all sources are considered, a temperature coefficient (T.C.) of as little as ± 8 parts per million per degrees centigrade over the range of 0° to 100° C. may be too high for the most critical applications. Moreover, these near zero T.C. glasses have been found to exhibit changes in unit delay time resulting from thermal after-effects of up to several hundred parts per million and from temporal instability effects (aging) of up to -40 parts per million per decade. (This latter number has been arrived at by plotting change in delay time in parts per million versus days on a log scale. For convenience, the term decade as used herein is intended to refer to the number of days along this log scale.) This amount of variation in delay time is a considerable contribution to the overall change in unit delay time tolerable, and thus too high for some critical applications. In the case of the alkali-lead-silicate glasses mentioned, it has been found that these instability characteristics are related to the glasses' thermal histories. This problem is treated in U. S. Pat. No. 3,173,780 issued to H. L. Hoover on Mar. 16, 1965, which describes a thermal treatment to reduce the propensity of the glass toward temporal changes or aging of delay time. As an additional step this thermal treatment to reduce aging is, of course, undesirable, since it increases the cost of producing the delay medium. Furthermore, it has been found that a moderately fine anneal results in less aging than a coarse anneal. The additional control required to achieve the fine anneal further increases the cost of producing the glass delay medium.

SUMMARY OF THE INVENTION

A new glass ultrasonic transmission medium has been discovered, which has the nominal composition in mole per cent 17 per cent lead oxide, 9.5 per cent barium oxide and 73.5 per cent silicon dioxide. This glass not only exhibits near zero temperature coefficient of delay time over the normally encountered temperature range of 0° to 100° C., but also exhibits substantial independence of thermal after-effects and of aging of delay time with the thermal history. That is, the thermal after-effect is not greater than 10 p.p.m. and the aging of delay time is less than -10 parts per million per decade of time, regardless of prior thermal treatment, thus making the glass suitable for critical ultrasonic applications, such as the delay medium in ultrasonic delay lines, without the need for a final thermal treatment of the glass.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a graph depicting BaO—PbO—SiO₂ glass compositions which are useful as ultrasonic transmission media according to the invention;

FIG. 2 is a schematic illustration of a delay line assembly incorporating the inventive material as a delay medium.

DETAILED DESCRIPTION OF THE INVENTION

FIG. 1 graphically illustrates the family of BaO—PbO—SiO₂ glasses which exhibit an average temperature coefficient of delay time of a maximum of ± 5 parts per million per degrees centigrade over the range 0° to 100° C. It has been determined that this family of glasses exhibit thermal after-effects not greater than 10 p.p.m. and an aging of delay time (temporal instability) of not more than -10 parts per million per decade.

The average temperature coefficient of delay time from 0° to 100° C. is plotted along the vertical axis and the mole ratio of PbO to [PbO + SiO₂] is plotted along the horizontal axis for three different series of compositions, each having a different but invariant proportion of BaO. Compositions along line A contain 9.5 mole per cent BaO, line B, 8.0 mole per cent BaO and line C, 11.0 mole per cent BaO. It may be shown that the parallelogram formed by lines B, C, D and E, corresponds to the area of a ternary diagram formed by connecting with straight lines the following point pairs:

1. 11.0 mole percent BaO, 0.155 mole ratio PbO/[PbO+SiO₂] and 11.0 mole percent BaO, 0.189 mole ratio PbO/[PbO+ ξ^{SiO_2}];
2. 11.0 mole percent BaO, 0.189 mole ratio PbO/[PbO+SiO₂] and 8.0 mole percent BaO, 0.221 mole ratio PbO/[PbO+ ξ^{SiO_2}];
3. 8.0 mole percent BaO, 0.221 mole ratio PbO/[PbO+SiO₂] and 8.0 mole percent BaO, 0.187 mole ratio PbO/[PbO+SiO₂];
4. 8.0 mole percent BaO, 0.187 mole ratio PbO/[PbO+SiO₂] and 11.0 mole percent BaO, 0.155 mole ratio PbO/[PbO+SiO₂].

These compositions fall within a much broader glass-forming region of the ternary diagram roughly defined by the ranges in mole per cent 0 to 40 BaO, 0 to 60 PbO and 40 to 90 SiO₂. Within this parallelogram, the thermal after-effect and the aging of delay time is substantially independent of the glasses' thermal histories and does not exceed 10 p.p.m. and -10 parts per million per decade respectively. Varying the BaO content so as to result in compositions outside the parallelogram adjacent to lines B or C may result in devitrification of the melt. Increasing the PbO content at the expense of SiO₂ increases the temperature coefficient of delay time linearly, as may be seen from FIG. 1. Varying the PbO/[PbO + SiO₂] content so as to result in compositions outside the parallelogram adjacent lines D or E of course results in average temperature coefficients of delay time in excess of ± 5 parts per million per degrees centigrade, which is too high for many ultrasonic applications. For the most critical applications, compositions within the parallelogram defined by lines B, C, F and G are preferred for their average temperature coefficients of delay time of not more than ± 2 parts per million per degrees centigrade. These compositions fall within an area of the ternary diagram formed by connecting with straight lines the following point pairs:

1. 11.0 mole percent BaO, 0.166 mole ratio PbO/[PbO+SiO₂] and 11.0 mole percent BaO, 0.177 mole ratio PbO/[PbO+ ξ^{SiO_2}];
2. 11.0 mole percent BaO, 0.177 mole ratio PbO/[PbO+SiO₂] and 8.0 mole percent BaO, 0.209 mole ratio PbO/[PbO+ ξ^{SiO_2}];
3. 8.0 mole percent BaO, 0.209 mole ratio PbO/[PbO+SiO₂] and 8.0 mole percent BaO, 0.199 mole ratio PbO/[PbO+SiO₂];
4. 8.0 mole percent BaO, 0.199 mole ratio PbO/[PbO+SiO₂] and 11.0 mole percent BaO, 0.166 mole ratio PbO/[PbO+SiO₂].

In general, minor amounts of additives or impurities, exclusive of the Group I alkali metals Li, Na, K, Rb, Cs, typically up to about 1 mole per cent total, may be present in the glass compositions without adversely affecting the acoustic properties. For example, fining agents such as As₂O₃ or Sb₂O₃, typically up to 1 mole per cent may be present. The alkali metals

should not be present in amounts greater than about 0.1 cation per cent, in order to avoid adverse thermal after-effects or aging.

The described glasses may be produced in any suitable manner known to the glass-making art, although some advantage may be gained by following the known methods of producing optical quality glass. Also a fine anneal may be desirable in reducing the level of acoustic loss. Although not a necessary part of this description, a fine anneal is described in U.S. Pat. No. 3,173,780, issued to H. C. Hoover on Mar. 16, 1965.

The molten glass may be shaped into blanks having roughly the desired form and subsequently finished by the usual cutting, grinding and polishing steps. The blanks may be annealed according to steps known in the glass-making art. However, as already noted, thermal after-effects and temporal instabilities are minimal and are substantially unaffected by the character of the anneal or other prior or post-thermal treatment.

EXAMPLE:

A glass having the final composition in mole per cent of 73.45 SiO₂, 17.05 PbO, 9.50 BaO, was melted in a 34-inch clay pot, into which 1 mole per cent As₂O₃ was added as a fining agent. Additional fining and oxidizing action was obtained by adding 4 weight per cent of the BaO in the form of Ba(NO₃)₂. The remainder of BaO was added as BaCO₃. Samples suitable for the obtaining of acoustic properties were prepared by optically polishing flat and parallel the opposite ends of ½-inch diameter right cylinders 1 inch in length. These were processed into one-ended delay lines and measured for the appropriate acoustic properties using pulse-echo techniques. The thermal after-effect was determined by measuring the unit delay time at 25° C. before and after an 18-hour soak at 125° C. Temporal instability was then measured at 25° C. as a function of time over a several-hundred-day period.

The following table sets forth the thermal after-effect and temporal instability of delay time as determined by the above procedure, together with some other significant acoustic properties obtained for these samples.

Shear Delay Time	9.67 microseconds/inch
Temporal Instability	less than -5 p.p.m./decade
Thermal After-effect	less than 10 p.p.m.
Temperature Coefficient of Delay Time	less than one part per million per °C.
(from 0° C. to 100° C.)	
Shear Attenuation (at 50 MHz)	2.5 decibels/centimeter
Frequency Dependency of Shear Loss	~ 1.3
Mechanical Impedance	9.7 × 10 ⁸ g./cm. ² sec.
Density	3.7 g./cc.

Referring now to FIG. 2 there is shown a schematic diagram of one embodiment of an ultrasonic delay line assembly, including delay medium 10 of the inventive material, piezoelectric transducers 11 and 12, in substantial contact with faces of medium 10, and leads 13 and 14 for electrical input and output means, not shown. Medium 10 may be cylindrical, rectan-

gular, polygonal or other delay medium shape, known or unknown.

What is claimed is:

1. A solid ultrasonic delay line comprising a solid ultrasonic transmission medium, means for converting electrical signals to acoustic pulses comprising two piezoelectric transducers affixed to opposite faces of said medium, and electrical input and output means attached to said transducers,

characterized in that said transmission medium is a barium-lead-silicate glass having an average temperature coefficient of delay time of up to 5 parts per million per degrees centigrade, a thermal after-effect of less than -10 parts per million per decade and consisting essentially of a composition within an area of the ternary diagram for barium oxide, lead oxide and silicon dioxide formed by connecting with straight lines the following point pairs:

1. 11.0 mole percent BaO, 0.155 mole ratio PbO/[PbO+SiO₂] and 11.0 mole percent BaO, 0.189 mole ratio PbO/[PbO+SiO₂];

2. 11.0 mole percent BaO, 0.189 mole ratio PbO/[PbO+SiO₂] and 8.0 mole percent BaO, 0.221 mole ratio PbO/[PbO+SiO₂];

3. 8.0 mole percent BaO, 0.221 mole ratio PbO/[PbO+SiO₂] and 8.0 mole percent BaO, 0.187 mole ratio PbO/[PbO+SiO₂];

4. 8.0 mole percent BaO, 0.187 mole ratio PbO/[PbO+SiO₂] and 11.0 mole percent BaO, 0.155 mole ratio PbO/[PbO+SiO₂];

said transmission medium additionally containing up to one percent of one or more fining agents selected from the group consisting of As₂O₃ and Sb₂O₃, and not more than one-tenth cation percent of the Group I alkali metals.

2. The solid ultrasonic delay line of claim 1 in which the transmission medium is a glass consisting essentially of a composition within an area of the ternary diagram for barium oxide, lead oxide, and silicon dioxide, formed by connecting with straight lines the following point pairs:

1. 11.0 mole percent BaO, 0.166 mole ratio PbO/[PbO+SiO₂] and 11.0 mole percent BaO, 0.177 mole ratio PbO/[PbO+SiO₂];

2. 11.0 mole percent BaO, 0.177 mole ratio PbO/[PbO+SiO₂] and 8.0 mole percent BaO, 0.209 mole ratio PbO/[PbO+SiO₂];

3. 8.0 mole percent BaO, 0.209 mole ratio PbO/[PbO+SiO₂] and 8.0 mole percent BaO, 0.199 mole ratio PbO/[PbO+SiO₂];

4. 8.0 mole percent BaO, 0.199 mole ratio PbO/[PbO+SiO₂] and 11.0 mole percent BaO, 0.166 mole ratio PbO/[PbO+SiO₂];

said transmission medium additionally containing up to one percent of one or more fining agents selected from the group consisting of As₂O₃ and Sb₂O₃, and not more than one-tenth cation percent of the Group I alkali metals.

3. The solid ultrasonic delay line of claim 1 in which the transmission medium is a glass consisting essentially of a composition in mole percent of 73.45 percent SiO₂, 17.05 percent PbO, 9.50 percent BaO.

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