UNITED STATES PATENT OFFICE

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guishers.

erally of two types,—one type having some perature prescribed. form of pumping mechanism for expelling One of the principal objects of this inven-10 type having some form of chemical charge a charge composed of materials which func- 60 of such characteristics that during use chemi-tion with high efficiency of reaction to proguishing liquid. This invention relates more writers. 15 particularly to the latter form of extin- Another object of the invention is to pro- 65

more general application.

20 guisher is typical.

Such an extinguisher as heretofore gener- Another object of the invention is to pro-25 water, a bottle of some acid, such as sulphuric perature. acid, being mounted within the container so Still another object of the invention is to 30 bon dioxide which in turn exerts a pressure chemically inert with respect to those con- 80 from the container. One principal objection forming reactions. to an extinguisher of this character is that the Still another object of the invention is to 35 stand very low temperatures. At tempera- guisher charge, a gas-generating material 85 solution) the carbonate will precipitate out formation. and the main extinguishing liquid will then Other objects and advantages of this in-40 freeze rendering the extinguisher incapable vention will be apparent from the following 90 of use. Not only does the bicarbonate solu- description, and claims. tion freeze at comparatively high temperatures, but furthermore at very low temperatures the chemical activity of sulfuric acid 45 is greatly decreased. This is of peculiar importance because the Underwriters' Labora-

tories refuse to certify as of a preferred char-

This invention relates to fire extinguishers, ficient for certification on two grounds,—first more particularly of the portable type, and that the carbonate solution would freeze at particularly to charges for such extin- a temperature much above that prescribed, and furthermore the sulphuric acid itself Portable fire extinguishers, as heretofore would become, for practical fire extinguisher 55 manufactured for many years, have been gen- operation, chemically inert at this low tem-

the fire-extinguishing liquid, and the other tion is to provide a fire extinguisher having

cal reaction will take place to produce a gas- duce a discharge pressure at the low temperaeous pressure for expelling the fire-extin- ture of -40° C. prescribed by the under-

guisher, although it is in some aspects of vide a charge for fire extinguishers of this character, comprising materials which are Of the latter class of extinguishers, that in liquid form, and are non-freezing at the generally known as the soda and acid extin- low temperature prescribed by the underwriters.

ally manufactured has consisted of a casing vide such a charge, the constitutent materials containing a fire-extinguishing liquid, ordi- of which are not only non-freezing but are narily a solution of sodium bicarbonate in chemically active at this low prescribed tem-

that when the extinguisher is inverted for provide a freezing temperature depressant, use the acid will escape into the carbonate for use in connection with the constituent solution and react therewith to generate car- materials within the extinguisher, which is upon the extinguishing solution to expel it stituents at least in so far as concerns gas-

sodium bicarbonate solution will not with provide as one constituent of a fire-extintures of approximately 32° F. (depending which when in solution contains for a given upon the concentration of the bicarbonate volume of solution a large capacity for gas

This application is in part a continuation of the application of Charles A. Thomas and Carroll A. Hochwalt, Serial No. 85,386, filed February 1, 1926, for Antifreeze mixture for 95 fire extinguishers.

As stated above chemical reaction fire exacter any extinguisher which will not with- tinguishers as heretofore used have been instand a temperature of -40° C. The ordi-capable of use at the extremely low temperanary soda and acid extinguisher has been det ture of -40° C., which the Board of Nation- 100

al Fire Underwriters prescribes as a prerequisite for granting an A-1 rating upon a fire extinguisher. A solution of calcium chloride in water will serve adequately as the 5 main fire-extinguishing liquid, at such low temperatures, a calcium chloride solution having a freezing point below -40° C. But no constituents have been heretofore known which were chemically active at this low temperature, to react at such a rate in the production of a pressure gas as would make an extinguisher containing calcium chloride solution suitable. With a view to meeting the requirements of the Board of Underwriters 5 and obtaining an extinguisher capable not only of withstanding a temperature as low as -40° C., but also of operating at high efficiency at that temperature we have, by searching and sustained experiments, ascertained o that a compound contaning a sulfonic acid radical, such as a halogenated sulfonic acid, will not freeze at extremely low temperatures, will react with any carbonate, either solid, in solution or in suspension, to produce carbon dioxide.

Such a halogenated sulfonic acid is chlorosulfonic acid, ClSO₂OH, fluorosulfonic acid, FSO₂OH, or, in fact, any sulfonic acid contaning any element of the halogen group. Chlorosulfonic acid, which will not freeze at extremely low temperatures, is admirably adapted to act upon a solid carbonate, such as sodium bicarbonate, NaHCO3, to produce carbon dioxide with adequate efficiency at temperatures much lower than -40° C. This reaction may be accelerated by water to which any non-freezing agent such as calcium chloride may be added.

It has been definitely ascertained that one molecule of chlorosulfonic acid acts with three molecules of sodium bicarbonate to produce three molecules of carbon dioxide, these agents resisting a temperature as low as −80° C.

An effective charge of these non-freezing agents for expelling a gallon and a half of liquid from a fire extinguisher, consists of 8 ounces of sodium bicarbonate and 2½ fluid

ounces of chlorosulfonic acid.

While we have found sodium bicarbonate to be an effective carbonate for reacting with chlorosulfonic acid to produce carbon dioxide at extremely low temperatures, any other carbonate, such as sodium carbonate, magnesium carbonate, potassium carbonate and ammonium carbonate may be used with a halogenated sulfonic acid for this purpose with highly satisfactory results.

We have also found that other materials containing a sulfonic acid radical an undesirably large portion of the total (-SO₂OH) such, for example, as the sul-space available inside the extinguisher, and fonic acid of acetic acid, CH2SO2OHCOOH, thus cuts down to an impracticable degree the and other sulfonic acid radical containing quantity of fire extinguishing liquid which

produce carbon dioxide at extremely low tem-

peratures.

The sulfonic acid compound when used with a carbonate, not in solution, will react satisfactorily at temperatures much below 70 -40°C. However, the underwriters object to the use of a solid, or non-solution, form of carbon dioxide producting material. This is partly due to the fact that the reaction between the acid material and the solid car- 75 bonate material may be non-uniform, and consequently may not generate a continuous gas pressure to effect uniform discharge of the fire-extinguishing liquid. Furthermore the solid carbonate material is apt to agglom- 80 erate into comparatively large lumps, which may acquire a hardened surface, so that the rate of reaction will be greatly slowed down due to the incapacity of the acid to contact with a large quantity of the carbonate ma- 85 terial in a short time. Consequently it is extremely desirable, and almost commercially necessary, that the carbonate material be in solution. However, all carbon dioxide producing materials heretofore used in fire ex- 90 tinguishers have been incapable of use at the low temperatures specified herein since they will freeze at those temperatures.

For example sodium bicarbonate in solution is inadequate because it freezes at a 95 temperature considerably above -40° C. But we have discovered that ethylene glycol ((CH₂)₂(OH)₂) when used with a carbonate in a water solution is chemically inert with respect to that carbonate, at least in so far 100 as concerns any reaction which results in liberating the carbon dioxide or rendering the carbonate incapable of subsequent reaction with an acid to produce carbon dioxide, and is at the same time of such character that 105 it will greatly lower the freezing temperature

of such a carbonate in water.

Not only is this true but ethylene glycol being an uninflammable material lends itself nicely as an anti-freeze for the carbonate 110 solution of the fire extinguisher. And a carbonate solution with ethylene glycol, with the water and the carbonate and ethylene glycol admixed in suitable proportions will have a considerably depressed freezing tempera- 115 ture.

However, a carbonate solution containing sodium bicarbonate, or any of the other usual carbonates, admixed with ethylene glycol is objectionable for use in a fire ex- 120 tinguisher, when used in a container separate from the fire-extinguishing liquid, because even though its freezing temperature may be lowered adequately, the volume of the resulting charge is so great that it occupies 125 65 compounds, will react with a carbonate to is to be expelled as a result of the chemical 130

reactions between this carbonate charge and point considerably below -40° C. Furtheracid charge. Of course the container could more these particular proportions afford the be filled with any suitable fire-extinguishing maximum weight of sodium potassium carliquid such as a solution of carbonate in water bonate that will remain in solution with 5 with sufficient ethylene glycol admixed there- ethylene glycol in water at -40° C. And be- 70 with to produce the desired depression of cause of what may be called the CO2 concenthe freezing point. At present, however, this tration of the resulting solution the quantity is commercially undersirable because of the of the solution necessary to produce the decomparatively high cost of ethylene glycol sired quantity of CO₂, when compared with 10 which would make the use of it, in the large a solution of an ordinary carbonate such as 75 quantities needful for sufficiently lowering sodium bicarbonate, is quite small; and conthe freezing point of such a large quantity of sequently a commercially feasible chemical carbonate solution as would constitute the reaction extinguisher may be provided, acmain extinguishing liquid of the extinguisher, tive at -40° C., and having an adequate 15 run the cost of the charging materials for supply of fire-extinguishing liquid in the 80 the extinguisher to a commercially un-casing. feasible point. However, if it is desired to Of course if the volumetric capacity of the use ethylene glycol as a freezing tempera- extinguisher permits, a lower percentage by ture depressant in the main extinguishing 20 liquid, the extinguisher would work satisfactorily, with only the substitution of chlorosulfonic acid, or some analogous compound, in the place of the sulfuric acid tions of the various constituents in either diordinarily used in the soda and acid ex- rection, from those above named as consti-25 tinguisher, where extremely low temperatures are to be met.

However, such a carbonate as is ordinarily used in a fire extinguisher, for example sodium bicarbonate, is of such character that when placed in solution and used in a smaller separate container as described immediately above in order that there may not be too great displacement of the main extinguishing fluid, there will not be enough CO2 gen-35 erated during the reaction with the acid from carbonate with 40% by weight of ethylene 100 each unit volumn of carbonate solution to glycol and 40% by weight of water give very provide from such small volume of sodium satisfactory results. But if the percentage of bicarbonate solution sufficient expelling gas, sodium potassium carbonate is increased maand as a consequence where any of the or-terially above the 25% referred to above, then dinary used carbonates constitute the car- the water and ethylene glycol would be rela- 105 bon dioxide producing material the quantity tively decreased accordingly, and the result of carbonate producing solution in the charge would be a raising of the freezing point. is excessive. We have found, however, that sodium potassium carbonate (NaKCO₃) is potassium carbonate is increased to 30% by 45 so constituted that when placed in solution weight and the water and ethylene glycol 110 in water the CO₂ content per unit of volume are present in the proportion of substantially will be quite high. Sodium potassium car- 35% by weight of each, the freezing point bonate is quite soluble in water as compared would be above -40° C., at which temperawith other generally used carbonates such as so sodium bicarbonate, approximately 185 parts ate will precipitate out of the ethylene gly- 115 of sodium potassium carbonate going into col-water solution which will then freeze. solution in 100 parts of water at 15° C. This The most desirable results so far attained compares with 35 parts of sodium bicarbonate which will go into solution into 100 parts 55 of water at 15° C.

mixed with a solution of sodium potassium ter, and 36% by weight of ethylene glycol. carbonate in water within a certain range Such a solution permits of a fire extinof proportions will not only lower the freez-guisher having all the desirable characterising temperature of that sodium potassium carbonate solution to below -40° C., but in the proportion of 25% by weight of sodium potassium carbonate, 39% by weight of water and 36% by weight of ethylene glycol will 65 form a eutectic mixture having a freezing

weight of sodium potassium carbonate may be used which would merely mean increasing 85 the quantity of carbonate solution forming the chemical charge. Varying the proportuting the eutectic mixture, of course raises 90 the temperature at which the carbonate will precipitate out and the solution freeze. However within the limitations of volumetric capacity in the extinguisher and the low temperature conditions which have to be os met, the relative proportions of the sodium potassium carbonate, the ethylene glycol, and the water may be varied as desired; for example 20% by weight of sodium potassium

For example, if the percentage of sodium ture some of the sodium potassium carbon-

by us have been with a solution of the proportions producing the eutectic mentioned above,—namely, 25% by weight of sodium 120 Furthermore ethylen glycol when ad-potassium carbonate, 39% by weight of wa-

tics that are present when a material such as 125 chlorosulfonic acid is used with a solid carbonate, and has in addition desirable characteristics that are not present when a solid carbonate is used.

Where the chlorosulfonic acid is to react 130

ate combined with ethylene glycol as a freezmay be secured through the use of approxi-said solution also containing a freezing tem- 70 to react with a solution of 7 ounces of so- ert with respect to said carbonate solution. dium potassium carbonate in 14 ounces of 3. A charge for fire extinguishers, which 10 tions as set out above being admixed with one of which consists of a compound con- 75 specified quantities of chlorosulfonic acid and admixed with ethylene glycol to lower the sodium potassium carbonate solution will freezing point thereof. liberate sufficient carbon dioxide gas to ex- 4. A charge for fire extinguishers, which so bon dioxide producing portion of the charge carbonate, admixed with ethylene glycol to 85 contains 14 ounces of water, 7 ounces of lower the freezing point thereof. of ethylene glycol, to be used for reaction guishers, consisting of ethylene glycol and with 1.72 fluid ounces of chlorosulfonic acid. a carbonate in a water solution. Such proportions will have a freezing point 6. An anti-freeze mixture for fire extin- 90 the prescribed temperature of -40° C.

30 above particularly with reference to cholorosulfonic acid as the acid constituent of the carbon dioxide forming charge, reference is made primarily to this particular acid as one 8. A charge for fire extinguishers, comor replacing a hydroxyl group similarly connected in an inorganic acid compound containing the sulfonic radical (-SO₂OH) will react with a carbonate with varying degrees of activity at varying temperatures.

While the forms of invention herein described constitute preferred embodiments thereof, it is to be understood that the invention is not limited to such precise forms, and that changes may be made therein without departing from the scope of the invention which is defined in the appended claims.

What is claimed is:-

1. A charge for fire extinguishers, which comprises two normally separated portions, one of which consists of an acid constituent gas but normally freezing at a higher tem- to lower the freezing point thereof. perature than -40° C., and a freezing tem- 13. A charge for fire extinguishers, which 125 spect thereto for lowering the freezing point of said solution.

with a solution of sodium potassium carbon-comprises two normally separated portions, one of which comprises a compound containing temperature depressant, satisfactory ing a sulfonic acid radical, and the other of production of expelling carbon dioxide gas which consists of a solution of a carbonate, mately 1.7 fluid ounces of chlorosulfonic acid perature depressant which is chemically in-

water,—ethylene glycol in suitable propor- comprises two normally separated portions, the sodium potassium carbonate solid to give taining a sulfonic acid radical, and the other suitable lowering of the freezing point. Such of which consists of a solution of a carbonate,

pel 2½ gallons of fire-extinguishing liquid. comprises two normally separated portions, As illustrating actual proportions that give one of which consists of a compound convery satisfactory results for expelling 2½ taining a sulfonic acid radical, and the other gallons of fire extinguishing liquid, the car- of which consists of a water solution of a

sodium potassium carbonate, and 11.3 ounces 5. An anti-freeze mixture for fire extin-

above the freezing point of the eutectic mix- guishers, consisting of ethylene glycol and ture specified above, but substantially below sodium potassium carbonate in a water solution.

While the invention has been described 7. An anti-freeze mixture for fire extinguishers, consisting of sodium potassium 95 carbonate by weight 25%, water by weight 39% and ethylene glycol by weight 36%.

which functions very satisfactorily, and is prising a carbonate solution of high carbon 35 commercially available. However all the dioxide concentration, and a freezing tem- 100 compounds secured from replacing the car- perature depressant chemically inert with bon atom normally attached to the sulfonic respect to carbon dioxide producing reacacid radical, in an organic acid compound, tions with said carbonate solution, comprising ethylene glycol.

9. A charge for fire extinguishers, which 105 includes a water solution of sodium potassium carbonate containing a freezing temperature depressant which is chemically inert

with respect thereto.

10. A charge for fire extinguishers, which 110 includes a eutectic mixture of water, sodium potassium carbonate, and a freezing temperature depressant which is chemically inert with respect thereto.

11. A charge for fire extinguishers, which 115 includes a eutectic mixture of water, sodium potassium carbonate, and ethylene glycol.

12. A charge for fire extinguishers, which comprises two normally separated portions, 55 chemically active at temperatures as low one of which comprises a compound contain- 120 as -40° C., the other of which comprises a ing a sulfonic acid radical and the other of solution of a second constituent adapted to which consists of a solution of sodium potasreact with said first constituent to generate sium carbonate containing ethylene glycol

perature depressant comprising a glycol in comprises three normally separated portions. said solution and chemically inert with re- one of which consists of a water solution of a freezing temperature depressant, said solution being non-freezing at very low tem-2. A charge for fire extinguishers, which peratures and being adapted to serve as a 130

fire-extinguishing liquid, the other two of which are normally separated gas-generating portions consisting of a constituent having a sulfonic acid radical, and a solution of sodium potassium carbonate containing a chemically inert freezing temperature de-

pressant therein.

14. A charge for fire extinguishers, which comprises an acid constituent and a solution of a carbonate constituted to liberate an expelling gas on reaction with said acid constituent, said acid and said carbonate solution being chemically active with respect to each other to produce such expelling gas at temperatures ranging downwardly from substantially 0° C., and a glycol inactive to effect gas generating reaction with said carbonate solution for lowering the freezing point of the solution of said second constituent.

15. A charge for fire extinguishers, which comprises three normally separated portions, one of which consists of a fire extinguishing liquid which is non-freezing at low tempera-25 tures, the other two of which are normally separated gas-generating portions consisting of an acid constituent and a solution of a carbonate constituted to liberate an expelling gas on reaction with said acid conso stituent, said acid and said carbonate solution being chemically active with respect to each other to produce such expelling gas at low temperatures ranging downwardly from substantially 0° C. and which solution nor-35 mally freezes at a temperature above said low temperatures, and a glycol in said solution chemically inert with respect thereto.

16. A fire extinguishing liquid comprising a gas generating water solution including a compound of an alkali metal element having high fire extinguishing properties at low temperatures and containing a glycol therein.

17. A fire extinguishing liquid comprising a gas generating water solution including a compound of potassium and containing a

glycol therein.

18. A charge for fire extinguishers having normally separated gas generating portions, comprising a gas generating water solution including a compound of potassium, and an acid compound containing a sulfonic acid radical.

19. The use in a fire extinguisher of a water solution of sodium potassium carbonate containing in excess of 15% by weight of

sodium potassium carbonates.

20. A fire extinguishing charge comprising a glycol mixed with a liquid having high fire extinguishing properties at low temperatures and chemically inert with respect thereto.

In testimony whereof we hereto affix our signatures.

CHARLES A. THOMAS. CARROLL A. HOCHWALT.