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FIRE EXTINGUISHING LIQUIDS AND  
PROCESS

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1

This invention relates to new fire extinguishing liquids and the method of using such liquids to extinguish incipient hostile fires.

It has long been recognized that effective means for extinguishing hostile fires at their inception is an important factor in reducing fire losses. Once a small fire has been allowed to continue growing, it can quickly and easily spread to the uncontrolled or even conflagration stage with serious loss or damage to property and life. Probably the two foremost extinguishing agents for attacking fires at their inception have been special liquids based on carbon tetrachloride, and the gas, carbon dioxide.

Neither of these materials has been completely satisfactory. For example, carbon dioxide has to be stored under considerable pressure, thus requiring the use of containers of high strength and weight. The discharge of such a gas is limited in its application because the gas cloud cannot be projected very far from the container, thus requiring the operator to approach the fire closely. In addition, the operation of such an extinguisher usually blankets the fire area with an opaque gas cloud which makes it difficult for the operator to observe quickly the complete effect of his attack on the fire.

On the other hand, carbon tetrachloride extinguishants and similar chlorinated liquids have a tendency to increase the density of the smoke from a fire, likewise obscuring to some extent from the operator's view the effects of his action. Carbon tetrachloride has also come into disfavor in some quarters because of the fear of formation of toxic gases due to the chlorine content of the liquid.

An ideal fire extinguisher for coping with a hostile fire at its inception should be lightweight and small in size for easy storage and handling, simple to operate even by a person of little skill, and effective against fires of all types regardless of the nature of the combustible material. Also, it should use an extinguishing agent which is effective in small quantities, does not produce toxic gases or conditions when applied to a fire, is stable chemically under the fire conditions, does not damage ordinary materials on contact with them and is capable of storage in a container or applicator without objectionable corrosion thereof.

An object of our invention is the provision of improved extinguishing liquids meeting these requirements to a high degree.

Another object is the provision of a method of using such a fire extinguishing liquid by applying it to hostile incipient fires.

2

We have discovered that methylene bromide, also known as dibromo-methane ( $\text{CH}_2\text{Br}_2$ ), either alone or mixed with small proportions of other constituents, is an excellent fire extinguishing agent for use on small fires of all types. This material in its pure state has a boiling point of  $97^\circ\text{C}$ . and a freezing point of  $-53.5^\circ\text{C}$ . It has great chemical stability which is very advantageous, both from the point of view of storage in a closed container, and for extinguishing fires. By reason of its high boiling point, it can readily be stored in closed containers as a liquid, it can be projected as a liquid stream for a considerable distance from the operator, thus making it possible to attack effectively fires which are dangerous to approach closely or are in relatively inaccessible locations. And it does not produce an opaque cloud or produce the kind of smoke which tends to obscure the fire any more than the smoke of the fire itself.

At the same time, a given quantity of this liquid is much more effective compared with carbon tetrachloride and other liquids in extinguishing various types of fires, such as fires in flammable liquids, wood, paper, textiles and electrical installations. Its superiority may vary with different types of fires, but there is always some degree of superiority. For example, burning gasoline, which cannot be extinguished with a given quantity of carbon tetrachloride, can be extinguished with the same quantity of the extinguishants of our invention. In the case of wood fires, it has been observed that the extinguishants of our invention do a more complete job, particularly with respect to glowing embers.

Our new extinguishants are also advantageous from the point of view of physical properties which are helpful in connection with the storage problem. For example, methylene bromide has a boiling point approximately  $20^\circ\text{C}$ . higher than carbon tetrachloride and has a freezing point sufficiently low to avoid the necessity of adding any freezing point depressor to the liquid to enable its storage under ordinary conditions.

While methylene bromide may be used alone, we prefer to employ a mixture of methylene bromide with a minor proportion of another brominated hydrocarbon, a preferred addition agent for this purpose being the chemical bromoform or tribromo-methane ( $\text{CHBr}_3$ ). In place of, or in addition to, bromoform, such other normally liquid brominated hydrocarbons as ethylidene dibromide ( $\text{CH}_3\text{CHBr}_2$ ), 1,2 dibromoethane or ethylene bromide ( $\text{CH}_2\text{BrCH}_2\text{Br}$ ), tri-

bromo-ethane ( $\text{CH}_2\text{BrCHBr}_2$ ), symmetrical or unsymmetrical tetrabromo-ethane ( $\text{CHBr}_2\text{CHBr}_2$  or  $\text{CBr}_3\text{CH}_2\text{Br}$ ), dibromo-ethylene ( $\text{CH}_2\text{:CBr}_2$ ), dibromo-ethene ( $\text{CHBr:CHBr}$ ), or tribromo-ethylene ( $\text{CHBr:CBr}_2$ ) may be used. Mixtures containing about 80 to 97% methylene bromide with 20–3% of another brominated hydrocarbon, preferably bromoform, have been found to be particularly effective. Examples of suitable proportions for such mixtures include 85%, 90% and 95% methylene bromide with most or all of the balance either bromoform or one of the other brominated hydrocarbons. In fact, such a mixture of methylene bromide and bromoform is actually more effective in extinguishing fires than either methylene bromide or bromoform alone.

The superiority of the mixture has been demonstrated, for example, on the gasoline fires. A small extinguisher was used that holds one quart of liquid and squirts it out in a stream during a period of six and one-half minutes. A pan 10" in diameter and 5½" deep was filled with two quarts of gasoline, fresh gasoline being used for each test, and the extinguisher was adjusted so that the stream from the discharge nozzle impinged against the inside wall of the pan. In each case the gasoline was ignited and allowed to burn for thirty seconds before application of the first extinguishing liquid. It was found that standard carbon tetrachloride fire extinguishing liquids would not put out this fire. Bromoform alone extinguished the fire in an average time of thirty-four seconds. Methylene bromide used alone extinguished this fire in an average time of eleven seconds. The mixture of methylene bromide and bromoform, however, extinguished it in still less time, averaging about 10 seconds.

Additional tests were made using an ordinary 30" diameter washtub with two gallons of gasoline in it as the fuel which as allowed to burn freely for sixty seconds. The ordinary carbon tetrachloride extinguisher of the one quart size would not put out this fire. Using the same equipment, methylene bromide extinguished the fire in thirteen seconds, and bromoform used alone extinguished it in about thirty seconds. The mixture, however, was found to extinguish the same fire in eleven seconds or, in other words, a shorter time than the use of either constituent alone. It should also be noted that, in addition to its quick action, only approximately one-half pint of the mixture was required to extinguish the fire in the tub in each case.

Both methylene bromide and a mixture of methylene bromide with one of the other brominated hydrocarbons have been found to be markedly superior as a fire extinguishing agent compared with other bromine compounds heretofore used, such as methyl bromide and chloro-bromomethane. Also, our new liquids, unlike some of the other bromine compounds are not injurious to a person's skin and clothes.

The high degree of chemical stability of this new extinguishant, along with its very effective fire extinguishing action, are most important in giving the operator, whether skilled or unskilled, confidence in his ability to attack a small fire effectively. At the same time, the liquids of our invention do not form or release any quantity of dangerous reaction products when applied to various types of fires, an important consideration for use in enclosed or confined spaces.

Both methylene bromide alone and mixed with one of the other brominated hydrocarbons can be readily stored without producing any unde-

sirable corrosion on the various metals and alloys commonly used for fire extinguisher construction. Here again, the chemical stability of these new extinguishants is of tremendous importance from a practical viewpoint, making it unnecessary to dilute or adulterate the extinguishing liquid with substantial quantities of corrosion inhibitors.

The desirable physical properties of methylene bromide have been mentioned. Bromoform, on the other hand, has an even higher boiling point of 150° C. but also has a less desirable higher freezing point of 8.5° C. The higher boiling point of bromoform apparently raises somewhat above 100° C., the boiling point of the mixture when used with methylene bromide. At the same time, the freezing point of the mixture remains sufficiently low for storage under most conditions. For example, a mixture of 85% methylene bromide with 15% bromoform has a freezing point of approximately -50° C., which is adequate for all ordinary storage purposes without the necessity of adding any freezing point depressant.

It will be apparent that the preferred proportions of methylene bromide and bromoform or other bromated hydrocarbon are not particularly critical but can be varied to some extent without sacrificing the desirable new results and benefits achieved by these new fire extinguishing liquids. In any case, however, it is desirable that methylene bromide constitute the principal ingredient of the mixture and that the liquid having a boiling point between about 97° C. and 140° C. with a freezing point below about -30° C.

The terms and expressions which we have employed are used as terms of description and not of limitation, and we have no intention, in the use of such terms and expressions, of excluding any equivalents of the features shown and described or portions thereof, but recognize that various modifications are possible within the scope of the invention claimed.

It is claimed:

1. A fire extinguishing liquid which comprises as its principal constituents a mixture of methylene bromide and a compound selected from the group consisting of bromoform, liquid brominated ethanes and liquid brominated ethylenes, said liquid having a boiling point between about 97° C. and 140° C. and a freezing point below about -30° C.

2. A fire extinguishing liquid which comprises a mixture of methylene bromide and a compound selected from the group consisting of bromoform, liquid brominated ethanes and liquid brominated ethylenes, the methylene bromide comprising at least about 80% of the mixture.

3. A fire extinguishing liquid which comprises as its principal constituents a mixture of methylene bromide and bromoform, the methylene bromide constituting the major proportion of said mixture.

4. A fire extinguishing liquid which comprises as its principal constituents a mixture of methylene bromide and bromoform, the mixture having a boiling point below about 140° C. and a freezing point below about -30° C.

5. A fire extinguishing liquid which comprises from about 3% to about 20% bromoform and the balance principally methylene bromide.

6. A fire extinguishing liquid which comprises essentially a mixture of about 85% methylene bromide and 15% bromoform with no more than minor proportions of other constituents.

5

7. A fire extinguishing liquid which comprises essentially a mixture of about 90% methylene bromide and 10% bromoform with no more than minor proportions of other constituents.

8. A fire extinguishing liquid which comprises essentially a mixture of about 95% methylene bromide and 5% bromoform with no more than minor proportions of other constituents.

9. A process of extinguishing a fire which comprises applying thereto a liquid composed principally of methylene bromide.

10. A process of extinguishing a fire which comprises applying thereto a liquid comprising as its principal constituents a mixture of methylene bromide and a compound selected from the group consisting of bromoform, liquid brominated ethanes and liquid brominated ethylenes.

11. A process of extinguishing a fire which comprises applying thereto a liquid containing methylene bromide as its principal constituent and a substantial proportion of at least one compound selected from the group consisting of bromoform, liquid brominated ethanes and liquid brominated ethylenes, said liquid having a boiling point between about 97° C. and 140° C. and a freezing point below about -30° C.

12. A process of extinguishing a fire which comprises applying thereto a liquid containing methylene bromide as its principal constituent and a substantial proportion of bromoform.

13. A process of extinguishing a fire which comprises applying thereto a liquid containing bromoform and at least about 80% of methylene bromide.

14. A process of extinguishing a fire which comprises applying thereto a liquid containing as its principal constituents a mixture of methylene bromide and bromoform, the liquid having a boiling point below about 140° C. and a freezing point below about -30° C.

15. A process of extinguishing a fire which comprises applying thereto a liquid containing about 3% to about 20% bromoform with the balance consisting principally of methylene bromide.

6

16. A process of extinguishing a fire which comprises applying thereto a mixture of about 85% methylene bromide and about 15% bromoform.

17. A process of extinguishing a fire which comprises applying thereto a mixture of about 90% methylene bromide and about 10% bromoform.

18. A process of extinguishing a fire which comprises applying thereto a mixture of about 95% methylene bromide and about 5% bromoform.

19. A fire extinguishing liquid which consists essentially of a mixture of methylene bromide and bromoform and contains substantial quantities of each ingredient.

20. A process of extinguishing a fire which comprises applying thereto a liquid consisting essentially of a mixture of methylene bromide and bromoform.

21. A fire extinguishing liquid which consists essentially of a mixture of methylene bromide and bromoform, the proportions of the constituents of said mixture comprising about 80-97% methylene bromide and about 20-3% bromoform.

22. A fire extinguishing liquid which consists substantially of methylene bromide and other liquid brominated hydrocarbons, the methylene bromide comprising from about 80 to 97% of the liquid.

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