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[72] Inventors **Thomas P. Dougan**
Corona Del Mar;
Samuel Chess, San Pedro, both of, Calif.

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[73] Assignee **The Upjohn Company**
Kalamazoo, Mich.

[54] **PROCESS FOR EXTINGUISHING FIRES BY DISPENSING RIGID POLYMER FOAM FORMING MIXTURES**
7 Claims, No Drawings

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[56] **References Cited**

UNITED STATES PATENTS

2,907,627	10/1959	Cummings	264/54X
3,158,667	11/1964	Michaels	264/45

Primary Examiner—John T. Goolkasian
Assistant Examiner—D. J. Fritsch
Attorneys—Eugene O. Retter and Denis A. Firth

ABSTRACT: A process for extinguishing fires burning on the surface of combustible liquids is disclosed. A thermally resistant rigid polymer foam forming reaction mixture is dispensed directly on to the burning liquid surface so as to form a continuous solid layer over the entire surface of the combustible liquid. At the time at which it reaches the foam surface the foam reaction mixture is in a state of reaction beyond the start of foam rise but prior to gelation. In addition to extinguishing the fire the polymer foam layer serves as a floating protective blanket over the combustible liquid, preventing contamination and/or reignition.

PROCESS FOR EXTINGUISHING FIRES BY DISPENSING RIGID POLYMER FOAM FORMING MIXTURES

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to an improved process for extinguishing fires burning on the surface of combustible liquids, and is more particularly concerned with a process for extinguishing fires by dispensing rigid cellular polymer forming reaction mixtures on to the burning surface of combustible liquids.

2. Description of the Prior Art

Chemical foams have long replaced water as effective weapons for extinguishing fires burning on the surface of volatile liquids (solvents, oils, etc.) and for extinguishing glowing fires (e.g., electrical, cotton, cloth, etc.). The chemical foams coat the burning surface thus preventing the ingress of oxygen and eliminating the possibility of after-glow and eventual reignition. Generally speaking, such chemical compositions are prepared by dissolving polymers or phosphate salts in water or halogenated hydrocarbons, see, for example, U.S. Pat. No. 3,345,289; British Pat. Nos. 1,071,660 and 1,079,633; and German Pat No. 1,219,331 and 1,250,274. Belgium Pat. No. 688,915 discloses extinguishing gasoline fires on airport runways by spraying an aqueous solution of urea-formaldehyde on to the burning surface.

The above types of chemical foam, although satisfactory for extinguishing most types of fire, generally cannot be used successfully in controlling fires burning on the surface of large volumes of combustible liquids such as those generally present in crude petroleum storage areas. When used on fires of the latter type the conventional chemical foams suffer the disadvantage that the carrier liquids (e.g., water and halogenated hydrocarbons) have a higher density than the burning liquid and therefore tend to sink to the bottom of the latter. During the course of settling to the bottom of the hot burning liquid the water or solvent vaporizes and can thereby cause "boil-over" of the combustible liquid with resultant spreading of the fire. In addition, fires of the above type are generally of such intense heat and of such high energy that conventional chemical foams are easily dispersed thereby and cannot be applied in sufficiently thick layers to blanket the burning surface against the ingress of oxygen. Further, conventional chemical fire extinguishants, when used on such fires in either powdered or solution form, contaminate the combustible liquids, and expensive separation procedures are required in order to salvage the combustible liquids after the fire has been extinguished.

The most usual method of dealing with fires on combustible liquids stored in bulk has been to protect the surround area (e.g., buildings and adjacent storage tanks) against spreading of the fire and to let the fire burn itself out. Such methods of operation involve tremendous loss of property and are obviously to be avoided if possible.

This invention provides, for the first time, a method of extinguishing fires burning on the surface of combustible liquids stored in large bulk. The method involves dispensing certain rigid cellular polymer forming compositions, in a particular state of reaction, directly on to the burning surface of the liquid. In addition to extinguishing the fire the process provides a thermally insulating continuous blanket over the combustible liquid surface which blanket serves to protect the stored liquid against contamination or reignition. It is to be noted that the formation of polymer foam blankets on the surface of stored combustible liquids; particularly those of high volatility, has been described previously; see, for example, U.S. Pat. Nos. 2,907,627 and 3,158,667. However, the use of rigid polymer foam in the manner described hereinafter has not been described previously.

SUMMARY OF THE INVENTION

In its broadest aspect, the invention comprises a process for extinguishing a fire burning on the surface of a combustible liquid which process comprises:

dispensing on to the surface of the burning liquid a rigid thermally resistant cellular polymer forming reaction mixture; said mixture being in a stage of reaction beyond the start of foam rise and prior to foam gelation at the time at which it contacts said burning surface; said mixture being dispensed in such a manner as to form a substantially continuous solid cellular polymer layer on the surface of the combustible liquid.

DETAILED DESCRIPTION OF THE INVENTION

The rigid cellular polymers which are utilized in the process of the invention are those polymers normally produced by bringing together two or more reactants which, either spontaneously or with the aid of suitable catalyst systems, polymerize and, at the same time, generate a gas which acts as blowing agent to produce a foam. The blowing agent in question can be carbon dioxide liberated in the polymerization reaction or can be a relatively volatile inert liquid such as freon which is added to the initial reaction mixture and is volatilized by the heat generated in the polymerization reaction. Typical of cellular polymers which can be produced in the above manner are polyurethane foams, polyurea foams, polyoxazolidinone foams, polyamide foams, polyimide foams and polyisocyanurate foams as well as foams produced by simultaneous production of two or more such foams (i.e., production of two or more types of foam by including in the one foam reaction mixture the ingredients necessary to produce different chemical types of foam).

The rigid cellular polymers which are preferred for use in the process of the invention are those which exhibit a high degree of resistance to degradation on exposure to heat. Preferably, the cellular polymers employed in the process of the invention are capable of withstanding any substantial amount of degradation on prolonged exposure to temperatures in excess of 400° F. and, most preferably, in excess of 600° F. In addition, the preferred rigid cellular polymers for use in the process of the invention resist combustion i.e. they are classified as "nonburning" when tested in accordance with ASTM D1692–59 and, more particularly, have a rating of 25 or less when subjected to the tunnel test in accordance with ASTM E84–61.

The methods for the preparation of the above types of rigid cellular polymers are well known in the art. Said polymers are generally prepared by the condensation, under foam producing conditions, of an organic polyisocyanate with one or more of the following reactants: (1) a polyol having two or more hydroxyl groups per molecule (yields a polyurethane), (2) a primary polyamine having two or more amino groups per molecule (yields a polyurea) (3) a polycarboxylic acid having two or more carboxylic acid groups per molecule (yields a polyamide) (4) a polycarboxylic acid anhydride having two or more anhydride groups per molecule (yields a polyimide) or (5) a polyepoxide having two or more oxirane groups per molecule (yields a polyoxazolidinone). The rigid foam forming reactions are carried out in the presence of a blowing agent, a catalyst and optionally, if desired, in the presence of surfactants, fillers, dyes, antioxidants, flame retardants and the like adjuvants commonly employed in the preparation of rigid polyurethane foams.

The preparation of the above rigid cellular polymers is more fully described in, for example, T. H. Ferrigno, "Rigid Plastics Foams," pages 51—61, Reinhold Publishing Corporation, New York, 1963; U.S. Pat. Nos. 3,198,851; 3,242,108; 3,282,863 and 3,300,420; British Pat. No. 1,070,581; and Australian application No. 4468/66. The above cellular polymers can be prepared employing one-shot, quasi-prepolymer, or prepolymer methods. Preferably, the polymers employed in the process of the invention are prepared using a one-shot technique i.e., a technique in which all of the reactants are metered in the appropriate proportions and mixed simultaneously. In a particularly preferred embodiment of the one-shot procedure the various foam forming ingredients are

supplied in premixed packages keeping the catalyst portion separate from either component. The components which are brought together in any given premix are confined to those ingredients which show no significant tendency to react one with the other.

In carrying out the process of the invention the rigid cellular polymer forming ingredients are brought together under foam producing conditions, as described above, using a one-shot, quasi-prepolymer or prepolymer procedure. The foam reaction mix is dispensed directly on to the surface of the burning liquid by means of any of the various dispensing equipment conventionally used in the art for dispensing such foam forming compositions. Such equipment is inclusive of conventional spray, pour and froth equipment, see, for example, T. H. Ferrigno, ibid; J. H. Saunders, et al., "Polyurethanes: Chemistry and Technology," Part II, Chapter XVI, Interscience Publishers, New York, (1964); and U.S. Pat. Nos. 2,955,058 and 3,091,551. The type of equipment used in the process of the invention is not critical.

Advantageously, the foam is directed on to the surface of the burning liquid continuously, or semicontinuously, in one or more streams in such a manner that a continuous layer of foam reaction mix is formed on the said liquid surface. For example, the foam mix can be dispensed from a standard mixing head mounted on a traveling boom. The boom is operated in such a manner that the mixing head constantly traverses a straight line path over the surface of the liquid. The mixing head is advanced in position at the end of each traverse so that each succeeding traverse is made along a path parallel to that taken in the previous traverse but spaced apart therefrom by a distance of about 6 inches to about 2 feet. It is to be understood that the latter distances are given for purposes of illustration and can be larger or smaller depending on the particular foam being used. The most appropriate distance apart of the parallel paths will vary according to the nature and characteristics of the foam reaction mixture which is being laid down. The distance is so chosen that the parallel pours of foam reaction mixture produce a unitary whole i.e., there are no gaps in the foam coverage of the surface.

When the above method, of laying down the foam reaction mix on the surface of the combustible liquid, is adopted it is found preferable to commence the dispensing of the foam reaction mixture at the periphery of the burning area and to advance the boom, or other means supporting the mixing head, in stages as described above, towards the opposite periphery of the burning area. In this manner a complete blanket of foam can be laid systematically over the whole of the area of the fire and can thereby extinguish the latter. Such an approach is preferable to a haphazard dispensing of the foam on the burning surface of the combustible liquid.

In a particularly preferred method of dispensing a foam reaction mixture, a plurality of mixing heads are employed, each head being mounted on a boom or like means so that it can be made to traverse an area of the burning surface in the manner described above. Each of the mixing heads is made to dispense foam reaction mixture and to lay a blanket of said mixture over a given area of the burning surface. By suitable arrangement of the paths of the various mixing heads it is thus possible to provide a complete blanket of foam reaction mixture over the entire burning surface in a very short period of time.

It will be readily appreciated that the amount of foam dispensed on to the burning surface must be sufficient to entirely blanket the area of surface which was burning originally. It is not necessary to cover the entire exposed surface of the liquid in order to extinguish the fire. However, such coverage of the entire surface is generally desirable in order to exclude oxygen and prevent any reignition of the blaze as well as to protect the liquid from further contamination.

While the manner in which the foam reaction mixture is dispensed on to the burning surface of the combustible liquid is important but not critical, the particular stage to which the foam forming reaction has advanced at the time at which the foam mixture contacts the burning surface is the key to successful operation. As is well recognized in the art there are a number of clearly marked stages in the preparation of a polymer foam based on chemical reaction between a polyisocyanate and a second polyfunctional compound. In the first stage of such a reaction the start of the polymerization reaction is marked by a substantial increase in viscosity without any evolution of blowing agent. The start of the second stage of the reaction, the beginning of the foam formation, is generally marked, particularly in the case of polyurethanes, by a pronounced color change caused by nucleation (formation of tiny gas bubbles) in the reaction mixture. This point in the reaction cycle is commonly known as the "cream" time because of the creamlike appearance which the reaction mixture assumes at this time. Thereafter the reaction mixture expands, i.e., foam rise begins. The point at which the foam begins to rise is known as the "rise time."

The third stage in the reaction sequence is marked by the occurrence of "gelation." Gelation is marked by a change of state and is generally defined as representing the point at which the first "structurally insoluble gel" appears; see, for example, Flory, J. Am. Chem. Soc. 63, 3083, 1941. The point of gelation in the case of a cellular polymer forming system is the point at which the formation of polymer has progressed to the stage at which a crosslinked space lattice network has been formed. At this point the foam exhibits substantial structural strength and integrity. It is important to note that further foam expansion can, and generally does, occur after gelation has taken place but the amount of such further expansion is very limited compared with the expansion which has taken place before gelation occurs. The fourth and final stage in the formation of the polymer foam is represented by the completion of foam rise, the "final rise" time. This is the point at which expansion of the foam reaction mixture is substantially complete.

The various stages of the polymer foam formation discussed above are readily recognized and can be determined by methods well known in the art; ASTM D2237–64T. The "cream," "rise," "gel" and "final rise" times of any given foam reaction mixture are a characteristic thereof and reflect the rate at which the various reactions are taking place within the polymer foam system, i.e., these times are a measure of the reactivity of the system. These reactivity characteristics are largely a function of the catalysts employed in the system and one or all of the cream, rise, gel, and final rise times of any system can be changed by appropriate adjustment of catalyst as is well recognized in the art.

The above explanation has been given at some length in order to provide a background against which can be understood more readily the particular point to which the polymer foam reaction mixture employed in the process of the invention must have progressed at the time at which it contacts the burning surface of the combustible liquid. If the said contact takes place before foam rise has commenced it is found that the foam reaction mixture is generally dispersed, at least in part, by the turbulent air flow surrounding the burning surface. This results in incomplete coverage of the burning surface and consequent failure to extinguish the fire. On the other hand, if the foam reaction mixture has reached the stage of gelation prior to the point at which contact of the mixture with the burning surface occurs, said mixture will not flow or expand laterally on the burning surface to form a continuous blanket covering said surface, i.e., the newly deposited foam reaction mixture will no longer be in a state in which it will unite with foam reaction mixture previously deposited.

Accordingly, at the time at which the foam forming reaction mixture contacts the surface of the burning liquid in accordance with the process of the invention it is required to be in a stage of reaction which is beyond the start of foam rise, i.e., beyond the "rise time," and yet is prior to gelation ("gel time"). Further the interval of time between the moment at which the foam reaction mixture first contacts the burning surface and the time at which said mixture reaches the get

time should be as short as possible. Advantageously, this time interval is less than about 15 seconds and preferably this time interval is less than about 5 seconds. The above requirements as to rise time and gel time can be met by appropriate adjustment of formulation particularly as to catalyst requirements. The required characteristics of the foam reaction mixture, within the above limitations, can be obtained readily by trial and error for any given polymer foam system. In determining the most suitable rise time to impart to said system it is necessary to take into account the time which must lapse between the moment at which the foam forming reactants are first brought together in the mixing head and the moment at which the resulting mixture contacts the burning surface. Factors influencing this time include the mixing time within the mixing head and the distance to be travelled between the outlet of the mixing head and the surface of the burning liquid. In general the latter distance is kept as short as possible to avoid prolonged exposure of the foam reaction mixture to the turbulent atmosphere above the burning liquid and thereby lessen the danger of dispersion of the foam reaction mixture before foaming has taken place. Generally speaking, the rise time of the polymer foam forming system employed in the process of the invention is within the range of about 2 seconds and 30 seconds and is preferably within the range of about 3 seconds and about 5 seconds. The interval between rise time and gel time for said system is advantageously within the range of about 1 second to about 90 seconds and preferably is within the range of about 2 seconds to about 5 seconds.

The amount of foam reaction mixture applied to the burning surface in accordance with the process will vary. Clearly, the minimum amount applied to the surface is important but the upper limit is dictated solely by reasons, such as economics, ultimate usefulness of the foam barrier and the like, other than those concerned with simply extinguishing the fire. The minimum amount of foam reaction mixture applied to the burning surface to extinguish the fire herein in accordance with the invention will vary depending upon the nature of the particular polymer foam system applied. The minimum amount of foam reaction mixture is dependent upon the density of the ultimate foam as well as the thermal resistance of said foam. In general, however, it can be said that the minimum amount of foam mix applied, assuming a density in the ultimate foam of about 2 p.c.f. to about 25 p.c.f., will be of the order of about 4 pounds per square foot of surface.

The foams which are employed in the process of the invention can be water-blown (i.e., water is added to the foam reaction mixture in an amount sufficient to produce the required quantity of carbon dioxide by action with polyisocyanate) or can be blown by incorporation of volatile inert solvents such as freon and like halogenated aliphatic hydrocarbons having a boiling point from about −40° C. to about 110° C. Alternatively a combination of water and halogenated hydrocarbon can be employed. The use of one as opposed to the other class of blowing agents does not matter so far as the effectiveness of the process of the invention is concerned. However, when a halogenated hydrocarbon is employed as blowing agent there is a danger that the heat to which the polymer foam is subjected in extinguishing the fire may be sufficient to convert some of the halogenated hydrocarbon to phosgene thereby creating an additional hazard to personnel engaged in fighting the fire. Accordingly, in a preferred process of the invention the polymer foam employed is one which is water-blown. It will be appreciated that this expression of preference is not predicated on the efficiency, or lack of efficiency, of the process of the invention as far as it is applied to nonwater blown foams.

As pointed out previously, the process of the invention has clear advantages over previous methods employed to extinguish fires burning on the surface of combustible liquids. Thus, the polymer foam reaction mixtures employed in extinguishing said fires in accordance with the invention are free from any significant amounts of water (other than that used as blowing agent) or other fluids which would sink below the surface of the burning liquid and thereby give rise to dangers of boil-up previously discussed. Further, the foam barrier formed in accordance with the process of the invention serves to form a permanent cover for the surface of the combustible liquid thereby preventing contamination of the latter by atmospheric pollutants, flying debris and the like. The formation of a solid barrier which is clearly not incorporated in the combustible oil avoids the necessity for expensive salvage operations which had to be performed to separate the oil from the fire extinguishing composition hitherto used.

The process of the invention will now be described with respect to a specific embodiment thereof. It is to be understood that this embodiment is given for purposes of illustration only and that the invention is not limited thereby.

A fire burning on the surface of an open crude oil storage tank of approximate surface dimensions 50×50 feet was extinguished as follows. A Binks Spray polymer foam mixing head capable of delivery of 20 pounds per minute of foam mix was mounted on a travelling boom such that the head could be made to traverse the width of the storage tank. The boom was positioned initially so that the first traverse of the mixing head covered one outside edge of the fire and the boom was moved toward the fire after each traverse so that the next traverse of the mixing head was 6 inches beyond the previous traverse. The mixing head was positioned approximately 4 feet above the surface of the oil and the foam mix discharged from the mixing head fell under gravity on to the surface of the foam. The polymer foam mix was prepared using a two-component system as follows, the mixing ratio of said components being such as to provide in the final mixture the proportions (by weight) of reactants set forth.

	Parts by weight
Component A:	
Polymethylene polyphenyl isocyanate (PAPI®)	315
Dimethylpolysiloxane polyethylene oxide block copolymer surfactant (SF-1109)	10
Stabilized trichlorofluoromethane (Isotron-11B)	65
Component B:	
Dipropylene glycol	32
Diglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane [DER 331]	32
Tris(2-chloroethyl)phosphate	28
N, N′, N″-(dimethylaminopropyl)-s-hexahydrotriazine	8

The above system had a rise time of approximately 6 seconds and a gel time of approximately 35 seconds. The foam mixture was discharged on to the surface of the burning oil at a rate of about 20 pounds per minute. The foam mix contacted the burning surface approximately 15—20 seconds after mixing. The speed of traverse of the mixing head was adjusted so that the amount of foam mix deposited on the oil surface was approximately 4 pounds per square foot. The dispensing of the foam was continued until the fire had been completely blanketed and extinguished. The resulting foam layer formed on the surface of the oil had an average density of about 4 p.c.f. and an average thickness of about 6 inches.

We claim:

1. A process for extinguishing a fire burning on the surface of a combustible liquid which process comprises:

dispensing on to the surface of the burning liquid a rigid cellular polymer forming reaction mixture wherein the polymer foam forming reaction mixture of ingredients is one necessary to produce a rigid, thermally resistant cellular polymer selected from the class consisting of cellular polyisocyanurates, polyurethanes, polyureas, polyoxazolidinones and polyimides;

said mixture being in a stage of reaction beyond the start of foam rise and prior to the point of foam gelation at the time at which it contacts said burning surface;

said mixture being dispensed in such a manner as to form a substantially continuous solid cellular layer on the surface of the combustible liquid.

2. The process of claim 1 wherein said polymer foam forming reaction mixture has a rise time within the range of about 2 seconds to about 30 seconds and on interval between rise time and gel time within the range of about 1 second to about 90 seconds.

3. The process of claim 1 wherein the time interval between the moment of contacting the burning surface and the point of foam gelation is less than 15 seconds.

4. A process according to claim 1 wherein the rigid cellular polymer forming reaction mixture is discharged from a foam mix delivery means on to the surface of the burning liquid initially at a point on the periphery of the burning area and the foam mix delivery means is subsequently advanced over the burning area so as to completely blanket the burning surface with cellular polymer.

5. A process according to claim 4 wherein a plurality of foam mix delivery means is employed.

6. A process for extinguishing a fire burning on the surface of a combustible liquid which process comprises:

dispensing from a foam mixing and dispensing head on to the surface of the burning liquid a rigid cellular polymer forming reaction mixture wherein the polymer foam forming reaction mixture of ingredients is one necessary to produce a rigid, thermally resistant cellular polymer selected from the class consisting of cellular polyisocyanurates, polyurethanes, polyureas, polyoxazolidinones and polyimides; said mixture being in a stage of reaction beyond the start of foam rise and prior to the point of foam gelation at the time at which it contacts said burning surface;

said foam mixing and dispensing head being made to traverse the burning surface of said combustible liquid in a series of parallel paths so as to dispense a continuous layer of polymer foam on said surface.

7. The process of claim 6 wherein the initial traverse of said foam mixing and dispensing head is made across a perimeter of said burning surface and subsequent traverses each advance said foam mixing and dispensing head incrementally across said surface towards the opposite perimeter thereof.