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OSRD list no. 3 dtd 2-11 Jan 1946; OTS index dtd Jun 1947

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NATIONAL DEFENSE RESEARCH COMMITTEE
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Division 11
NATIONAL DEFENSE RESEARCH COMMITTEE
of the
OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT
CHEMICAL IGNITION OF FLAME THROWERS

by
DR. G. Kirkpatrick, Chemist
E. I. du Pont de Nemours and Company
Ammonia Department

Report OSRD No. 3507

Copy No. 45

Date, April 20, 1944

Copy Nos.

- 1-28 Dr. Irvin Stewart
- 29 Commandant, U. S. Marine Corps Headquarters
Attention: Lt. Col. L. E. Marie
- 30 Office of the Chief of Chemical Warfare Service
Attention: Technical Division, Liaison Branch
- 31-34 Chemical Warfare Center, Edgewood Arsenal
Attention: Brig. Gen. W. C. Kabrich
- 35 Mr. E. P. Stevenson
- 36 Division 11 Files

Total Number of Copies - 45

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Division 11
NATIONAL DEFENSE RESEARCH COMMITTEE
of the
OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT
Section 11.3

CHEMICAL IGNITION OF FLAME THROWERS

Service Directive; CWS-10

Endorsement (1) From E. P. Stevenson, Chief, Division 11 to Dr. Irvin Stewart, Executive Secretary of the National Defense Research Committee.

Forwarding report and noting:

"Chemical methods of igniting flame thrower fuels are reviewed without any definitely promising possibilities coming to light. Certain oxidizing agents, such as chromyl chloride and chromic oxide, and certain fluorinating agents, such as antimony pentafluoride, bromine fluoride, et al. appear as possibilities. Spontaneous ignitable substances, such as zinc diethyl, were not considered as promising."

This is a Final Report under Contract 11-364, OEMsr-744 with E. I. du Pont de Nemours and Company.

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Ammonia Department
E. I. du Pont de Nemours & Co., Inc.

Chemical Division
Du Pont Experimental Station
Wilmington, Delaware

Chemical Ignition of Flame Throwers.
A Critical Review of Proposed Techniques.

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Ammonia Department
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Chemical Ignition of Flame Throwers.
A Critical Review of Proposed Techniques.

ABSTRACT

Chemical methods of igniting flame thrower fuels are reviewed. It is recommended that oxidizing agents such as chromyl chloride or chromic oxide and fluorinating agents such as fluorine, antimony pentafluoride, oxygen fluoride or bromine and chlorine trifluoride mixtures be evaluated. The use of a platinum catalyst to inflame a gasoline spray is suggested. Less promising techniques considered include the use of spontaneously ignitable substances, metallic driers, sulfur compounds, nitrogen-containing compounds, and ignition of a gasoline pilot flame by a hot filament or chemical agents.

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E. I. du Pont de Nemours & Co., Inc.

Chemical Division
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Chemical Ignition of Flame Throwers.
A Critical Review of Proposed Techniques.

February 22, 1944

I. Introduction

On October 25, 1943, Mr. F. S. Bacon, assistant to the Chief, Division 11, N.D.R.C., requested by letter that this group, under N.D.R.C. Contract OFMSr-744, undertake a critical survey of chemical means of producing ignition in flame throwers. In a search for ignition agents the literature on fire hazards, spontaneous ignition and antiknock studies on gasoline was reviewed. The chemistry of the materials suggested by the above preliminary search was then studied and the properties of related compounds were reviewed. Candidate agents fell into several distinct classes of compounds, the properties of which were then discussed when security regulations so allowed with other groups in this Company. An attempt was made to visualize the mechanical adaptation of various chemical ignition systems to present flame throwers.

II. Summary and Recommendations

1. A set of field requirements on flame throwers as they pertain to the ignition system has been outlined. The degree to which existing devices meet these requirements indicates that a chemical ignitor must be foolproof to warrant adoption.

2. It appears feasible to induce ignition by the reaction between the unsaturated fraction of the fuel and strong oxidizing agents. Based on stability, potency, and ease of handling chromyl chloride (CrO_2Cl_2), a liquid, and chromic oxide (CrO_3), a solid, dispersed as an aerosol are judged the most promising oxidizing agents for this purpose. Fortification of the fuel with unsaturates, preferably acetylene, or certain reducing agents is desirable.

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3. Fluorine or fluorinating agents react violently with saturated hydrocarbons, yet are non-inflammable and stable when properly contained. If these materials were used as ignition agents they could be stored safely in the flame thrower away from the fuel. When mixed at the nozzle of the gun even with unfortified fuel, they would react with sufficient energy to cause ignition. The following compounds are suggested for further evaluation: fluorine, antimony pentafluoride (SbF_5), oxygen fluoride (OF_2), and bromine and chlorine fluoride mixtures (BrF_3-ClF_3). Oxygen fluoride is stable in the presence of moisture.

4. The use of high concentrations of metallic soaps to catalyze the air oxidation of flame thrower fuels appears unreliable and impractical. This system might be improved by modification of the fuel.

5. Sulfur-containing compounds which have caused spontaneous ignition react slowly and with but little energy release.

6. Nitrogen-containing compounds which will ignite gasoline gels are unstable in storage. The use of amines (reducing agents) which might function as ignition aids would peptize Napalm gels.

7. Possible techniques of safely handling spontaneously ignitable substances such as metal alkyls, phosphene and silane are reviewed.

8. The primary ignition of a gasoline flame ignition system by chemical ignitors, metallic catalysts or a hot filament may offer a simple solution to the problem. A platinum catalyst protected from major contamination should insure reliable ignition of a gasoline pilot spray.

9. If an experimental appraisal of chemical ignition is to be undertaken, the systems outlined in items 2, 3 and 8 above appear most promising as initial lines of attack.

III. Discussion of the Problem

In order to compare the relative merits of various proposed chemical ignition systems, it is necessary to define more fully the field requirements

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on flame throwers. The extent to which these requirements are fulfilled in existing weapons indicates that to warrant adoption a chemical ignition system can fail none of the indicated tests.

As a basis for this review the following requirements were visualized.

1. Functioning. The ignition system must function in the field at all temperatures between -10°F . and 125°F .

2. Durability. The ignition requirements must hold after the assembled gun has been given rough handling, has been carried in any position, has been immersed in water, and after the fuel has been held in high and low temperature storage.

3. Servicing. It should be possible to service the gun with fuel and ignition agent by simple means at forward bases. Once the gun has been serviced it should be possible to maintain it loaded and ready to fire for at least a month.

4. Safety. If the fuel and ignition systems are hit by small arms fire the operator should not be endangered. The filling operation should involve hazards not greater than those experienced in handling gasoline.

5. Surveillance. The fuel and ignition agent should be stable in storage for at least a year during some period of which the temperature might reach -40°F . or 150°F .

6. Design. The design should be simple to facilitate manufacture and reduce malperformance. The ignition system must not add materially to the weight of the gun.

7. Operation. To maintain ignition of the fuel the ignition device must function during the entire period the gun is operated. If fired in one burst the fuel in a portable unit can be ejected in from 10 to 12 seconds. It should, however, be possible to divide the charge into several shorter shots and attain ignition with each burst.

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The ignition systems in portable flame throwers now in the field or under development depend either on slow burning flare mixes mounted in a cartridge or on a gasoline flame which is ignited by a high tension electric spark. Both of these systems meet nearly all of the above-outlined stringent requirements. The first method (see Bibliography, Section V, reference 9) has been criticized because the duration of fire cannot be controlled, the flame from the cartridge ignitor reveals the position of the gun to the enemy, and because there is some uncertainty concerning the stability at high temperatures of the black powder in the mix. The high tension electric spark system has not been accepted due to possible failure of the electrical system on exposure to water.

IV. Review of Chemical Agents

The use of chemical ignition agents is most conveniently reviewed by classifying them according to their chemical action or their chemical composition. Of the various types of materials discussed, only fluorinating agents appear certain to induce ignition. In all other cases the information available allows only a qualitative estimate of their worth to be made. With the more promising candidates a laboratory evaluation is required. Since the use of spontaneously ignitable fuels appears hazardous during the filling operation, the major effort was directed to a search for materials not spontaneously flammable but which would only ignite when mixed with the fuel.

A. Oxidizing Agents

When mixed with gasoline many oxidizing agents liberate heat but to obtain spontaneous ignition the most vigorous agents are required. The reaction involves principally the unsaturated fraction of the fuel so that the reaction can be made more energetic by altering the fuel composition. The most effective means appears to be incorporation of acetylene in the gasoline. Due to its low molecular weight a small proportion of acetylene in gasoline should markedly improve its ignitability. Other additaments in decreasing order of effectiveness are olefines, turpentine, alcohols and antiknock agents. Satisfactory Napalm gels have been prepared in turpentins. Possibly alcohols and antiknock agents would peptize the gel. The reduction of the autoignition temperature of

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gasoline by antiknock agents is not large and the effect is not proportional to the quantity added. It is believed that some improvement in ignitability could be effected by the addition of minor amounts of carbon disulfide, tetranitromethane (U.S. Patent 2,185,157) or iron pentacarbonyl to the fuel. The presence of reducing agents would markedly enhance the reaction with oxidizing agents but with all materials considered gel stability appears uncertain. It is suggested that as new types of gelling agents are considered their stability towards hydrazine, ammonia or hydrogen sulfide should be determined.

The choice of an oxidizing agent will be determined not only by its reactivity but also by its stability. It is felt that organic peroxides, persulfuric acid, Caro's acid, and perchloric acid are not sufficiently stable in storage to warrant consideration. While hydrogen peroxide and nitric acid have both been known to cause spontaneous ignition of organic material, the reactions appear slow and uncertain. The most promising oxidizing agents uncovered in this search are chromic oxide (CrO_3), chromyl chloride (CrO_2Cl_2), permanganic acid anhydride and trichloromethyl perchlorate (Cl_3CClO_4).

Chromyl chloride is a dark mobile liquid (boiling point 116.7°C ., freezing point -96.5°C ., specific gravity 1.96) throughout the temperature range under consideration. It is stable to heat and can be stored indefinitely in steel without pressure development. It is hydrolyzed by water and water vapor. It should therefore be packaged in a steel container to be opened at the time of use. This technique is described more fully in Section F. A preliminary test of the reaction between chromyl chloride and Napalm gel was made at Edgewood Arsenal by the Technical Division of C.W.S. While the heat of reaction was appreciable, ignition did not result. It is believed that with an increase in the unsaturate content of the fuel ignition could be achieved. This point warrants further study. Chromyl chloride is now manufactured commercially.

The reactivity of chromic anhydride (CrO_3) may be greater than that of chromyl chloride since only the former causes the ignition of aromatic substances. In the absence of moisture chromic anhydride is stable. It is a dense solid (melting point 196°C ., specific gravity 2.7) and is soluble in halogenated hydrocarbons.

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It is suggested that it be transported as a solution in a volatile solvent which on evaporation would liberate the anhydride in an aerosol-like system (liquid finely dispersed in air). Suitable solvents would be tetrafluormethane and tetrafluordichlorethane. These mixtures would be noxious but not hazardous if exposed to the air inadvertently. The solution would be carried in a steel container. The vapor pressure of the low boiling solvents would eject the mixture into the nozzle area of the gun; no air pressure would be required.

The most reactive material considered is permanganic acid anhydride (Mn_2O_7). This oxide is a liquid which freezes below $-20^\circ C$. It decomposes at $70^\circ C$. but has been heated safely to $50^\circ C$. This material has been little studied so that its storage stability is unknown. At room temperature in the absence of moisture the literature states it is stable for many weeks. The oxide reacts explosively with reducing agents and a few drops are sufficient to cause inflammation of turpentine, benzene, alcohol and oils and fats. With this ignition agent it would probably be unnecessary to fortify the Napalm gel. It is suggested that methods of preparation and stability of the oxide be determined.

The reaction of sodium perchlorate with carbon tetrachloride yields trichloromethyl perchlorate ($ClCClO_4$), a powerful liquid oxidizing agent. Stability data are lacking. One might predict it would be stable in the absence of organic materials but sensitive to shock.

The other oxides or oxyhalides of the heavy metals appear from the literature to be less stable or less reactive than those listed above. While ozone might be an effective ignition agent, high concentrations would be required.

B. Fluorinating Agents

The reaction of elementary fluorine with organic substances is violent. Small amounts of fluorine will ignite completely saturated hydrocarbons. Explosion has resulted from mixing turpentine and liquid fluorine at $-210^\circ C$. Since the reaction does not depend on the unsaturate content of the fuel, ignition of any gasoline gel should be satisfactory.

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The choice of a suitable ignition agent containing fluorine depends on stability and ease of handling. The following compounds are suggested for further evaluation: fluorine, antimony pentafluoride (SbF_5), oxygen fluoride (OF_2), and bromine and chlorine trifluoride mixtures (BrF_3-ClF_3). Oxygen fluoride, a gas boiling at $-167^\circ C.$, has the interesting property of being stable in the presence of moisture. The other fluorinating agents hydrolyze to liberate ozone and hydrogen fluoride. In the temperature range under consideration traces of oxygen fluoride have ignited saturated hydrocarbons in the laboratory. The material is stable and can be compressed. Antimony trifluoride is a liquid boiling at $150^\circ C.$ and freezing at $5^\circ C.$ The freezing point could be readily lowered by addition of small amounts of the more volatile fluorides. Its properties closely resemble those of bromine trifluoride which boils at $135^\circ C.$ and freezes at $5^\circ C.$ Mixtures of bromine and chlorine fluorides (BrF_3-ClF_3) have very low freezing points.

All of these compounds can be stored indefinitely in steel containers. At high concentrations they are toxic. In the extremely low concentrations required for ignition some lachrymatory effect might be felt by the operator when the gun is fired directly into the wind. Due to hydrolysis even large concentrations of the gases are rapidly dissipated in the air. When fluorinating agents attack metal they form an impervious fluoride film which prevents further action. After formation of such a film iron is not attacked by fluorine at temperatures below $400^\circ C.$ It is therefore believed that these materials will not have a corrosive action on the gun.

In view of the availability of liquid and gaseous agents, the use of solid fluorinating agents such as chromium trifluoride appears unnecessary. If the fluorides appear too violent, their reactivity may be decreased by dilution with the corresponding chlorides. The compounds suggested are all soluble in fluorinated hydrocarbons like tetrafluoromethane and could therefore be generated as aerosols in the gun. It is suggested that these agents be handled in cylinders, capsules or squibs as discussed in Section F and that ignition be actuated by breaking the container.

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C. Metallic Driers and Unsaturation

The air oxidation of unsaturated materials can be catalyzed by soluble metallic salts. The cobalt, manganese, chromium and lead salts of such acids as naphthenic acid, stearic acid and rosin are used for this purpose in paints. Concentrated solutions of these "driers" are commercially available and are in general stable. In normal paint mixtures the rate of the catalyzed oxidation is slow. To obtain ignition of flame thrower fuels it would therefore be necessary to use high concentrations of the driers and to increase the unsaturated content of the fuel. If this technique is studied, it is suggested that the rod of fuel be coated with a film of a concentrated drier solution to obtain a high local concentration of catalyst on the surface of the gel. This technique has been developed to "lubricate" mechanized flame thrower fuels.

The most effective additaments to the fuel would be hydrocarbons containing conjugated unsaturation such as butadiene or drying oils like tung oil. Due to lack of stability in storage, the use of by-products from the synthesis of neoprene does not appear feasible. Thus monovinyl acetylene, divinyl acetylene and their low molecular weight polymers are readily ignited but during storage develop a skin of polymeric material which is ignited only with much difficulty. If these materials are peroxidized, they become sensitive to shock.

It has been suggested (letter F. S. Bacon to E. C. Kirkpatrick, 12/10/43) that an atmosphere of oxygen rather than air in the shield surrounding the nozzle of the gun would aid ignition. It is felt that the rate of flow of the fuel is such that the time of exposure to the oxygen atmosphere would be too short to be effective.

In general, the use of driers does not appear as promising as the two ignition techniques previously outlined unless a special flame thrower with delayed ignition is desired. This type of reaction is being studied by the Chemical Warfare Service for another purpose in which the fuel has greater contact with the air and ignition is not required until after the gel reaches the target. The results of their study when completed should be determined. It is also suggested that the manufacturers of metallic driers be canvassed in a search for a more potent catalyst.

D. Sulfur Compounds

The literature cites many organic sulfur compounds as exhibiting spontaneous ignition. This is especially true in the presence of oxygen or ultraviolet light. Thiophosgene (CSCl_2) has the lowest ignition temperature (30°C .) disclosed (Delephine Bull. Soc. Chimie 31, 762 (1922)). We are informed that while spontaneous ignition of organic sulfur compounds is an industrial hazard, the reactions involved are slow and not reliable.

E. Organic Nitrogen Compounds

Hydrazine will peptize Napalm gels but when added to other viscolized fuels should markedly enhance their reactivity towards oxidizing agents. Chromyl chlorids will react violently with hydrazine hydrate even when the latter is in a dilute aqueous solution. Mixtures of hydrazine and chlorine inflame spontaneously. It is suggested that the action of hydrazine on aluminum naphthsnate gels be determined. Solutions of polyvinyl ether in gasoline are not affected by the presence of this reagent.

The nitrogen halides react violently with unsaturated materials. Ignition resulted when turpentine, grease or soaps of oleic acid were brought in contact with nitrogen trichloride. The nitrogen halides are hydrolyzed by cold water and are sensitive to shock. They therefore are unsuitable in that form as ignition agents. Nitrogen trichloride may be generated by the action of hypochlorites on urea or ammonium chloride. It is felt that a generating unit might be cumbersome and not sufficiently durable.

The other types of organic nitrogen compounds which will cause ignition include nitroso, azo and diazo compounds and azides. A review of this field has indicated that the known compounds which are sufficiently reactive would be unstable in surveillance. Many compounds in these classes would produce a detonation which would blow out incipient ignition.

F. Spontaneously Inflammable Substances

Ignition of flame thrower fuels could be obtained by reaction with inflammable substances like the metal

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alkyls (zinc diethyl, boron trimethyl), phosgene, silanes and their derivatives. Since these materials ignite when exposed to air, their use is hazardous during and after loading of the gun. The problem is therefore to devise mechanical techniques to handle these materials. A few are outlined below.

Small carbon dioxide cylinders of approximately 20 cc. capacity have been marketed for home production of Seltzer water. In use the cylinder is opened by puncturing one end. Such cylinders would fit into the forward handle of the gun. Replacements could be readily inserted at any time. Just prior to firing the gun the ignition system would be actuated by screwing the forward handle and thus forcing the cylinder against a centered sharpened point. It could be desirable to have a valve to control the flow of the agent into the nozzle area. The cylinder container must therefore retain pressure for a short period. Any leaks will result in a flame which will draw enemy fire and might injure the operator. If this technique is applied to non-inflammable agents as suggested in earlier sections, the above objections do not hold and a valve might not be required in the system if the capacity of the cylinder will allow the contents to be released over a considerable period. This release requires control only when it exposes the location of the gun.

When only small concentrations of the agent are required, it could be fed to the nozzle in small increments. The agent would be handled in a series of containers resembling cartridges, capsules, dynamite squibbs or even a continuous compartmented tube. The individual containers would be opened mechanically by a trigger operated pin. If necessary, the pin could be driven by a spring actuated by the trigger. The above technique is the one used in the existing pyrotechnic ignitors and for spontaneously ignitable reagents suffers the same disadvantage of lack of control within the size of each individual unit.

Continuous control might result if the chemical were stored in a collapsible tube containing a permeable plug or membrane in the neck and sealed by a spring-driven cap. A turn of the forward handle would release the cap but the porous plug would prevent rapid dissipation of the agent in the tube. Additional turns of the forward handle of the gun would mechanically squeeze or roll up the rear end of the flexible tube and force the agent

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into the nozzle area. The rate of flow of the agent would be determined by the rate at which the operator turned the handle. A turn in the reverse direction should recap the tube. It would be possible to use agents developing moderate pressure in the tube if it were supported in a rigid case along the lines of a fountain pen (a collapsible bladder in a rigid shell). The mechanical features of such a device appear complex. The tube to be flexible must be constructed of rubber, plastics or tin-lead alloys. Rubber or plastic tubes might either be slowly permeable to moisture or allow slow leakage of the reagent in the tube. The metal alkyls are stable only in glass. Gaseous materials such as phosphene and silane would probably require excessive pressures for economic filling. Reaction of monochlorosilane with ammonia, however, yields nitrilotrisilane ($N(SiH_3)_3$) a spontaneously inflammable liquid which might prove suitable for this purpose. If fluorinating agents were used in such a device, they would react with a container fabricated from organic material and above $100^\circ C$. would attack tin or lead.

G. Primary Ignitors other than a Spark

The gasoline flame in the E-2 flame thrower gives reliable ignition. The criticism against this unit is the use of a high tension spark to ignite the gasoline torch. The primary electrical ignition system could be replaced by chemical ignitors.

Cigarette lighters have been devised in which air and alcohol vapor is drawn over a platinum or platinum-iridium alloy catalyst (British Patent 462,717). If such a catalyst were supported in the path of the gasoline spray, ignition should result. The reaction of the gases on the catalytic surface heats the metal until the ignition temperature of the fuel is reached. At very high gas flow rates the combustion heat is dissipated. This might require that the spray be split into two streams, the catalyst igniting a pilot light utilizing only a small portion of the gasoline vapor. We are advised that catalysts which will initiate combustion at room temperature and below are sensitive to poisoning. They are somewhat sulfur-tolerant since platinum catalysts have been used to light household gas kitchen stoves. Immersion in water or exposure to powder fumes would probably destroy their activity but they can be regenerated

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by heat. This latter factor insures continued combustion during a shot once the flame is ignited. The possibility of simplifying and decreasing the weight of the gun by replacing the electrical system with a small catalyst pellet is, however, intriguing. The following procedures to protect the catalyst might be considered: Support the catalyst inside the tube carrying the spray to the nozzle area and seal the end of this tube, the seal to be broken by operation of the safety switch. Alternatively the catalyst might be supported in a sheath in a water-tight container and inserted through a special fitting into its location in the nozzle area of the gun just before use. Spare catalyst cartridges should be carried.

A gasoline flame could be ignited by an agent liberated from a capsule as discussed in the previous section. Under such conditions the chemical agent would be used only to initiate the gasoline flame and after-burning would be eliminated. This technique is not recommended since it involves two complicated ignition systems and would therefore increase the chances of mechanical failure.

In an electrical ignition system the use of a hot filament rather than a high tension spark might be considered. Reliability of such a system would be improved if the autoignition temperature of the gasoline were reduced possibly by addition of carbon disulfide. After immersion in water a hot filament would dry itself out and then function. The danger of a short circuit is reduced. It is not known whether light weight batteries with sufficient capacity to heat resistance wire are available.

Prepared by *E. C. Kirkpatrick*
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Approved by *John S. Beekley*
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Official Investigator

2/23/44

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A few specific references have been included in the body of this report. In general, however, the data in the literature are not immediately applicable to the particular problem. For the properties of the various compounds discussed the reader is referred to the standard reference books such as J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Longmans Green and Co., London, 1922, and Beilstein Handbuch der Organischen Chemie, Springer, Berlin, 1918, 1929. Articles of particular interest on existing flame throwers, autoignition temperatures, spontaneous ignition and industrial hazards include the following:

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Restricted War Dept. Technical Manual
TM 3-376 December 10, 1943

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TITLE: Chemical Ignition of Flame Throwers

ATI- 31600

REVISION

(None)

ORIG. AGENCY NO.

(None)

PUBLISHING AGENCY NO.

OSRD-3507

AUTHOR(S): Kirkpatrick, E. C.

ORIGINATING AGENCY: E. I. du Pont de Nemours and Co.

PUBLISHED BY: Office of Scientific Research and Development, NDRC, Div 11

DATE	DOC. CLASS.	COUNTRY	LANGUAGE	PAGES	ILLUSTRATIONS
April '44	Confid'l	U.S.	Eng.	13	tables

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DIVISION: ~~Ordnance and Armament~~ (22)

SECTION: ~~Chemicals and Incendiaries~~ (11)

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SUBJECT HEADINGS: Flame throwers - Fuels - Ignition (37319.7)

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- (23) * Flamethrower Fuels
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