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FIRE
RETARDANT
PAINTS

A collection of papers comprising the
Symposium on Fire Retardant Paints,
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Introduction

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The subject of fire retardancy through the use of protective coatings should be approached a little to the right of center -- that is, with cautious but definite enthusiasm. As with so many other chemical developments, including plastics, medicines, drugs, insecticides, soil conditioners, even chlorophyll, a favorable beginning for a product that seems to meet a long-felt pressing need of the consuming public is soon overpromoted. For fire-retardant paints, as for so many of these other badly needed products, overpromotion can be more harmful than underpromotion. An example of overpromotion is to claim absolute fireproofness for a product, and then rig a demonstration that appears convincing. No paint film can be expected to withstand a fiery holocaust for an extended period of time without yielding. Not even a sheet of steel, many times thicker than the average paint film, could live up to such claims. If, in addition, the so-called "fireproof" paint is deficient in a host of normal paint properties, the public is doomed to disappointment. People are led to expect so much, and then receive so little, even in this age of chemical miracles.

This matter of misleading and deceptive wording is extremenly important, not only for the ad writer, but also for the chemist, the engineer, the underwriter, and the author of a building code. The use of the term "fire-retardant" itself has confused paint research. Fire-retardant action over steel is altogether different in principle from fire-retardant action over wood or vegetable fiber wallboard. Is any one fire-retarding agent to be preferred over another? It all depends on what you want to prevent from becoming fuel to feed the flames -- is it the paint itself, or is it the construction material underneath the paint?

It cannot be emphasized too strongly that dried paint films, instead of tending to spread flame, actually retard it when compared with the same unpainted surface. Therefore, it serves no good purpose for the purchaser of paint to consider replacing all of his conventional painting with special fire-retardant coatings. For special uses in hazardous areas where it is imperative to take all possible safeguards, such special types of coatings have a definite utility.

Ordinary paints, particularly those with pigmentation intermediate between flat and full gloss, possess a fair amount of fire retardance when exposed to conditions existing during the first stages of a fire. This can be checked at a bonfire by throwing on painted and unpainted boards, and observing which catches fire first and which is consumed first.

The really worth-while features of improved types of actual paints that possess considerable fire retardancy have not yet received enough attention. Special pigments that fuse, release smothering gases, or react with the combustible substrate -- combined with special puffing vehicles to provide insulation -- can be used to make coatings

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that are both fire-retardant and acceptable paints in themselves. A special top coat then becomes unnecessary.

If these two features were better known -- that ordinary paints as applied to ordinary construction do not constitute an additional hazard; and that special paints can be used to provide an extra measure of protection at critical points by retarding the initial rate of spread of fire -- the proper climate of public opinion would prevail that would ensure the further development and use of true fire-retardant paints.

This symposium is a compilation of both new and review information, laboratory data and field experience, the practical viewpoint together with theoretical reasoning. Well-rounded and representative as it is, this symposium would have been strengthened by two additional papers. Circumstances prevented the invited authors from participating, but fortunately they have both published articles recently that are available in the literature.

The requirements of a good test for fire-retardant paints should be known to all those concerned with their evaluation and usage. This problem of what constitutes a proper test is a very serious one when it stands as a roadblock in the path of progress. A poor test is worse than no test at all. Too mild -- it is dangerous to life and property. Too severe -- it stifles progress. Too costly -- it becomes impractical and is rarely used. R. C. Hubbard covers this philosophy of testing as related to fire-retardant paints in excellent fashion (2, 3). H. L. Aldrich (1) covers the role of paint in atomic warfare, as well as in peacetime disasters, in a sobering but definite manner in six articles. His main thesis is that very little can be done about preventing ignition in the primary blast zone, but that the radius of conflagration can be reduced considerably by the use of heat-reflecting paints, thereby reducing the possibility of setting up large uncontrollable fire storms.

At the FATIPEC Conference held in Paris, June 3 to 6, 1951, an international group of experts pooled their information. The papers were combined and published under the French title, "Journées d'Étude sur les Peintures et Vernis dans la Lutte contre le Feu," describing the role of paints and varnishes in the war against fire. John C. Moore and myself were honored to be invited to present some of the work done at the laboratories of the Scientific Section of the National Paint, Varnish and Lacquer Association.

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Value of Fire-Retardant Paints

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To determine whether paint may aid in reducing fire damage -- in 1950 some 600,000 building fires resulted in $700,000,000 fire loss -- the process of combustion, types of fires, and theoretical role of paints under fire conditions have been examined. Properly designed paints will reduce fire damage, even though the degree of protection may be subject to question. A properly designed paint should be nonflammable or of a low order of flammability, smooth out the surface of the substrate to reduce surface area exposed to the air, insulate the substrate by being heat-reflective or of an insulation nature, retain insulation and nonflammable characteristics under direct fire attack, and be sufficiently decorative and protective to be practical coating material.

In 1950 some 600,000 fires caused almost $700,000,000 damage to buildings, 4% more than 1949. In Table I, the percentage of dollar fire losses by occupancy is summarized for 1950. This table is based on data from 13 states and, therefore, is only indicative of the relative importance of type of structure on potential fire losses. Private dwellings account for one fourth of the total fire losses.

A claim that paints would eliminate this $700,000,000 annual loss would be considered unrealistic. However, by examining the various factors of this fire damage in the cold light of reality, it should be possible to decide the most effective places to use paints for reduction of fire damage, and the more promising development approaches to be used to obtain such a paint or paints.

Therefore, let us examine the process of combustion, types of fires, and the theoretical role of paints under these conditions.

Process of Combustion

Combustion results from the union of a three-component system. Remove any one of the components and a fire either does not start or when started is extinguished. These components are fuel, air, and temperature of sufficient degree to enable combustion to take place.

A match is fuel. It is surrounded by air in sufficient volume to support combustion. But it is not burning because the temperature is not sufficiently high to produce combustion. If we abrade the match, we generate sufficient heat to cause

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the chemicals in the match head to ignite. This heat is then sufficient to cause the match to continue to burn.

How do we extinguish a burning match? We can let it burn itself out -- in other words, we remove the fuel by permitting it to be entirely consumed. We can smother it by dipping the match in water. This removes the air necessary to support combustion. Or we can blow it out. This process blows away the burning gases, so that the other volatile gases are cooled below ignition temperature.

But what has this match to do with a burning house? The principles that govern the burning of a match also govern the burning of a house. The burning of a house is the same phenomenon, only increased an infinite number of times over that of a match.

If the house contains no combustible material, it will not burn. If the burning area could be tightly sealed, it would smother itself. This is the principle of foam extinguishers. We cannot reduce the temperature below the ignition point by blowin the fire out, but we do have another way of reducing temperature. This is water. Every calorie of heat absorbed by the noncombustible water and steam removes that calorie of heat from the fire's ability to propagate itself.

Therefore, three major means exist for reducing fire damage -- removing the fuel, removing the air, and lowering the temperature. For each means, there are several approaches. The success of each approach is influenced by the type and nature of the fire.

Table I. Percentage of Fire Losses by Occupancy

Government buildings	0.1		Metalworkers	0.8	
Hospitals	0.4		Woodworkers	2.4	
Schools and colleges	2.4		Grain mills	3.0	
Churches	1.6		Packing	0.1	
Theaters	0.8		Bakeries	0.1	
Amusement halls	1.6		Textiles	0.1	
Total public buildings		6.9	Printing	0.1	
			Laundries	0.5	
Hotels	2.0		Cleaners, tailors	0.2	
Boarding, rooming houses	0.4		Miscellaneous	11.0	
Apartments	2.4		Total manufacturing		18.3
Dwellings	25.6				
Total residential		30.4	Barns	8.8	
			Outbuildings	1.2	
Offices	4.0		Lumber and coal yards	0.6	
Restaurants	2.4		Railroad property	0.4	
Miscellaneous	12.8		Oil refineries and storage	0.2	
Warehouses	4.0		Garages	3.0	
Total mercantile		23.2	Filling stations	0.2	
			Power plants	0.4	
			Creameries, dairies	0.2	
			Miscellaneous	6.4	
			Total miscellaneous		21.4

Types of Fires

If building fires are classified by the severity of the fire, three types may be enumerated:

1. Isolated, one building or less.
2. Multiple, more than one building.
3. Conflagration, a sweeping fire that spreads beyond control to destroy cities or large areas of built-up property.

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The isolated fire starts from any number of causes. The fire feeds upon fuel that is readily available and causes the surrounding temperature to rise. With a sufficient increase in temperature, flames and sparks may ignite nearby structures and start multiple fires, which may, at times, spread in ever-widening circles and eventually reach a conflagration proportion.

A conflagration resulting from a mass incendary bomb attack, or an atomic bomb attack, would probably burn itself out by its sheer magnitude. Air is pulled into the burning area with such a force that the fire is kept from spreading out of the burning area.

Role of Paints

Considering a conflagration as the most severe condition of combustion, let us examine the role of paint. In the fire area itself, paint would be of little or no significance. But the same thing is true for any of the more usual fire-fighting methods.

Around the perimeter of the burning area, however, paint may play several roles.

1. If the paint is of a flammable nature with a low ignition point, it may materially aid the spread of fire.
2. If the paint is completely inert, it may have little or no influence.
3. If the paint is of a heat-reflecting nature, it may keep the temperature of the combustible substrate and the paint itself below its ignition temperature. Therefore, it will either prevent the spread of the fire or reduce the rate at which it spreads.
4. If the paint is of an insulation nature, it may keep the temperature of the combustible substrate below the ignition point.

Therefore, properly designed paints can, at least reduce the rate of fire spread from a burning to a nonburning area.

Studies of fire damage from atomic bomb attack and incendiary bomb attack have shown this reduction of flame spread to be a significant and measurable fact. However, variations in burning conditions, types of structures, types of paints, condition of the paint at the time of exposure to fire, etc., will always leave the true value of protective paints open to question and subject to opinion.

Delayed ignition of a house on the perimeter of a conflagration may be of academic interest only. This supposition is based on the premise that the overtaxed fire department is unable to take advantage of this delayed ignition. But, if the fire department is not overtaxed, delayed ignition may mean the difference between a fire loss or no fire loss. Therefore, the smaller the fire, the less overtaxed is the fire department, and the greater is the importance of delayed ignition. This, then, may be the means of keeping an isolated fire isolated.

Let us now examine the possible roles of paints under conditions of isolated fires. In building fires, this combustion may start from cigarettes, electrical short circuits, matches, spontaneous combustion, lightning, Christmas trees, or explosions.

These causes are arbitrarily listed in an order representative of the magnitude of the fire at first ignition.

It is apparent that the same factors govern these fires:

1. If the paint is flammable, it may aid the spread of the fire.
2. If the paint is inert, it may have little or no influence. But one additional factor is worth mentioning at this point. Unfinished wood permits fairly rapid flame spread across the surface of the wood because of loose slivers of wood protruding from the rough surface. An inert paint, that would bind together or cover over all these

wood particles, would reduce flame spread by reducing the surface area of exposed combustible material.

3. If the paint is of a heat-reflecting nature, the temperature may be kept below the ignition point.
4. If the paint is of an insulation nature, it may keep the temperature of the combustible substrate below the ignition point.

Therefore, paints may perform a positive role in reduction of fire damage. This realization that paints may reduce combustion has led to several methods for measuring this phenomenon. All the tests have one thing in common: They use an uncoated substrate as the base standard. They differ in their duration and severity of direct flame exposure.

One thing should always be remembered. Under direct attack of the most severe fire, paint and many other forms of fighting fire have limited value. At the edges of the fire, however, the combustion may be equivalent to a finite number of matches. The combustion of a finite number of matches is controllable. Properly designed paints will, in any case reduce the rate of fire spread. The reduction may make it possible for additional fire-fighting techniques to take effect quicker as well as having a fire of smaller magnitude to combat.

To accomplish this goal, a properly designed paint would probably possess the following characteristics:

1. Be nonflammable or of low order of flammability.
2. Smooth out the surface of the substrate to reduce the surface area exposed to the air.
3. Insulate the substrate by being either heat-reflective or of an insulation nature.
4. Retain this insulation characteristic and nonflammable characteristic as long as possible under direct fire attack.
5. Possess sufficient decorative and protective characteristics of the usual paints to be a practical coating material.

Acknowledgment

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Some Theoretical Aspects of the Flameproofing of Cellulose

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Several theories have been proposed to explain how flaming is inhibited in the many processes used to flameproof cloth or cellulosic materials. Such materials do not continue to flame after being removed from a source of ignition. Study of these theories of thermal decomposition of treated and untreated cellulose, the latter also involving burning, leads to the conclusion that only one chemical mechanism, dehydration, aided by a physical mechanism, accelerated gas production, explains the behavior of all known flameproofing agents. This chemical mechanism, elaborated in the light of current concepts of organic chemistry, explains the flameproofing reaction on the basis of catalytic dehydration. through a Lewis acid-base interaction via a carbonium ion or carbanion mechanism. Accelerated gas production plays an important part in providing the over-all protection. Much of the reasoning involved in the theory of catalytic dehydration should apply also to the flameproofing of wood.

Man's concern with the hazards associated with the combustibility of cellulosic materials, including textiles and wood, has been continuous since the discovery and utilization of fire. Many of the household and industrial uses of cotton fabrics require that they be efficiently flameproofed for the protection of clothing, equipment, and personnel. The need of efficient flameproofing of military textiles for protection of both personnel and matériel is self-evident and the hazards encountered are well understood. The wider use of incendiaries in modern warfare has increased the need for adequate protection against flame.

Neither cotton nor wood celluloses can be made fireproof in the sense that glass or asbestos fibers are, as they cannot be prevented from charring; but they can be made "flameproof" in that they will not support combustion after removal of the source of ignition. According to federal specifications (27), flameproofed cloth must not propagate a flame after exposure under standard conditions for 12 seconds to the luminous flame of a Bunsen burner.

The theoretical aspects of flameproofing cellulose, considered in the present paper, are based mainly upon experience with the flameproofing of cotton textiles. However,

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much of the theory applicable to the flameproofing of cotton is also applicable to the flameproofing of wood. A flameproofing material, whether it is applied to cotton or to wood, must have two characteristics. It must not support combustion by itself -- that is, it must not continue to burn after being subjected to flame or other sources of ignition -- and it should so affect the cellulose that it will not support combustion after removal of the flame. If such flameproofing material can be added to the cotton, or to wood, and contains ingredients which change the course of the reaction, ideally to a decomposition of the cellulose to carbon and water, flameproofing has been accomplished. In the case of wood, much attention is being given to the possibility of flameproofing through the use of paint. The goal sought is a paint which, in addition to fulfilling the normally expected requirements such as weather protection, resistance to rotting, and decoration, will at burning temperatures bring about at least a surface change which will stop or retard complete burning of the wood.

Since the burning of the study of methods for flameproofing cellulosic materials, various theories have been suggested to explain the mechanism by which the materials were prevented from burning. It has generally been assumed that a different theory was necessary for each class of flameproofer -- that is, no one theory accounted for the results obtained with all known flameproofers. However, if flameproofing is the result of a chemical reaction, a single theory based on a single type of chemical mechanism should apply in all cases. It is not intended that such theory apply to natural and synthetic noncellulosic fibers such as wool, silk, and nylon. Some of the reasoning may apply, but in general other materials would not be expected to undergo the same decomposition reactions as cellulose.

This paper presents a brief outline of the theories which have been proposed and uses the modern concepts of organic chemistry to explain the mechanism of the chemical reaction involved. Although the remarks in this paper are concerned mainly with the flameproofing of cotton, they should be equally applicable to the flameproofing of wood. Only the flaming stage of burning is considered, as glowing is a separate process and a different mechanism is involved.

Thermal Decomposition and Combustion of Untreated Cellulose

The burning of cellulose is due to the formation and combustion of flammable vapors when the cellulose is exposed to high temperature -- that is, cellulose, a solid with no appreciable vapor pressure, does not burn as such but rather decomposes into flammable fragments which, in burning, generate heat, and this heat further decomposes the cellulose to carry on the process. The burning of untreated cellulose has been studied thoroughly (3, 20) and it has been established that the complete burning takes place in two stages: First, with a source of ignition, which may be either an open flame or a hot surface above 300 C., thermal decomposition begins, and the cellulose decomposes heterogeneously into gaseous, liquid, tarry, and solid products. Combustion of the flammable gases takes place and the liquids and tars volatilize in part to give more volatile fractions which burn and in part to give a carbonized residue which does not burn readily. The process continues in this manner until only carbonaceous matter is left. Then the second, or glowing, stage begins. In this stage the residual carbonaceous matter oxidizes and glows and continues to glow until the organic matter is consumed, leaving only a fluffy ash. This is shown schematically as follows:

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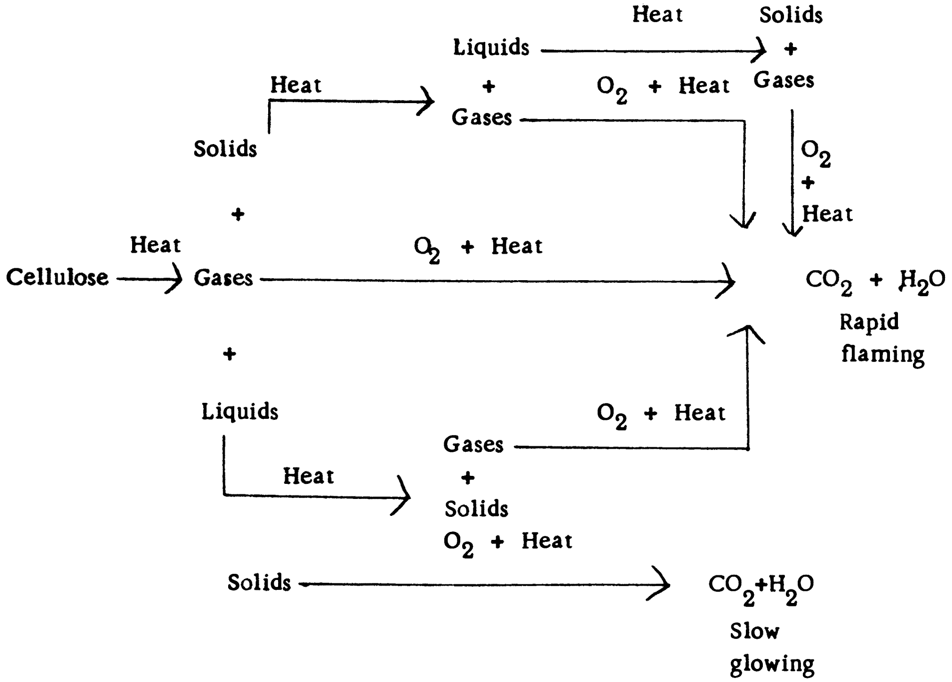

While it is difficult, if not impossible, to duplicate experimentally the conditions of burning in air and to collect intermediate reaction products, it has been possible to change the conditions in such a way as to retard the process to the point where some intermediate products may be isolated (3, 20). Studies on the composition (13) of the products from the destructive distillation of cellulose have shown that the gaseous and liquid portions formed in the first stage of burning are comprised of such low molecular weight volatile compounds as acetic acid, methyl ethyl ketone, formaldehyde, and methane, and that the tars give rise to aliphatic, aromatic, and heterocyclic compounds.

Although cotton textiles and wood burn in a similar manner, the cotton fibers catch fire and burn more readily than wood, once the ignition temperature is reached, because the fibers are sufficiently exposed to the air to make rapid combustion possible. However, this is somewhat offset by the presence in woods of lignin and other aromatic organic compounds which, under the influence of heat, can give rise to highly flammable gases.

From consideration of the combustion of untreated cotton and wood, it is evident that, fundamentally, the same type of reaction takes place and that the solution of the problem of flameproofing lies in the direction of reduction of the flammable vapors and a corresponding increase in the carbonaceous residue or coating on the surface, thus preventing continued burning. In the flameproofing of wood, the rapid formation of a carbonaceous residue upon the surface of the wood is particularly important. A paint capable of producing this effect by chemical mechanism, such as outlined below, should be a step in the right direction.

Some Flameproofing Agents for Cellulose

Perhaps the first noteworthy recorded attempt to flameproof cellulose was that of

Wilde (25) in 1735 in England, whose patent covering a flameproofing mixture composed of alum, ferrous sulfate, and borax gave impetus to later efforts. Gay-Lussac (8) in France in 1821 studied the application of many different salts for the flameproofing of linen and jute fabrics and found that ammonium phosphate, ammonium chloride, and borax mixtures could be used. In 1638 Nikolas Sabbattini (25) in Italy suggested obtaining a flameproof paint by mixing the pigments used with clay or gypsum. In 1859 Versmann and Oppenheim (29) in England reported that out of about 40 compounds studied, only ammonium phosphate, sodium ammonium phosphate, ammonium sulfate, sodium tungstate, and a mixture of ammonium phosphate and ammonium chloride were effective. Later Kling and Florentine (16), in France, showed that mixtures of borax and boric acid were effective. Such mixtures are still in use today. An extensive review of soluble salts used for flameproofing has been made by Ramsbottom (23).

The first successful launder-resistant flameproof finish for cloth was probably that suggested by Perkin (22) in 1912. The active principle here was stannic oxide precipitated within the fiber. Although cloth so treated was flameproof in that it did not burst into flame, it was consumed by glowing, which was greatly aided by the presence of the stannic oxide.

Not until attention was given, about 1930, to the use of halogenated organic compounds in conjunction with metallic salts or oxides were truly durable flameproof finishes obtained. Examples of this type are the use of a mixture of chlorinated paraffins and antimony oxide fixed on the fabric with resinous binders (4, 5, 18, 28).

Although the material so treated is generally stiff and has an unpleasant, waxy feel, this type of treatment was of great value in World War II, particularly for tarpaulins and tentage.

In the late 1930's interest developed in treatments involving reaction of the flameproofer with the cellulose molecule. An example of this type is the reaction of cellulose with urea phosphate to yield a cellulose phosphate (7, 20). Although only about 1 to 1.5% phosphorus is necessary to impart flameproofness, the drastic reaction causes degradation of the fiber with resultant brittleness and loss of tear strength and wearability. A more recent and entirely different type of treatment involves the apparent reaction of mixed titanium and antimony oxides with the cellulose (10). With a pickup of about 15% of the combined oxides, the cotton is flameproof and only a small amount of degradation accompanies the treatment. Although durable to ordinary home laundering, the metallic oxides are removed by the acid sours used in commercial laundering, such as the sodium acid fluoride-sodium silicofluoride sour employed in the standard Army mobile laundering (26).

Very recently, attention has been given to producing a durable flameproof finish on cotton fabrics through the use of organic compounds which are held on the fibers by polymorization and not through reaction with the cellulose molecule. Many advantages are claimed for this type of treatment. Walter (30), in recent patents, describes unsaturated alkyl phosphate esters containing bromine, a process which has been further described in a recent news article (2). The similarity between these textile-treating materials and flameproof paint is striking. The material does not penetrate the individual fibers, and therefore coats the surface as a paint would. Furthermore, being unsaturated, the material further polymerizes to give an impervious paintlike coating. These materials, before final polymerization, are soluble in organic solvents and may offer some possibilities as ingredients of paints. Finally, the cured insoluble

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material might be finely ground to be added to the pigments to produce flameproofing paint.

Thermal Decomposition of Treated Cellulose

The theories so far proposed for the flameproofing of cellulosic materials have been reviewed by Coppick (20). They may be broadly classified under four headings: coating theories, gas theories, thermal theories, and chemical theories.

Coating Theories. Gay-Lussac (8) had suggested that flameproofing was due to the coating of the fiber with a layer of fusible material which melted and excluded the air necessary for burning to take place. The basis for his belief was the efficiency of some easily fusible salts as flame retardants. This theory is still held by some, as in the report of Ramsbottom and Snead (24), and is said to explain the superior behavior of borax-boric acid mixtures over either separately.

Some of the salts used as coating materials, particularly carbonates, borates, and ammonium salts, in the course of melting produce a foam on the fiber through the liberation of such gases as carbon dioxide, water vapor, ammonia, and sulfur dioxide. These gases, being incombustible, retard burning by a process similar to that proposed in the gas theory as discussed below.

Gas Theory. This hypothesis presumes that if the flameproofer decomposes at burning temperatures to give gases which do not burn, these vapors will dilute the flammable gases produced by decomposition of the cellulose to a concentration below the flaming point. Here again the flameproofer must decompose during burning to produce the various nonflammable vapors to such an extent that its presence makes it impossible for gases to flame. This theory has been used to explain the action of sodium or ammonium carbonate, ammonium halides, phosphates, sulfates and sulfamates as well as the chlorides of zinc, magnesium, and calcium.

The gas theory is obviously not capable of general application, since many excellent flameproofers -- for example, titanium-antimony oxide mixtures -- do not evolve gases on heating. The theory has been criticized as untenable (20), based on the amounts of gas produced. Nevertheless, the gases produced are worthy of careful study as contributing in a subsidiary manner to the flameproofing of cellulose.

In considering the application of the gas theory, it is necessary to discuss the "limits of flammability" of the flammable gases -- that is, the concentrations beyond which the gas is either too diluted or too concentrated to burn, as well as the effect of a nonflammable diluent on these limits. The flammable limits of some of the gases produced burning the thermal decomposition of cellulose are shown in Table I (6).

Table I. Effect of Diluents on Flammable Limits of Some Gases

Gas	Limits in Air, % by Volume	Minimum % of Diluent Required to Make Mixture Nonflammable in All Proportions			
		H_2O vapor	CO_2	CH_3Br	CCl_4
Carbon monoxide	12.5 - 77.5	54	52	6.2	2.0
Methane	5.3 - 16.0	29	24	4.7	12.5
Ethane	3.0 - 12.5	--	33	---	---
Ethylene	3.1 - 32.0	--	40	11.7	---
Benzene	1.4 - 7.1	35	31	7.8	---
Acetaldehyde	4.1 - 55.0	--	79	---	---
Acetone	3.0 - 11.0	--	--	---	---

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In their treatise on the subject of limits of flammability, Coward and Jones (6) state: "A flammable mixture (of gases) may be rendered nonflammable by (a) a suitable increase in the amount of either constituent, (b) the addition of a suitable amount of chemically inert substance, and (c) the addition of a flammable substance in sufficient amount to exceed the higher limit of the resultant mixture."

This gas theory then demands the fulfillment of requirement (b) of Coward and Jones. From Table I it can be seen that to prevent the burning of the gases from cellulose by dilution with carbon dioxide would require a prohibitive amount of sodium carbonate. The relatively small amounts of methyl bromide and carbon tetrachloride required would indicate that a flameproofing agent liberating these would be of great value, but no such substance is known.

However, the increasing use of organic polymers as flameproofers or supporters of flameproofers leads to further consideration of the gas theory. A specific case is an organic polymer containing an efficient flameproofing group, such as a phosphate. When the skeleton of this polymer consists only of carbon and hydrogen atoms, the cellulose cannot be flameproofed. Chlorination of the polymer depresses only slightly the flaming tendency of cotton cloth. If, however, bromine is substituted for the chlorine, the polymer becomes an excellent flameproofer. In all three cases the amount and nature of the chars resulting from burning a treated cloth sample are similar and contain no halogen. It must be concluded that all three polymers "flameproof" the cellulose, but the first two evolve flammable gases which support the flame beyond the source of ignition, while the third emits noncombustible gases.

The extent of reduction of flammable limits by diluting gases is dependent on the flammable limits of the diluent (6). With this in mind the flammable limits of a number of halogenated hydrocarbons should be considered. The limits given in Table II were determined by Coward and Jones (6) in a standard apparatus. It can be seen that the increase in halogen content in an organic molecule narrows the flammable limits. The substitution of bromine for chlorine brings about a profound change in these limits. This effect is confirmed by the experimental evidence mentioned above.

Table II. Flammable Limits of Some Halogenated Hydrocarbons

Gas	Limits in Air, % by Volume	Gas	Limits in Air, % by Volume
Methyl chloride	10.7 - 17.4	Allyl bromide	4.4 - 7.3
Methyl bromide	Noncombustible	Ethylene chloride	6.2 - 16
Ethyl chloride	3.8 - 15.4	Methylene chloride	Noncombustible
Ethyl bromide	Noncombustible	Chloroform	Noncombustible
Allyl chloride	3.3 - 11.1	Carbon tetrachloride	Noncombustible

Thus the conclusion is that the gas theory of flameproofing has little application to the burning of cellulose, but may be of great importance in preventing flaming of the flameproofing agent. If this agent is so constituted that its thermal decomposition produces a mixture of noncombustible gases, it then fulfills the requirement that an effective flameproofing agent must be nonflammable.

Thermal Theories. Two thermal mechanisms have been proposed by which flaming of cellulose might be retarded. In one of these it is suggested that the caloric input from a source is dissipated by an endothermic change in the retardant. Thus, in fusion and sublimation of the flameproofer, enough energy would be absorbed to prevent propagation of the flame. This mechanism would seem to apply only to those compounds capable of fusing or subliming and could not have universal application, as it would not apply to the majority of known flameproofers.

The second mechanism suggests that the heat supplied from the source is conducted away from the fibers so rapidly that the fabric never reaches combustion temperature. Consideration of the small amount of flameproofing agents required in some cases makes this mechanism obviously inadequate for most flameproofers.

Chemical Theories. Most of the efficient flameproofing materials tend to degrade cellulose, particularly under the influence of heat. Many of the strong acids, bases, metal oxides, and the usual oxidants degrade cellulose and also confer some degree of flameproofness to the cellulose. It is postulated that this is due to a catalytic action of the flameproofer upon the cellulose to promote a dehydration reaction. Leatherman (19) and his coworkers and others (3) have proposed that flameproofing is a rapid dehydration caused by such well-known dehydrating agents as sulfuric and phosphoric acids produced during the burning. In these cases the normal combustion reaction of untreated cellulose to produce carbon dioxide and water is changed to one that produces mainly carbon and water. However, no explanation of the mechanism has been offered.

It has been suggested that a majority of the known flameproofers are strong hydrogen-bonding agents and this has led to the idea that when the bridging medium of water between cellulose chains is lost at high temperatures, the linkage may be maintained by the strong hydrogen-bonding activity of the flameproofer, thus stabilizing the volatile, flammable fragments to reduce their volatility and so reduce their combustibility.

While this idea seems to have some validity, it must be rejected on the following grounds. The strength of hydrogen bonds is dependent upon the electronegativity of the atoms involved (9). Even the strongest bonds, such as in the F-H-F bond, have a bond energy of only 9 to 10 kcal. per mole. It is not likely that such bonds could exist at 400° to 500° C. With most flameproofers weaker hydrogen bonds (4 to 6 kcal. per mole) would be formed.

Status of Theories. It appears that the coating, thermal, and gas theories are inadequate to explain the profound differences observed in the combustions of treated and untreated cellulose. Subsidiary beneficial effects may be contributed by tendencies of the flameproofing compound to coat the fiber and to produce nonflammable gases. The production of nonflammable gases particularly may be beneficial with regard to the flameproofing of organic flameproofers. It seems reasonable, however, that only a chemical theory can be applicable to all or nearly all of the flameproofing materials used. The basic ideas in the chemical theory of dehydration are restated and elaborated below in the light of current theories and recent developments in the field of organic chemistry.

Revised Chemical Theory

Organic compounds when subjected to sufficiently high temperatures will decompose, generally into smaller and simpler molecules (14). The course of the reaction as well as the nature of the products can be controlled to some extent. Commercially such processes are carried out every day with many classes of organic compounds, as well as with naturally occurring complex materials such as wood, coal, and crude oil.

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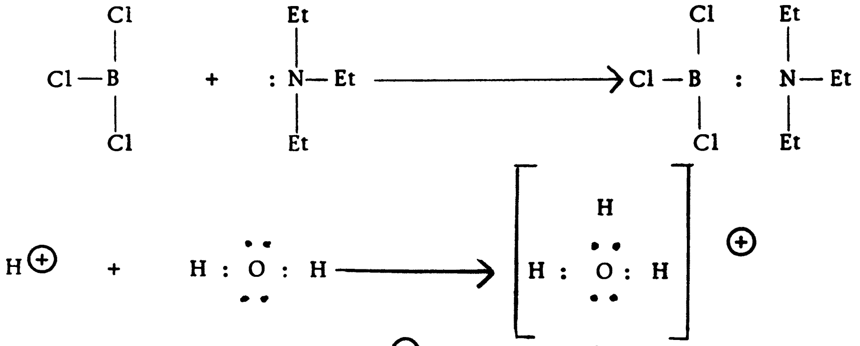
In recent years great strides have been made in the study of reaction mechanisms in organic chemistry, and these studies have been applied to many reactions including pyrolytic, cracking, and dehydration reactions.

It seems that the principles which appear to govern the known organic reactions should apply in the thermal decomposition of cellulose. Cellulose is a polyhydric alcohol; therefore, it is reasonable to believe that as such it should enter into reactions common to this class of compounds. As an alcohol, cellulose is subject to catalytic dehydration and this, it is thought, is the major reaction involved in the flameproofing of cellulose. Broadly, it may be stated that the flameproofing of cellulose is brought about by a dehydration process operating by acid or basic catalysis through a carbonium or carbanion mechanism. Obviously, some dehydration must take place even when pure cellulose burns, as a carbon residue is present at least at some time during the burning. However, the reaction is comparatively slow and dehydration is accompanied by many side reactions, as evidenced by the numerous compounds produced (20).

In experiments at this laboratory, when samples of untreated and treated cloth were submitted to burning or charring on a surface controlled at 400° C., the treated cloth gave larger amounts of carbonaceous residue, indicating a reduction in the amounts of low-molecular-weight flammable gases. This result could fulfill requirement (a) of Coward and Jones (6) by indirectly increasing the percentage of air in the mixture. On the other hand, in these experiments, the flameproofed fabric "burned" or decomposed to equilibrium in one third to one fourth the time required for untreated samples. Thus the gases evolved must have been at least twice as concentrated as those from the untreated samples, even if the residual char accounted for 50% of the cellulose involved (a high estimate). It could be theorized, therefore, that the difference in the rates of burning of treated as compared to untreated cellulose fulfills requirement (a) of Coward and Jones by increasing the concentrations of the gases beyond their flammable limit. When these gases were diluted with air, the mixture could be ignited with almost explosive violence. This indicates that the gases in the vicinity of the cloth were too concentrated to burn.

Lewis has defined acids and bases in a general way as electron acceptors and donors, respectively (21). Accordingly, a compound or element capable of accepting electrons (electron seeking) is termed a Lewis acid. Conversely a compound or element capable of giving (or sharing electrons) is a Lewis base. In other words, those elements which are deficient in electrons -- that is, have unfilled electron shells -- will seek out those elements carrying extra electrons (lone pairs). This is the basis for the Lewis concept of "acid-base interaction." Thus:



$$\mathrm{Cl{-}BCl_2} + \mathrm{:N(Et)_3} \longrightarrow \mathrm{Cl{-}BCl_2 : N(Et)_3}$$

$$\mathrm{H^{\oplus}} + \mathrm{H:\ddot{\underset{..}{O}}:H} \longrightarrow \left[\mathrm{H:\ddot{\underset{..}{O}}:H}\ \text{with H above O}\right]^{\oplus}$$

$$\mathrm{AlCl_3} + \mathrm{COCl_2} \longrightarrow \mathrm{COCl^{\oplus}} + \mathrm{AlCl_4^{\ominus}}$$

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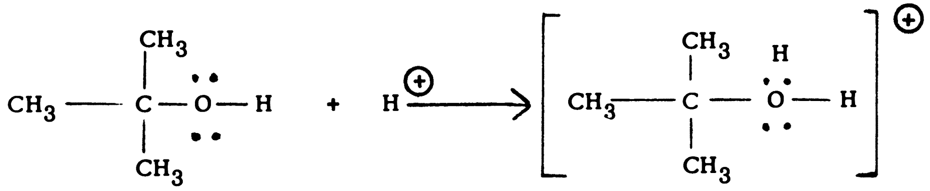
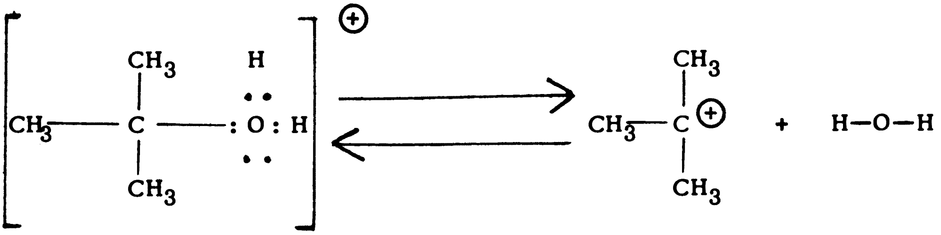
When such processes involve the carbon atoms of organic compounds, carbonium ions or carbanions are formed.

Whenever an acid is brought into the vicinity of a compound which can furnish a pair of electrons, carbonium ion formation is possible.

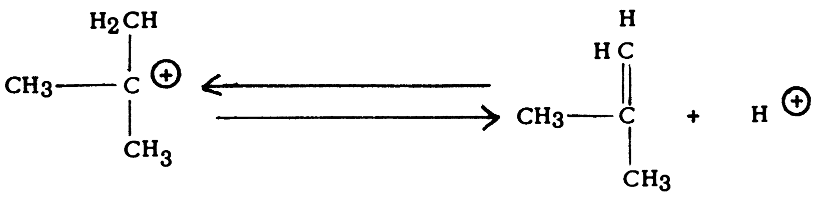
These reactions are the results of the complexing of the electron-poor atoms of the acid with the electron-rich atoms of the base through the lone pairs of the latter. Thus:



The addition of the proton (electron-seeking atom) disturbs the electronic system by drawing the pair of electrons between carbon and oxygen toward the oxygen, making it easy for water to be eliminated. This gives rise to a carbonium ion.



The carbonium ion now being unstable, if not stabilized by resonance or by hyperconjugation, rearranges electronically to split out a proton, which is ready to repeat the process at another electron-rich point.



Thus the dehydration is completed.

The driving force in this type of reaction -- that is, the energy for the reaction -- resides in the affinity of the proton for the oxygen electrons.

In the Lewis sense acids include not only protons but also certain compounds, such as halides and oxides, of elements which have only six electrons in their outermost valence shell.

Thus aluminum chloride aluminum oxide, phosphoric oxides, stannic oxide, etc., are Lewis acids and can catalyze dehydration reactions. Thus:

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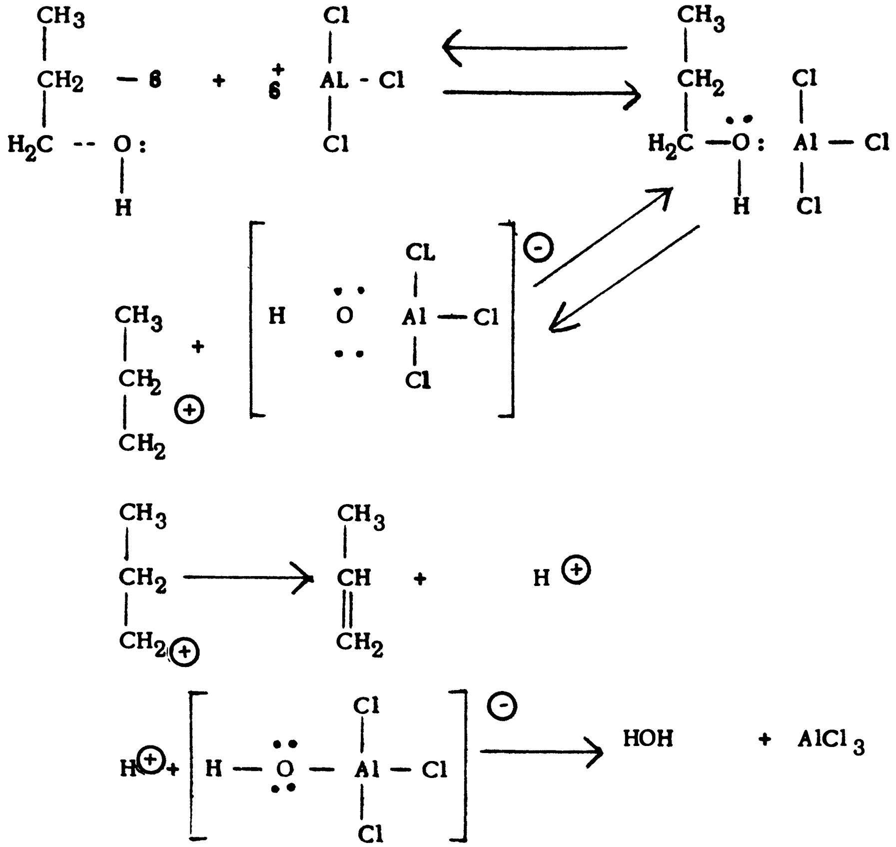
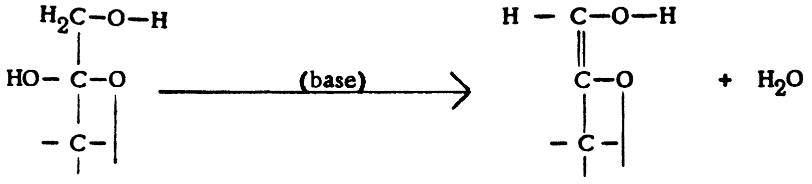


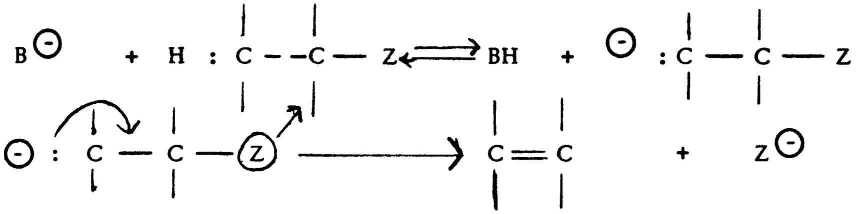
The basic principles illustrated above are applied in explaining the mechanism of many common organic reactions (11). Whitmore, in explaining the 1, 2 shift in dehydration and the rearrangements of glycols (pinacols), applied this mechanism with success (31, 32).

While it is well known that water can be eliminated from organic compounds more easily by acid catalysis than by basic catalysis (12), mechanisms involving the latter should not be overlooked.

The flameproofing of cellulose by bases like sodium hydroxide or calcium hydroxide can be explained on this basis. Examples may be cited where the elimination of water from carbohydrate materials by the action of bases is postulated (17).

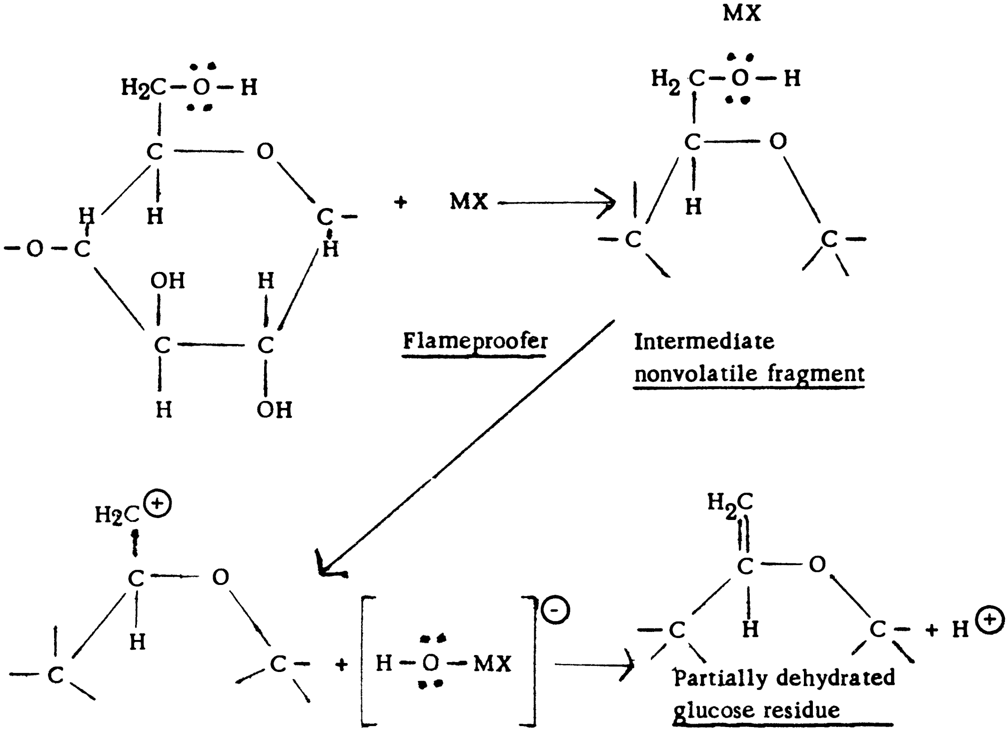


The mechanism of this dehydration is more complex than the corresponding acid-catalyzed dehydration. The proposed mechanism involves the formation of a transitory carbanion usually at a β-carbon atom, with the simultaneous displacement of the ion or mulecule being eliminated (1).

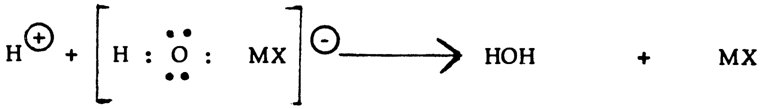


The mechanism of acid-catalyzed dehydration as described above can be applied to the flameproofing of cellulose. But flameproofed cellulose constitutes a heterogeneous solid-solid system. For this reason the amount of catalyst required is far in excess of that generally used in the homogeneous systems cited above.

Considering one of the glucose residues in a cellulose chain, the mechanism can be pictured as follows:



Then:



$$H^{\oplus} + \left[H : \ddot{\underset{\cdot\cdot}{O}} : MX\right]^{\ominus} \longrightarrow HOH + MX$$

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This process can be visualized as continuing until all available hydroxyl groups have been involved, leaving a residue which because of its high carbon content is difficultly combustible.

While the structure of this residue is not known, it is reasonable to expect that it would have a thermal stability much higher than a corresponding hydroxylated compound. For example, polyvinyl alcohol decomposes completely when subjected to 260° C. for 5 hours, while polyethylene is unaffected (14).

The interpretation of this is that the active principle of the flameproofer is an acceptor (Lewis acid) which is either present as such or produced at the flaming temperature. This agent ties up some of the volatile fragments as nonvolatile intermediates, which then enter into known catalytic dehydration reactions to produce a charred residue and water.

An alternative picture of this may be the possibility that the intermediate volatile fragments do not form as such and the cellulose is catalytically dehydrated by the same reaction mechanism as that generally accepted for dehydration of alcohols.

In the past few years much attention has been given to the use of organic compounds as flameproofers. The purpose here is to overcome the difficulties encountered in producing a finish on textile fabrics which can withstand laundering. Such compounds must, according to this theory, be capable of producing at burning temperatures a compound which will be a relatively strong Lewis acid. In choosing such a compound it is important to consider the possibility of Lewis acid formation under the conditions of burning.

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Summary

The working hypothesis used to explain the flameproofing of cellulose can be stated as follows:

1. The flameproofing is brought about by the catalytic dehydration of the cellulose through the reaction of the flameproofing agent with the cellulose via a carbonium mechanism probably identical with that proposed for the dehydration of monohydric alcohols and glycols.
2. The flameproofer may either be present or must be produced from its "precursor" at a temperature close to that of burning cellulose.
3. The flameproofing agent must not be volatile at 300° to 500° C.
4. The agent (or its precursor) must not burn readily by itself.
5. The flameproofer must be a Lewis acid or capable of forming a Lewis acid at the temperature of burning cellulose.

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Effectiveness of Fire-Retardant Paints in Fire Prevention

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Disastrous night club and circus fires have emphasized the fire hazard in highly combustible decorative materials and fabrics used in connection with public assemblage. The use of high-grade fire-resistant paints would materially aid in fire suppression by restricting combustion and retarding the spread of fire, would reduce the annual national fire loss by millions of dollars, and would save hundreds of lives. The field for such paint is unlimited. Some success has been achieved, but many of these paints are water-soluble, and others do not have the valuable features of high-quality paints. One stumbling block in the development of fire-retardant paints is the lack of standards by which their effectiveness can be tested, evaluated, and classified.

For centuries man has attempted to devise an effective process by which combustible materials could be rendered noncombustible or at least fire-resistant, but until about 10 years ago progress in this field was very limited and the effectiveness of the processes was questionable. Back in the days of the Roman Empire, efforts were made to reduce the fire hazard in props, curtains, and decorative-effect materials used in stage and theatrical plays by impregnating the fabrics with fine clay, and at about the same time clay, gypsum, and other types of plaster were used to coat wood, in an effort to make it resistant to fire. Since that time there has been steady progress in the field of fire-resistive and fire-retardant treatment processes, but it has been slow and the field of activity has been rather limited.

The Boston night club fire, the Natchez, Miss., night club fire, and the Ringling Brothers Circus fire, which together resulted in the loss of 867 lives and serious injury to hundreds of other persons, drew particular attention to the extreme fire hazard of highly combustible fiber and plastic materials. Public sentiment was aroused, and legislators and public safety officials decided that something must be done to eliminate this dangerous threat to human life. Laws were enacted; fire-resistant standards were established, and the public demand for an effective fire-retardant treatment for fabrics and other decorative materials, that would not discolor, deteriorate, stiffen, or otherwise affect the quality of the material, has resulted in the development of some good treatment processes that practically eliminate the fire hazard in these

In FIRE RETARDANT PAINTS;
Advances in Chemistry; American Chemical Society: Washington, DC, 1954.

materials. Many of the processes prolong the life of the fabric by making it resistant to the action of mildew, fungi, and the acids that are found in smoggy atmospheres. Until we suffered such severe losses in our Navy ships during and immediately following Pearl Harbor, no one would believe that the multiple coats of paint on the steel in our ships would furnish sufficient fuel for fire to destroy them, but again, experience was the teacher, and many of our fine fighting ships went to the bottom of the sea because of fire that was fed by multiple coats of combustible paint. Again, manufacturing chemists and industry have met the challenge by developing paints which will not in themselves contribute fuel for fire.

Structural engineers and fire insurance underwriters recognized many years ago the need for fire-resistive protection for steel beams, columns, and other structural framing of buildings, to protect them from the heat of a fire in the building that might cause the steel to lose its strength and collapse. Numerous methods have been developed and various types of material used to protect steel in buildings against the heat of fire. Standard tests and fire-resistive classifications have been developed to rate these protective materials and assemblies, and engineers, architects, and building officials recognize these fire-resistive classifications as essential in planning and constructing buildings.

With the advent of dry wall finishes that replace the wet plaster wall finish, additional fire safety problems were presented. The lime, cement, and gypsum plaster previously used provided an incombustible surface and afforded some fire protection to the wood or steel framing of the building; but many of the dry wall finishes are themselves combustible, offer little if any resistance to fire, and tend to increase the intensity of a fire by contributing additional fuel.

Testing Procedures

The development of fire-retardant paints and treatment processes has done much to reduce the fire hazards of combustible interior finishes, and recognized testing procedures have been adopted to evaluate the degree of flame-spread resistance in any dry wall finish. The "tunnel test" developed by the Underwriters' Laboratories, Inc., produces a flame-spread rating using cement asbestos board as 0 flame spread and red oak as 100. By this method the flame-spread rating of a material can be accurately measured and evaluated. The National Bureau of Standards has also adopted a testing procedure by which the flame-spread characteristics of acoustical tile and cellulose fiber wallboard can be determined. This test (8) establishes four classes of fire resistance: incombustible, fire-retardant, slow-burning, and combustible. There has been no correlation of test results between the two test procedures.

The experience gained in developing these tests will be of extreme value in developing a standard testing procedure for evaluating and classifying fire-retardant paints, impregnation treatments, or a combination of both. Until a standard test and evaluation procedure is established, full credit cannot be given to fire-resistive paints and treatment processes by fire insurance underwriters and building codes.

Definitions

The terms "incombustible," "fire-resistive," "fire-retardant," and "slow-burning" have been used rather promiscuously.

"Incombustible" means a product made from an incombustible material that

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will not contribute fuel for fire, such as asbestos, glass, concrete, gypsum, and similar materials.

"Fire-resistive" is a relative term used to designate the resistance of a material or an assembly to intense heat and fire. Incombustible materials are not necessarily fire-resistive, as they may, when subjected to heat and fire, decompose, be distorted, or lose their strength.

"Fire-retardant" means a product that provides a high degree of resistance to ignition or decomposition when exposed to fire for a substantial period of time.

"Slow-burning" means a product which, even though it is combustible, will provide a measurable resistance to both ignition and the rapid spread of fire over its surface but which has a lesser degree of resistance than fire-retardan' materials.

"Fireproof' paint" is a paint which in itself does not (after application) contain any material or substance that will contribute fuel to a fire but which does not necessarily impart any fire protection to the material to which it is applied.

"Fire-retardant paint" is a surface coating or impregnation that will impart a substantial degree of protection from flame or fire to the material to which it is applied.

Qualities Required

It now seems probable that an effective fire-retardant paint can be developed which will combine the qualities of weather and fire protection for wood. Several compounds now available for the treatment of fabric render it resistant to flaming to the degree that flame and afterglow will not spread beyond the original area of flame contact. The same result can also be obtained by applying certain chemicals to wood. Most fire-retardant chemicals are not true paints, in that they fall short of providing the required protection against the elements or they are impregnations rather than surface applications, but substantial progress is being made in developing fire-retardant paints with most of the qualities of a good paint.

Regardless of its ability to inhibit or prevent flaming, a true paint must provide effective protection against the elements. Conditions will be more severe in exterior service but must also be considered in interior applications, especially if an interior service requires periodic washing.

Some factors included in high quality paint are coverage, viscosity, brush marks, finish, gloss, bonding ability, hardness, color integrity, brightness, washability, blistering, checking, eroding, and resistance to the elements.

Paint compounds which do not provide these features to a satisfactory degree are either low-grade paints or merely coatings. A number of coatings have been offered on the market to provide protection against fire. Some of these are effective fire-retardant compounds, but the majority will not withstand weathering and thus have limited interior use only. To overcome this deficiency, manufacturers recommend a second or protective coat of moisture-resistant material. As an alternative means of achieving this same result, fire-retardant chemicals can be sprayed or brushed on wood and protected by a normal paint after the chemical dries.

The majority of these chemicals are water-soluble. Among the chemicals which may be used in this manner are ammonium phosphate, ammonium sulfate, ammonium borate, ammonium chloride, magnesium chloride, and boric acid. Some of these chemicals have certain disadvantages, such as increasing the hygroscopicity of the wood, since they attract moisture, corroding metal, dulling cutting tool edges, or being fugitive owing to their tendency to leach out. Monoammonium phosphate has the least tendency to absorb moisture and at the same time has the least corrosive effect and is the most stable chemically.

Fire-retardant paints for wood have been developed using urea-formaldehyde resins and ammonium phosphate. Heat causes this compound to intumesce and develop an insulating layer for the surface upon which it is applied. Oil-based fire-retardant paints usually contain organic materials such as resins, paraffins, or chlorinated rubbers combined with inorganic vehicles, or they may be compounded of inorganics such as ammonium compounds.

Some confusion has existed as between paints which are in themselves noncombustible and those which have the ability to prevent wood from entering into combustion. The Navy uses a noncombustible paint for metal to prevent flash fires following explosions. This paint was designed to protect metal against the elements and not contribute fuel to fire situations, as would ordinary oil paint, enamel, and varnish.

A fire-retardant paint for wood must be capable of withstanding temperatures of 2200° to 2422° F. in structural fires and prevent the wood from flaming. It cannot reasonably be expected that this painted wood will be undamaged where the temperature is sufficiently elevated and the exposure is of critical duration. It is enough that the wood cells be protected for a reasonable period and that they be prevented from contributing fuel to the initial flame or fire.

Wood ordinarily follows the following course when heated: It gives off considerable moisture until 212° F. is reached, when it undergoes further chemical changes with disintegration beginning. At about 400° F., wood discolors, and as the temperature continues to rise, flammable gases such as carbon monoxide, methane, terpenes, esters, and tars are distilled and given off. If sufficient air is available to combine with these gases when the ignition temperature is reached (about 575° to 600° F. for woods ordinarily used in building construction), flaming occurs. This constitutes active combustion and liberates additional heat, gas, and smoke.

Some of the same mechanics of fire-retardant treatment, so successful in treating (impregnating) fabrics, may be used with wood. However, there is this to be taken into account: Unlike fabric, wood presents a much greater mass at any given point where it may be exposed to an igniting flame. Thus, any effective fire-retardant treatment with a paint must successfully cope with a greater volume of flammable gases and higher temperatures of longer duration. This is the reason why the chemicals that are used to permit fabric to decompose in the presence of heat before the ignition temperature is reached, are only partially effective in preventing flaming of wood. Applied as a coating rather than as an impregnation, the chemical potentiality is quickly exhausted and, after its value is lost, additional gases enter into flaming combustion. The same limitations apply to other theories used to explain flameproofing functions -- for example, where oxygen is excluded by chemicals which coat individual fabric fibers, or where flammable fabric gases are diluted by nonflammable gases evolved from the flameproofing chemical, such as carbon dioxide, hydrogen chloride, ammonia, or sulfur dioxide, or where the chemical may develop the ability to absorb heat when exposed to fire (as endothermic reaction) and heat is conducted away from the ignition area so rapidly that combustion does not occur.

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Certain chemicals intumesce and form a heat-insulating mat of spongy tough cells. Experiments with various fire-retardant coatings and paints indicate this to be the most effective type of protection so far developed. If the "paint" qualities can be improved to meet requirements for high-quality exterior paint without sacrificing any of the fire-retardant ability, there is no question of a wide market for the product.

Application of Paint

When considering fire-retardant paint, account must be taken of its application. No fire-retardant compound, whether for wood or fabric, is better than the applicator's integrity. Unless the wood is in proper condition for painting, poor bonding can result, as in painting wet or even damp exteriors. Then, too, rate of application is critically important to ensure adequate chemical deposit (called "add-on" when treating fabrics). In some instances prescribed amounts of fire-retardant coatings have been cut by applicators, so that instead of using the full amount they "stretched" the chemical and had some left over.

Tests of finished work are generally impractical, for unlike drapes and curtains from which small test samples can be cut, a wooden wall, ceiling, or other structure will seldom lend itself to sampling.

For these reasons, any official approval of fire-retardant paint will specify coverage requirements as to gallon-per-square-foot ratio. And, as in the case of flame-retardant chemical application to fabrics, corresponding regulation will be necessary for those who apply fire-retardant paint in occupancies governed by statute and where credit is given by building codes or insurance underwriters.

With fire losses increasing as they have been for the past decade, there is urgent need for a true paint which will render homes and other structures resistant to fire.

When one considers the millions of non-fire-resistive substandard buildings in use today, it appears obvious that the field of opportuniyt is unlimited for marketing a good, reliable fire-retardant paint. A paint that would retard the ignition and spread of fire to a measurable degree would render many of these substandard buildings reasonably safe, and a paint or mastic that would increase the fire-resistance of an ordinary wood-studded, wood lath and plaster partition to 1-hour resistance, would find an immediate demand.

Conclusions

After considering the many factors relating to the development of high-quality fire-retardant paint and treatment processes and the effect such development would have upon the annual loss of life and property by fire, the writer has arrived at the following conclusions.

The loss of 867 lives and the injury to hundreds of other persons in the Boston night club fire, the Natchez, Miss., night club fire, and the Ringling Brothers Circus fire would not have occurred if the highly combustible materials used had been treated with proper fire-retardant treatment processes.

There now exists a public demand for a high-quality fire-resistive paint or treatment process which combines the essential qualifications of good grade paint with the ability to prevent ignition of combustible surfaces it protects.

There now exists a definite need for standards and testing procedures whereby the qualities of fire-resistive paint may be tested, evaluated, and classified.

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If an effective evaluation and classification procedure was established, acceptance and recognition by fire insurance underwriters, building safety officials, architects, and the general public would be assured.

The use of high-grade fire-resistive paints would materially aid in fire suppression by restricting combustion, thus retarding the spread of fire. This would enable firemen to concentrate their efforts on extinguishing the original fire and reduce the problem of controlling exposure fires, especially where wood frame construction and wood shingle roofs were used.

Eventually the increased acceptance and use of first quality fire-resistive paints and treatment processes could reduce our annual national fire loss by millions of dollars and save hundreds of lives each year.

Commercial and industrial possibilities for a high-grade fire-resistive paint are unlimited. Such a paint would find a definite and desirable market in every type of occupancy, from the modest home through the largest factories and warehouses. It could become a major factor in developing our national and civil defense programs. Its greatest asset would be the fact that the safety factor in existing non-fire-resistive structures could be increased measurably.

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Fire-Retardant Coatings on Acoustical Surfaces and Test Methods for Their Evaluation

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Large quantities of fibrous materials are installed annually in this country in the acoustical treatment of the interiors of public and private buildings. Surface coating of such products offers a practical method of imparting improved flame resistance. A number of types of such coatings are discussed, as well as some of the test methods used to determine the degree of flame resistance.

With the increase in knowledge in the field of acoustics and the awareness of the need for the control of sound, various acoustical products have appeared for employment by the public. This paper covers architectural acoustical materials only. The architectural acoustical products now on the market can be divided into two general classes, the inorganic and the organic type of product.

The inorganic classification includes the metal pan type, consisting of a perforated metal pan with a sound-absorptive mineral wool pad; the perforated cement-asbestos type, consiting of a perforated cement-asbestos sheet with a sound-absorptive mineral wool pad; acoustical plasters; and tile prepared from mixtures of inorganic or mineralized fibers with or without asbestos and other fillers. In general, acoustical products in this classification possess good fire and flame resistance, but are relatively expensive and difficult to manufacture and apply.

The organic classification includes acoustical tile board prepared from vegetable or wood fiber. These acoustical products are produced in greater volume than the inorganic type, are easier to manufacture in large quantities, are easier to apply, are cheaper, but are not as fire- or flame-resistant as the inorganic type, although they are not highly combustible. If the organic-type acoustical product could be rendered more fire- or flame-resistant, (and the potential is present), this would be a valuable service to the public and the building industry.

Considerable work has been done to improve the flame resistance of organic fiber acoustical tile by both integral and surface treatments. Results by both methods have been very promising. However, surface treatments have been much easier to apply, are less expensive, and do not require as much special equipment as does the integral treatment. The fire-retardant surface treatments have definitely increased the fire and flame resistance of the organic-type board, particularly by markedly retarding spread of flame. For complete insurance against fire, particularly behind those acoustical treatments which are not fastened directly to the ceiling, integral treatments are also required.

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Types of Integral Treatments

Many simple and complex treatments have been devised through the years to increase the fire and flame resistance of vegetable and wood fiber acoustical title by impregnating the board with the treatment or forming the board in the presence of the treatment.

These treatments may be divided into three main classifications -- treatment of the fiber with soluble salts, treatment of the fiber by processes wherein various water-insoluble chemical complexes are precipitated around the fiber or dispersed throughout the fiber mass, and treatment of the fiber by chemical reaction between the cellulose and/or other fiber components by suitable reactants. The last two classifications are the most permanent of the treatments.

Treatments of fiber with soluble salts would include:

Ammonium salts, which liberate free ammonia or sublime.

Boric acid or borax, which liberates free moisture and tends to fuse around the fiber.

Carbonates or bicarbonates, which liberate carbon dioxide and possibly moisture.

Hydrated salts, which liberate moisture.

Treatments with insoluble complexes would include:

The metallic oxide-chlorinated body type (7), which reduces flammability by the rapid liberation of hydrogen chloride.

The precipitation of insoluble borates, oxides, carbonates, etc., upon the fiber, which reduces flammability by the liberation of moisture, smothering gases, etc.

The dispersion of water-insoluble phosphorylamides throughout the fiber, which is claimed to increase the fire resistance by liberating smothering gases and by the formation of a glasslike material around the fiber (10).

Treatments of fiber by chemical reaction would include:

The reaction of polybasic acids, such as phosphoric, with cellulose in the presence of an organic base such as urea (5, 8). The urea acts as a buffer in the formation of the cellulose-phosphate reaction products, reducing the weakening of the fiber. The flame resistance of this type of treatment is claimed to result from the inorganic or acid anhydride itself.

The reaction of phosphoryl chloride with cellulose in the presence of a nonaqueous solvent such as carbon tetrachloride or pyridine and subsequent reaction with ammonia to form a cellulose phosphoramide (9).

In general, all the above treatments affect the decomposition products, by heat, of the fibrous material. After treatment, the solid carbonaceous residue from combustion of fiber tends to increase and the quantity of tarry by-products to be reduced.

Types of Surface Treatments

Many chemicals and chemical complexes have been evaluated in various coating formulations, with detailed study of pigmentation. The quality of these formulations varies from poor to excellent, depending on materials employed. In general, these formulations can be divided into two classifications, aqueous type and nonaqueous type, each exhibiting either nonintumescing or intumescing characteristics.

By an intumescent-type coating is meant a coating that will swell, char, bubble, and produce a firm, charred ash when a flame is impinged upon it, immediately shielding the fiber board from the flame.

Under the aqueous-type classification, the nonintumescent types would include:

Borax or borax-boric acid coatings containing a carbohydrate binder, with selected pigments. The borax or borax-boric acid combination will liberate the usual moisture when heated, with the binder and pigment furnishing some insulation. This type of coating has fair flame resistance.

Coatings containing ammonium salts of polyhydric acid -- e.g., monoammonium phosphate -- with pigments, sodium alginate, and a carbohydrate binder. The effectiveness of these coatings depends on the liberation of a flame-smothering gas and the insulating effect of pigments and binder. This type of coatings has fair flame resistance.

A highly pigmented coating containing mica, asbestos, etc., with a carbohydrate binder. This type of coating depends on insulation effect only and possesses fair flame resistance at high coverages.

Coatings combining sodium silicate with asbestos and various pigments. This type of coating will liberate moisture and produce insulation effect from the asbestos and pigment. It gives good initial flame resistance, but the silicate is changed gradually to sodium carbonate and silica by the atmosphere, which causes this type of coating to lose flame resistance and film qualities with the passage of time.

Intumescent types of aqueous coatings have been produced containing an amine aldehyde, the ammonium salt or salts of polyhydric acid, selected pigment, starch, and thickener. When formulated properly, this type of coating possesses excellent fire- and flame-resistant properties, but would be rated as a relatively poor paint film. A coating of this type is manufactured by the Albi Chemical Co. (6) under the name of Albi-R and has had extensive acceptance.

In the nonaqueous classification, nonintumescent types would include:

Borax and borax-boric acid paint with appropriate pigments and linseed oil (13). This type of coating has only fair fire and flame resistance.

Antimony oxide, various pigments, and chlorinated paraffin or rubber, etc., blended to form a coating. This type of coating has only fair fire and flame resistance.

Intumescent types of nonaqueous coatings have been produced containing an amine aldehyde resin, ammonium salt of polyhydric acid, and pigments, with an appropriate binder. This type of coating possesses excellent fire and flame resistance and good paint properties. There are probably other types of intumescent paints, but their exact composition is not available.

All the above formulations have been investigated and evaluated on perforated and unperforated Celotex fiberboard. Results demonstrate that a satisfactorily formulated intumescent water- or oil-base paint is the best type of paint to apply to acoustical fiber board to secure optimum fire or flame resistance. These paints, by their intumescent nature, tend to close the openings in the acoustical fiber board and insulate the basic fiber under the coating.

The nonintumescent-type coating does not produce as successful results, as the heat from the flame easily passes through the thin coating, permitting the basic fiber to char and burn more easily than with the intumescent coating.

Just because a paint itself will not burn, it does not follow that it will produce desirable fire or flame resistance on an acoustical fiber board.

For unperforated board, intumescent paints still produce optimum fire and flame resistance. However, because the painted surface is continuous, the simpler less flame-resistant borax-boric acid pigmented paint produces satisfactory results.

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A successful factory-applied intumescent paint has been developed by the Celotex Corp. for application to acoustic board. In addition, a satisfactory package paint, Due-Tex flame-retardant paint, is available for application over old fiberboard installations, wood, etc. This product bears an Underwriters' Laboratories label.

Surface Finish Characteristics

In addition to possessing the desired fire and flame resistance, the acoustical fiberboard paints and finishes must possess other requirements of an acceptable paint and finish.

The paint or coating must be capable of satisfactory application by the desired method and it must have satisfactory shelf life.

The paint finish after application must possess the following properties.

It must maintain the desired fire and flame resistance with age -- approximately 5 years.

It must be attractive.

It must have good color retention with age -- it must maintain its original color or show only slight color change after approximately 3 years from the date of installation.

It must maintain good film qualities with age -- not crack, craze, chalk, blister, etc.

For highest quality, the finish must be washable -- possess at least 200-cycle washability (4).

It must be mildew-resistant -- not permit the growth of Aspergillus oryzae, Aspergillus niger, and other common organisms when exposed under the normal recommended range of atmospheric conditions.

It must be capable of being repainted -- with the common interior, high-quality oil- and water-base paints and high-quality interior flame-resistant paints.

It has been very difficult to produce intumescent coatings which possess excellent washability. The Celotex finishes mentioned possess a reasonable washability. Active work is now in progress to obtain finishes with even better washability and at a lower cost.

Fire- and flame-resistant paints for acoustical fiberboard are now being satisfactorily applied by spray, brush, and roll.

Flame-Resistance Tests

Many tests have been devised to evaluate the fire and flame resistance of surface-treated acoustical fiberboard. The most widely accepted test, recognized by both the building industry and the building code agencies, is the fire-resistance test specified in federal specification (3). Other tests under consideration, but not universally adopted, are the tunnel test of the Underwriters' Laboratories, Inc. (11), and the Factory Mutual room burn out test (2). A small scale test that is being employed for plant control and quick finish evaluation is the Class F fire test (12).

Basically, all the above tests evaluate the flaming tendency -- e.g., flame type, flame spread, flame duration, etc.

Fire-Resistance Test (3). In this test method the preconditioned specimen, or specimens, to be tested are mounted on an incombustible backing to form a 3 x 3 foot test pannel. This panel is then mounted in a horizontal position, with the specimen panel facing downward, on supporting 2 x 2-1/8 inch steel angles framed to form a clear opening of 30 x 30 inches. The flame from a gas-air pressure burner, mounted 28-3/4 inches below the surface of the panel at the center of the panel, is then directed against the specimen panel face following a specified time-temperature curve. These temperatures are measured with a specified thermocouple, mounted under the test panel. Observations are made periodically during the test.

Based on observations of the behavior of the test specimen and the length of exposure, the material is assigned one of four classifications. If the test is conducted for 40 minutes, following the Columbia curve (3), and no flame issues from the specimen itself, nor does glow extend beyond the area of the test flame, the material is rated as "incombustible." If, during the same exposure, any intermittent flaming issues from the specimen, but is limited to the area covered by the test flame, and such flaming does not last longer than 2 minutes after the test flame is extinguished, the material is classified as "fire-retardant."

For the third classification, known as "slow burning", the exposure is 20 minutes following the standard time-temperature curve (3). No flame from the specimen may reach the angle frame at any point, and all flaming must cease within 5 minutes after the test flame is discontinued. If a material fails to meet these test requirements, it is rated as "combustible." For all classifications, there are restrictions as to the amount of material which may fall from the test panel during the exposure period.

A large number of testers of this type have been built and are being operated in both private industrial and commercial testing laboratories. Several points in the test method need clarification. At least two committees in the American Society for Testing Materials, and the Federal Specifications Board, are working on the problem of revising this test method. Under consideration are such items as a standard pre-conditioning requirement for the samples, the effect of using different gages of thermocouple wire, the effect of using fuels with different B.t.u. values, the interpretation of "sustained flame," and the length of time during which the panel should be observed after the test flame is discontinued.

Underwriters' Laboratories Tunnel Test. In this test the samples are exposed to flame impingement in a special fire test chamber which consists of a duct, rectangular in cross section, with a width of 17 inches and a length of 25 feet. The duct has a removable top, against the lower face of which the test samples are attached. At one end of the chamber the test burners are located, delivering flames vertically upward against the samples. At the other end of the chamber there is a vent pipe and the velocity of air through the chamber is adjusted to 200 feet per minute. This tends to draw the test flame down the tunnel, and under the test condition the test flame extends about 4-1/2 feet beyond the burners. Adjustments are made so that a test sample of Grade A red oak will become involved in flame throughout its entire length in 6 minutes. Following this, a test sample of cement-asbestos board is exposed to the same conditions, and the length of the test flame with this material establishes the zero classification.

Test samples are preconditioned in a specified atmosphere before exposure, and the test flame exposure is continued for 10 minutes unless the sample is completely consumed before that time. Observations of the spread of flame are made at 15-second intervals during the test. If the flame spread reaches only part of the distance between the end of the test flame and the end of the sample, the percentage of the distance traveled establishes the classification. If the flame spread reaches the end of the tunnel, the percentage of the time required against the time for the red oak

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sample establishes the classification. Smoke density and temperature readings of the combustion products are also recorded.

The American Society for Testing Materials (1) has described this test. The Underwriters' Laboratories, Chicago, has test equipment as described above. The Forest Products Laboratory, Madison, Wisc., has built a smaller tunnel, approximately 1 foot wide and 8 feet long. As far as the writers know, this type of tester has not been installed in any private industrial or commercial testing laboratories. This severely restricts the rate of accumulation of test data by this method. In spite of this, classifications by this method are being incorporated in various building codes.

Factory Mutual Room Burn Out Test. This method involves the use of a special test room. The particular one referred to is located at Factory Mutual Laboratories, Norwood, Mass. It is 14 x 20 feet in area and 12 feet high, constructed of spruce studs and roof joists, with a floor of Douglas fir sheathing on spruce runners laid on a concrete floor underneath. The interior surfaces of walls and ceiling are covered with 1/4 inch soft asbestos board. Thermocouples are located so as to record temperatures in the corners and center of the room at both the ceiling and breathing levels.

Test samples are attached to the ceiling, or walls, or both. A fuel pan is placed in one corner of the room, and a specified quantity of wood brands and ethyl alcohol is placed in it and ignited. The test continues until the fire extinguishes itself. Photographs are taken at 1-minute intervals, as well as before and after the test.

This is rather bulky test setup, but it seems to be a realistic approach to the problem of observing what happens to exposed materials when a fire starts somewhere in the room. The extent of spread of flame beyond the test flame area is observed, and the thermocouple readings indicate the potential life hazard from breathing in the atmosphere in the test room. Perhaps the dimensions of the test room could be reduced and thus bring about the installation of this type of equipment at other laboratories.

Class F Fire Test of Commercial Standards (12). The test specimen, preconditioned at a temperature of 70° to 75° F. and a relative humidity of 48 to 52%, is supported on the specified test rack at the specified 45° angle with the horizontal, with the board face downward, in a draft-free location.

A flat-bottomed sheet iron cup of 5/8 inch internal diameter, 9/32 inch depth, and 1/32 inch thickness is placed on a support composed of material of low thermal conductivity. It is supported so that the center of its base is 1 inch vertically below a point on the lower surface of the test specimen, 3 inches from its lower horizontal edge, and midway between the inclined edges.

One cubic centimeter of absolute ethyl alcohol is placed in the cup from a suitable pipett or other means, and ignited with the test specimen in place with a suitable practical flame, which is removed as soon as the alcohol is lighted. One minute after the fuel has been exhausted, any flame and glow on the specimen are extinguished and reported and the area of char is measured.

In accordance with the test specifications, the area of char is that portion which shows definite decomposition or shrinkage, and is black to dark brown in color. However, the extent of the charred area is not always clearly distinguishable and this leads to variable reporting of the same charred area. The Class F fire test has been very useful in mill control work, permitting quick evaluation of mill surface coatings.

Conclusions

Considerable time and effort have been employed to improve the fire and flame resistance of the organic-type acoustical board, with both wood and vegetable fibers, employing both the integral and surface coating methods. Thus far, considerable progress has been made in developing and introducing into production excellent flame-retardant coating surface treatments, which have improved the fire and flame resistance of the organic-type board. The most promising has been the intumescent type, in both the aqueous and nonaqueous classifications. Some progress has been made with the integral treatments, but the economics, process difficulties, and deleterious effect of those treatments on the fibers have not been completely overcome.

Additional work is now in progress to improve further the qualities of these fire-retardant coatings, particularly in finish washability and in reducing the coating cost. Several promising coatings are now in the laboratory stage. Additional laboratory work is also in progress with integral treatments.

Several tests have been developed to evaluate fire-retardant coatings on acoustical fiberboard surfaces. These tests are being reviewed and modified where there is necessity for standardization of the test.

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Practical Aspects of the Formulation of Fire-Retardant Paints

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An effective fire-retardant paint for use on burnable substrate must have the following properties: The dried film should be incombustible. It should liberate heavy inert or noncombustible gases, which tend to smother flame. The film should contain materials to give a glasslike flux by low-melting organic compounds which tend to seal the underlying surface from flame. A cellular mat should be formed, which serves to insulate the underlying surface. The paint film should be reasonably insoluble in water, so that interior paints will withstand washings and exterior paints withstand weather conditions. Vehicles and pigments have been selected to give these characteristics and at the same time produce practical protective and decorative coatings for interior and exterior use. Considerable thought was given to the evaluation of various formulations. Federal Specification TT-P-141 was adhered to as far as possible for test methods. The New York Production Club cabinet, with modifications by the Engineer Research and Development Laboratories, was utilized for the fire-retardant evaluations and a leaching test was introduced to determine the water solubility of the films.

Through the past 50 to 75 years, considerable interest has been demonstrated in paints or coatings that might be used as protection against fire.

The methods of approach to the problem vary widely. However, Ware and Westgate (2) cover the fundamentals adequately with four principles: (1) replacement of combustible organic matter in the vehicle by less combustible or incombustible material, (2) liberation of inert or noncombustible gases which tend to smother flames, (3) formation of glazes by low-melting inorganic compounds which flux and tend to seal the underlying surface from flame, and (4) formation of thick cellular mats which serve to insulate the underlying surface.

A fifth function might very well be included, and that is the charring of a cellulosic surface by the action of corrosive acids such as sulfuric or phosphoric, which are released by decomposition of the film. This latter function provides a surface very similar to charcoal, which has the well-known property of glowing without flaming.

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At this point a differentiation should be made between a nonflammable and a fire-retardant film. On the one hand, the coating is designed to be applied on a nonflammable substrate and, in this case, the film itself should be as near nonflammable as possible. On the other hand, a fire-retardant film is designed to retard the spread of flame through a flammable substrate. Most commercial paints are fire-retardant to a degree; an unpainted wood or wall board surface will burn much more freely if unpainted than if coated with an ordinary flat wall paint such as TT-P-47. There has been a widespread misconception that the dried paint film is a fire hazard, when actually a wood or cellulosic wallboard surface is considerably more readily combustible uncoated than when coated with the average wall paint.

The test apparatus used in this work was the New York Production Club cabinet developed by the New York Paint and Varnish Production Club and modified by Engineer Research and Development Laboratories, Fort Belvoir, Va. It consisted essentially of two parallel iron bars set 6 inches apart and extending upward at a 45° angle from the lower side of the cabinet, and an adjustable cross bar to support the test panel in the desired position. The flame source consisted of absolute ethyl alcohol contained in a brass cup supported on a cork-insulated metal pedestal.

The test panel was placed in position on the angular supports. Five milliliters of absolute ethyl alcohol was measured into the brass cup by means of a buret. The cup was then placed on the cork-insulated pedestal and placed in a position exactly 1 inch from the face of the panel.

The panel used was cut from selected poplar wood to the dimensions, 6 x 12 x 1/4 inches. Two coats of paint were applied to these panels to provide a dry film thickness of 0.004 inch.

Included in the work was a leaching test consisting of complete immersion of the painted panels in distilled water for 48 hours at 120° F. The panels were than removed and dried at 120° F. for 72 hours before being submitted to the burn test.

This test was considered important in the prediction of the effect of washing on an interior paint and it is obvious that the effect of rainfall should be predetermined on an exterior paint.

Ten typical pigments and/or extenders have been tested in an alkyd vehicle in both the presence and absence of chlorinated paraffin. These results were determined at pigment loadings of 40% and 60% PVC.

Table I shows that, of all the pigments tested, zinc borate showed the best fire-retardant properties. Calcium carbonate showed valuable retardant properties, its effectiveness increasing with increased concentration. This would indicate that it functions by decomposition with subsequent release of carbon dioxide.

In view of all of the references to be found in the literature, results with antimony oxide seem disappointing. However, most of the data on this pigment have been developed on fiber or fabric and it is obvious that these data would not necessarily apply to fire-retardant performance of supported films.

Ten different vehicles or vehicle combinations have been studied for fire-retardant properties. This study was conducted with a constant pigment combination and at a constant pigment volume concentration. The pigment loading concentration of 34% was chosen because it was believed that this concentration would fall below the critical range indicated in Table I. The combination of pigments was chosen to provide adequate hiding which had been indicated up to this point in the investigation.

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The pigments were combined in the following ratio:

Titanium dioxide	42.0%
Zinc borate	38.0%
Calcium carbonate	12.5%
Asbestine	7.5%

Examination of Table II will show that, of all the vehicles tested, the alkyd resins produced the best fire-retardant properties. All these films were air-dried at room temperature in the absence of any catalysts other than lead and cobalt where appropriate.

As might be expected, pigment volume concentration is shown in many instances to have definite effect on fire-retardant properties. This effect appears to be specific for each pigment. In general, this work shows better results at lower pigment volume concentration, but, as is shown in Table I, there is departure from this rule sufficient to indicate the probability of a critical pigment -- binder ratio for each pigment. When this ratio is exceeded, film porosity is increased, thus detracting from the retardant effectiveness.

Intumescent Agents

Perhaps the most important single property for a fire-retardant film is intumescence, the property of swelling or puffing when exposed to the heat of flame. Such swelling providing a thick cellular insulating layer between the fire and the flammable substrate.

During the course of this work, the following compounds were tested as intumescent agents in various formulations and concentrations both alone and in combination with each other.

Ammonium phosphate
Vermiculite
Casein
Starch
Benzene sulfonyl hydrazide
Isano oil
Carbamide phosphoric acid
Polyamide resin (No. 93, General Mills)
Urea
Paraformaldehyde
Aminoacetic acid
Victamide (Victor Chemical Works)
Methylene disalicylic acid

All these materials produced intumescence to some degree, but only a few showed enough to be of real value. The most effective was a combination of paraformaldehyde, urea, and ammonium phosphate. This confirms the work of Jones and Soll (1). The combination of isano oil with polyamide resin gave best results in exterior paint formulations. Amino acetic acid with starch and also with ammonium phosphate gave good results.

The better intumescent agents are water-soluble and therefore produce paints having poor water and scrub resistance. The Victamide is a relatively new product and has not been completely evaluated as yet. It is less water-sensitive than most of the other compounds.

An effort has been made to decrease water sensitivity when using water-soluble

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Table I. Pigment Study

Pigment	Average Wt. Loss Grams		Average Wt. Loss %		Average Char Area Sq. Inches		Average Char Volume Cu. Inches	
	60% PVC	40% PVC	60% PVC	40% PVC	60% PVC	40% PVC	60% PVC	40% PVC
Zinc borate, no Cl	19.75	14.7	11.4	9.1	24.3	25.5	4.27	4.56
Zinc borate, plus Cl	15.5	14.55	8.96	8.4	25.1	36.3	3.8	6.82
Calcium carbonate, plus Cl	17.2	25.8	9.9	15.3	22.5	38.1	4.22	6.65
Lead silicate, no Cl	25.4	23.1	14.0	13.67	45.7	39.3	7.33	6.83
Lead silicate, plus Cl	18.2	20.4	10.4	11.5	39.1	39.3	7.4	7.4
Magnesium silicate, plus Cl	20.4	18.0	12.1	10.8	36.6	31.5	6.91	5.95
Blanc fixe, plus Cl	21.7	31.9	12.5	17.6	39.8	45.0	8.16	9.15
Zinc oxide, no Cl	31.0	26.0	17.1	15.5	42.7	34.5	7.98	6.53
Zinc oxide, plus Cl	27.2	20.2	13.5	11.5	46.2	36.3	8.0	6.82
Antimony oxide, no Cl	21.1	21.0	11.45	11.53	41.9	41.3	7.8	7.78
Antimony oxide, plus Cl	20.0	19.9	11.1	10.54	39.0	31.8	7.34	6.0
Calcium pyrophosphate, plus Cl	39.3	38.5	21.2	22.7	55.8	49.0	10.9	9.23
Lead carbonate, plus Cl	39.3	29.3	19.6	16.2	50.8	50.4	10.2	8.31
Lithopone, plus Cl	19.9	28.2	14.6	16.5	38.0	58.0	7.11	8.31

Table II.* Recapitulation of Average Burn Test Data on Vehicles

Vehicle	Av. Wt. Loss, Grams	Av. Wt. Loss, %	Av. Char Area, Sq. Inches	Av. Char Vol., Cu. Inches
VE 1 refined linseed oil plus chlorinated paraffin	20.3	12.2	39.0	7.36
VE 2 alkyd resin plus chlorinated paraffin	16.0	9.63	32.6	6.2
VE 3 alkyd resin plus silicone resin	16.8	9.8	28.1	5.44
VE 4 alkyd resin plus chlorinated rubber	24.6	14.6	47.5	8.94
VE 5 vinyl chloride acetate resin	25.8	14.93	48.3	9.0
VE 6 oil-modified epichlorhydrin resin	28.1	16.54	45	9.04
VE 7 urea-formaldehyde resin	33.4	19.98	53	12.18
VE 8 alkyd resin plus ethyl silicate	23.64	14.4	42.8	7.96
VE 9 acrylic resin plus chlorinated rubber	28.8	18.9	52	9.7
VE 10 polystyrene resin emulsion	33.7	22	53	12.18

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intumescent agents. To accomplish this, relatively low concentrations of silicone resin were used. The result is demonstrated by reference to the washability values for formulations for interior paints 1, 2, and 3. Interior paint 1 containing no silicone withstood 600 scrubbing strokes on the Gardner instrument; interior paint 3 containing 2.5% silicone withstood 1436 strokes; interior paint 2 with 30% silicone took 2275 strokes.

Interior Paint Formulations

Interior Paint 1

PVC, 72%. Wt./gal., 11.3 lb.
Viscosity, 110 KU

	Pounds
Titanium dioxide	125.0
Starch	167.0
Ammonium phosphate	250.0
Chlorinated paraffin 70%	50.0
Aluminum stearate	2.0
Aminoacetic acid	200.0
10 cps. chlorinated rubber	121.0
50% alkyd resin solution	104.0
Hi Flash naphtha	204.0
- - - - - - - - - -	- - - -
Hi Flash naphtha	83.5

Interior Paint 3

PVC, 67%. Wt./gal., 11.2 lb.
Viscosity, 112 KU

	Pounds
Titanium dioxide	144.0
Starch	57.5
Ammonium phosphate	330.0
Aminoacetic acid	61.5
10 cps. chlorinated rubber	119.0
50% alkyd resin solution	115.0
Hi Flash naphtha	206.0
60% silicone resin solution	8.2
- - - - - - - - - -	- - - -
Hi Flash naphtha	82.5

Interior Paint 2

PVC, 64%. Wt./gal., 11.7 lb.
Viscosity, 99 KU

	Pounds
Titanium dioxide	200.0
Starch	65.0
Ammonium phosphate	380.0
Aminoacetic acid	100.0
50% alkyd resin solution	280.0
60% silicone resin solution	104.0
- - - - - - - - - -	- - - -
Mineral spirits	70.0
2% cobalt	7.0

Interior Paint 4

PVC, 67%. Wt./gal., 12.2 lb.
Viscosity, 110 KU

	Pounds
Titanium dioxide	175.0
Paraformaldehyde	51.0
Neutralized ammonium phosphate (Fyrex, Victor Chemical Works)	
Urea	64.0
Starch	40.0
Chlorinated paraffin 70%	55.0
10 cps. chlorinated rubber	145.0
50% alkyd resin solution	125.0
Hi Flash naphtha	250.0
- - - - - - - - - -	- - - -
Hi Flash naphtha	90.0

For the evaluation of paints for interior exposure, JAN-P-702 was taken as a reference standard.

During the course of this work, 27 interior fire-retardant paints have been developed and evaluated. Formulations and test results are shown for two of the best of these (Tables III and IV), together with the results obtained for JAN-P-702 (Table VII). Formulation and fire-retardance test results are shown in Table V for interior paint 3, while data for interior paint 4 are given in Table VI.

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Table III. Burn Test Data on Interior Paint 1

Panel	Wt. before, Grams	Wt. after, Grams	Wt. Loss, Grams	Wt. Loss, %	Char Area, Sq. Inches	Char Volume, Cu. Inches	Discolor Face, Sec.	Panel Flame, Sec.	Alcohol Flame Out, Sec.	Panel Flame Out, Sec.
					Before Leaching					
1190	163.5	153.0	10.5	6.44	15.7	3.0	10	29	489	485
1191	169.1	159.1	10.0	5.92	15.7	3.0	11	27	482	478
1192	175.0	160.3	12.0	6.85	17.2	3.2	11	23	478	472
1193	171.3	161.1	10.2	5.95	16.7	3.1	13	85	484	487
1194	163.8	151.7	12.1	7.40	15.8	3.0	16	27	486	485
Av.	168.54	157.04	10.96	6.512	16.22	3.06	12.2	38.2	483.8	481.4
					After Leaching					
1195	156.6	138.6	18.0	11.50	30.3	7.6	14	17	454	448
1196	154.3	125.6	28.7	18.60	43.0	10.8	11	15	462	460
1197	151.6	125.6	26.0	17.15	44.0	10.3	11	14	464	460
1198	153.8	125.2	28.6	18.60	41.2	10.3	11	16	463	459
1199	159.6	140.0	19.6	12.30	32.5	8.1	15	18	452	449
Av.	155.18	131.0	24.18	15.63	38.2	9.4	12	16	459	455

Washability, 600 strokes.

Table IV. Burn Test Data on Interior Paint 2

Panel	Wt. before, Grams	Wt. after, Grams	Wt. Loss, Grams	Wt. Loss, %	Char Area, Sq. Inches	Char Volume, Cu. Inches	Discolor Face Sec.	Panel Flame, Sec.	Alcohol Flame Out, Sec.	Panel Flame Out, Sec.
					Before Leaching					
1272	183.4	172.4	11.0	6.00	14.5	2.7	21	40	488	484
1273	171.5	161.2	10.3	6.00	15.4	2.6	16	27	482	477
1274	174.1	164.4	9.7	5.57	15.7	2.7	18	35	491	488
1275	180.5	166.7	13.8	7.65	20.5	3.9	17	27	485	486
1276	176.3	162.8	13.5	7.65	20.2	3.8	19	28	476	472
Av.	177.16	165.5	11.66	6.57	17.3	3.1	18	31	484	481

Washability, 2275 strokes.

Table V. Burn Test Data on Interior Paint 3

Panel	Wt. before, Grams	Wt. after, Grams	Wt. Loss, Grams	Wt. Loss, %	Char Area, Sq. Inches	Char Volume, Cu. Inches	Discolor Face, Sec.	Panel Flame, Sec.	Alcohol Flame Out, Sec.	Panel Flame Out, Sec.
					Before Leaching					
1292	178.6	169.7	8.90	4.98	13.9	2.6	16	28	450	460
1293	183.0	172.6	10.40	5.68	16.4	3.1	19	28	487	481
1294	166.4	157.6	8.80	5.29	14.8	1.9	16	28	463	460
1295	174.3	165.3	9.00	5.16	17.4	3.2	17	30	476	477
1296	167.5	159.1	8.40	5.01	15.0	2.6	16	26	469	465
Av.	173.96	164.86	9.10	5.22	15.5	2.7	17	28	469	468

Washability, 1436 strokes.

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Table VI. Burn Test Data on Interior Paint 4

Panel	Wt. before, Grams	Wt. after, Grams	Wt. Loss, Grams	Wt. Loss, %	Char Area, Sq. Inches	Char Volume, Cu. Inches	Discolor Face Sec.	Panel Flame, Sec.	Alcohol Flame Out, Sec.	Panel Flame Out, Sec.
					Before Leaching					
1201	160.5	150.7	9.8	6.10	16.2	2.0	13	34	462	460
1202	182.1	172.6	9.5	5.20	13.5	2.5	14	22	483	480
1203	167.5	159.0	9.5	5.07	13.5	2.5	17	25	487	484
1204	165.7	155.1	10.6	6.40	16.5	3.1	15	27	482	480
1205	174.3	151.7	12.9	7.40	17.1	3.2	16	23	481	482
Av.	170.02	157.82	10.26	6.03	15.36	2.66	15	26.2	479	477.2
					After Leaching					
1206	162.5	146.7	15.8	9.73	32.0	7.0	12	20	483	478
1207	170.0	152.0	18.0	10.60	30.0	7.5	11	16	457	453
1208	166.8	149.4	17.4	10.45	24.0	6.0	11	15	465	461
1209	155.0	130.0	25.0	16.10	44.5	11.1	12	18	457	453
1210	----	----	---	----	Defective panel (split)		--	--	---	---
Av.	163.57	144.52	19.05	11.72	32.6	7.9	11	17	465	461

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Table VII. Burn Test Data on JAN-P-702

Service and Application Properties

Washability - Not determined.
Brushability - Very good.
Opacity - Equal to acceptable commercial interior paint.
Drying time - Six hours.

Panel	Wt. before, Grams	Wt. after, Grams	Wt. Loss, Grams	Wt. Loss, %	Char Area, Sq. Inches	Char Volume, Cu. Inches	Discolor Face Sec.	Panel Flame, Sec.	Alcohol Flame Out, Sec.	Panel Flame Out, Sec.
1	175.0	147.1	27.92	16.0	38.1	3.02	320	100	445	445
2	170.5	132.0	48.5	28.4	50.8	3.0	286	42/122*	477	480
3	175.0	132.5	42.5	24.3	46.8	3.7	235	27/86*	410	573
4	170.5	133.4	37.1	21.8	44.2	3.49	240	38/139*	445	543
5	162.0	135.4	26.6	16.4	43.3	3.42	260	38/87*	405	405
Av.	170.5	136.1	36.55	21.38	44.65	3.33	268	29/107*	440	490

*First traces of smoke.

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For the formulation of fire-retardant paints for exterior exposure, considerable work has been done with isano oil. This oil, expressed from a nut native to French Africa, foams violently when exposed to flame temperature. This foaming appears to have definite fire-retardant value.

Formulations for two fire-retardant exterior paints are shown here. Exterior paint 1 contains no isano oil, while exterior paint 2 does contain isano oil.

For some reason, not yet established, a combination of lead sulfate with lead carbonate produced considerably better fire-retardant results than when either of these pigments was used alone. For that reason, this combination has been used in the formulations reported here (Tables VIII and IX).

Exterior Paint Formulations

Exterior Paint 1

PVC, 34%. Wt./gal., 14.8-14.9 lb.
Viscosity, 87 KU

	Pounds
Titanium dioxide	100.0
Zinc borate	379.0
Lead sulfate	168.5
Lead carbonate	168.5
Zinc oxide	95.0
Chlorinated paraffin 70%	67.5
XX refined linseed oil	340.0
- - - - - - - - - - - - - -	- - -
60% alkyd resin solution	98.0
Mineral spirits	39.0
2% cobalt	5.5
8% lead	24.0
2% manganese	3.5

Exterior Paint 2

PVC, 34%. Wt./gal., 15.9 lb.
Viscosity, 98 KU

	Pounds
Titanium dioxide	100.0
Zinc borate	292.0
Blanc Fixe	148.0
Lead sulfate	168.5
Lead carbonate	168.5
Zinc oxide	95.0
XX refined linseed oil	170.0
Isano oil	170.0
Chlorinated paraffin 70%	70.0
- - - - - - - - - - - - - -	- - -
40% polyamide 93 resin solution	160.0
2% cobalt	5.5
8% lead	24.0
2% manganese	3.5
Mineral spirits	20.0

Conclusions

Of the pigments and extenders tested, zinc borate is the most effective as a fire retardant. Calcium carbonate has good fire-retardant properties, especially in the limitation of the char area. Antimony oxide, whether in presence or absence of chlorine, is not particularly effective as a fire-retardant pigment in paint.

Pigment volume concentration has a definite effect on fire-retardant properties of paint films. This effect appears to be specific for each pigment or pigment combination.

With the exception of isano oil and combinations of isano oil with nitrogen-bearing resins, alkyds gave better fire-retardant results than the other vehicles tested.

Washability is greatly improved by the incorporation of relatively small amounts of silicone resins in paints containing water-soluble intumescent agents.

The best fire-retardant experior paint resulting from this work is exterior paint 2. The best fire-retardant interior paint produced in this investigation is interior paint 3.

Table VIII. Burn Test Data on Exterior Paint 1

Panel	Wt. before, Grams	Wt. after, Grams	Wt. Loss, Grams	Wt. Loss, %	Char Area, Sq. Inches	Char Volume, Cu. Inches	Discolor Face, Sec.	Panel Flame, Sec.	Alcohol Flame Out, Sec.	Panel Flame Out, Sec.
Before Leaching										
802	174.3	160.8	13.5	7.75	22.2	4.2	12	19	472	461
803	170.0	157.0	13.0	7.65	22.8	4.3	12	18	465	460
804	186.3	170.6	15.7	8.45	22.8	4.3	13	18	468	472
805	168.7	155.2	13.5	8.00	22.8	4.3	13	19	457	452
806	164.8	149.8	15.0	9.10	24.4	4.6	13	19	464	465
Av.	172.8	158.7	14.1	8.19	23.0	4.34	12.6	18.6	465	462
After Leaching										
807	162.0	146.7	15.3	9.45	25.0	4.7	14	18	465	462
808	170.5	152.2	18.3	10.70	30.8	5.8	12	15	459	456
809	160.4	146.4	14.0	8.75	24.0	4.5	11	15	455	454
810	160.0	143.0	17.0	10.60	30.0	5.7	10	14	439	436
811	165.1	145.1	20.0	12.10	36.0	4.5	12	16	450	444
Av.	163.6	146.7	16.9	10.3	29.1	5.0	12	15.6	453	450

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Table IX. Burn Test Data on Exterior Paint 2

Panel	before, Grams	after, Grams	Wt. Loss, Grams	Wt. Loss, %	Char Area, Sq. Inches	Char Volume Cu. Inches	Discolor Face, Sec.	Panel Flame, Sec.	Alcohol Flame Out, Sec.	Panel Flame Out, Sec.
					Before Leaching					
933	197.0	188.0	9.0	4.57	13.1	1.65	11	22	481	474
934	182.8	173.2	9.6	5.25	12.5	2.40	13	20	478	471
935	184.7	173.8	10.9	5.90	15.1	2.90	14	19	470	473
936	182.5	172.3	10.2	5.60	14.3	2.70	17	22	473	470
937	190.7	177.3	9.92	5.33	13.75	2.41	14	19	475	470
Av.	186.75	176.82	9.92	5.33	13.75	2.41	14	20	475	471
					After Leaching					
938	197.0	185.7	11.3	5.74	11.2	2.5	13	17	490	492
939	174.8	163.5	11.3	6.48	17.9	3.6	11	15	458	464
940	175.0	164.6	10.4	5.95	14.5	2.9	14	18	475	470
941	193.0	184.2	8.8	4.55	12.5	2.5	12	19	452	451
942	181.4	171.1	10.3	5.68	13.4	2.5	12	16	455	453
Av.	184.24	173.82	10.42	5.68	13.9	2.8	12	17	466	466

So far as has been determined, outstanding fire retardance is not obtained without some degree of intumescence.

Use of lead carbonate and lead sulfate in proper proportions improves exterior fire-retardant paints.

Literature Cited

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Testing Fire-Retardant Paints under Simulated Service Conditions

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Simulated ship structures at the Naval Damage Control Training Center, Philadelphia, Pa., are available for studying the behavior of materials in fires of the type to be expected in service. This investigation was planned to compare the flammability of several existing government paint formulations and proposed commercial fire-retardant products with the navy standard fire-retardant inside white, and to determine whether any of the paints may serve as a means by which fire could spread from one compartment to those adjacent. Single exposures conducted within the hangar deck demonstrated large differences in flammability, for example, between the standard fire-retardant inside white and white enamel. Minor differences cannot be conclusively demonstrated without some replication of the test procedure. The degree of replication is not known. Several of the paint systems approach or exceed the navy standard in fire retardancy. Thin films of inherently flammable paints can be ignited by the heat transmitted through a bulkhead or deck.

Certain structures at the Damage Control Training Center at this Naval Base are primarily useful for training service personnel to fight fires on ships. The arrangement of certain parts of ships is reproduced. Large scale fires can be set off in these structures, which are also useful for investigating the behavior of materials under conditions closely similar to those encountered during actual fires on ships.

In previous tests, the structures have been used to evaluate the performance of a fire-retardant plastic salt-water piping system as compared with that of piping of copper-nickel (70:30), the type currently used, and piping of aluminum alloy. A second series of tests rated the comparative fire-retardancy of a variety of deck coverings which included ordinary battleship linoleum, fire-retardant linoleum, rubber and synthetic matting, various fire-retardant nonskid deck treads, and several types of vinyl tile and decking. This paper presents information acquired during an investigation of fire-retardant paints by exposing painted steel panels to fires in these structures. Such investigation demonstrate the behavior which can be expected in actual fires, and provide a basis for correlation with laboratory data.

Throughout the paper, the term "fire-retardant paint" means a paint which does not flash or flame when exposed to a source of ignition. The intended purpose of

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such a paint is to limit the spread of fire, as the paint will not add any significant fuel, nor transmit the fire to adjacent compartments. As used, the term does not mean that the paint will protect a combustible substrate, such as wood, or that the paint will be unaffected by the fire. Fire-retardant paints, as here defined, usually char and disintegrate during fires, but do so without flaming or flashing.

Review of the Problem

Paint is necessary on interior steel surfaces of ships to prevent corrosion. In addition, properly selected paints augment illumination, assist in sanitation, and provide decoration.

The presence of thin coats of the usual flammable paints is not ordinarily regarded as a fire hazard. But for the practice -- prior to World War II -- of repeated paintings of ship's compartments, until heavy layers of paint were built up, the possible danger from flammable paints might have been overlooked. Ample evidence of this danger was provided to battle-damage crews fighting fires on ships after the Japanese attack at Pearl Harbor. Not only did paint on hot bulkheads take fire, but sheets of burning paint fell from the overhead, hindering those trying to bring the fires under control.

An initial corrective action was to scrape off all interior paint. The obvious necessity to repaint gave impetus to the development in 1942 of a fire-retardant paint (2), which continues in use as the standard finish coat on the bulkheads and overheads of surface ships of the Navy. It is fire-retardant by virtue of its high pigment volume (and consequent reduction in available combustible organic binder), and by incorporation of antimony oxide as part of the pigment. The vehicle is a medium-long oil alkyd resin. This paint is satisfactorily fire-retardant. It is deficient in resistance to staining, as its high pigment content produces a somewhat porous film.

No reliable data existed in 1942 on temperatures that might be found during fires on ships, and no standard laboratory tests for measuring the fire-retardancy of paints were available. The first laboratory tests used gas flames and muffle furnaces. Later, a more satisfactory device, whereby the paints were applied to thin steel strips, was devised (1). The painted strips were then repidly heated by shorting an electric current through them. Because of the shape and size of the strips, the center and narrower portion is rapidly heated, and the paint is quickly exposed to contact with red-hot metal. This source of ignition was envisaged as duplicating the severe conditions which might result from enemy action.

To supplement laboratory tests, practical trials of this paint were made at the Navy Fire Fighter Schools at Norfolk, Va., and Boston, Mass. These trials were somewhat crudely conceived, as might be expected from the state of knowledge at that time, but the satisfactory performance demonstrated by the fire-retardant paint was sufficient, under the pressure of circumstances then existing, to warrant its adoption. Actual experience has amply demonstrated that it functions exceptionally well as a fire-retardant coating, but the same experience has equally shown the need for improvement in ease of cleaning.

In 1942, various materials, such as resinous chlorinated paraffin, chlorinated rubber, chlorinated alkyd resins, and vinyl and vinylidene resins were unavailable for use in fire-retardant paints. Such chlorinated binders as were available were in critical demand for flameproofing fabrics. The present availability of such materials

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has permitted considerable improvement in fire-retardant paint formulations, so that it is now no longer necessary to sacrifice gloss, washability, stain resistance, and decorative value in order to have fire-retardance. This situation, together with an increased commercial interest in fire-retardant paints (because of their use on the SS. United States), has created a situation where re-evaluation of such paints seems desirable.

The present investigation was planned, therefore, to compare the behavior in large scale fires, of the former standard with that of newer formulations based upon chlorinated binders and with commercially available fire-retardant finishes.

Materials Evaluated

The paint systems evaluated consisted of five formulations conforming with existing government specifications, one experimental laboratory formulation, and four commercial products. The stock paints were of the type normally found aboard ship and included fire-retardant interior white, white enamel, gray deck, gray vinyl-alkyd combination, and gray alkyd-chlorinated rubber combination. The fire-retardant white, and light gray and green counterparts, are present standards for painting interior bulkheads. The chlorinated rubber paint and the vinyl-alkyd paint were assumed to have a degree of fire-retardancy because of their chlorine content. The enamel and gray deck paints were not formulated to possess any appreciable resistance to burning and represent flammable controls.

The experimental laboratory formulation is a proposed fire-retardant red deck paint. A primer not formulated to be fire-resistant is employed with this system.

The commercial samples were proposed essentially for use on interior bulkheads and the overhead. Each of the four systems employed one coat of a fire-retardant primer prior to the application of the fire-retardant top coat.

All the above paint systems are identified in Table I.

Tests in Forecastle

Test Site. The initial phase of this investigation was conducted on the overhead, bulkheads, and deck comprising the middle compartment on the main deck of the simulated forecastle structure at the Naval Damage Control Training Center. Figure 1, a sectional view of the main deck, illustrates the position of the compartment relative to those adjacent. The deck and overhead in the chamber are fabricated of 1/2 inch steel plates welded into a smooth, continuous surface. The overhead is supported by four beams so arranged that the main support longitudinally divides the area into two sections, each of which is subdivided by three lateral members into four equal segments. The fore and aft bulkheads also are of steel. Their exteriors, facing the adjacent compartments, are smooth; their interior surfaces are sectioned by upright stiffeners into panels approximately 2 feet wide. The port and starboard bulkheads are of brick. The entire deck and overhead surfaces and four adjacent panels on both the fore and aft bulkheads were employed in the evaluation. In addition, the roof of the forecastle directly above the compartment was considered as representing a weather deck and was used for testing deck paints.

Paint Application. Figure 2 illustrates and identifies the relative position of the bulkhead and overhead paint systems; Figure 3 likewise identifies the deck paints. Only the navy formulations, paint systems 1 to 6, were evaluated in this trial. Samples 1, 3, 4, and 6 were brushed on the bulkheads and overhead and samples 2, 4, and

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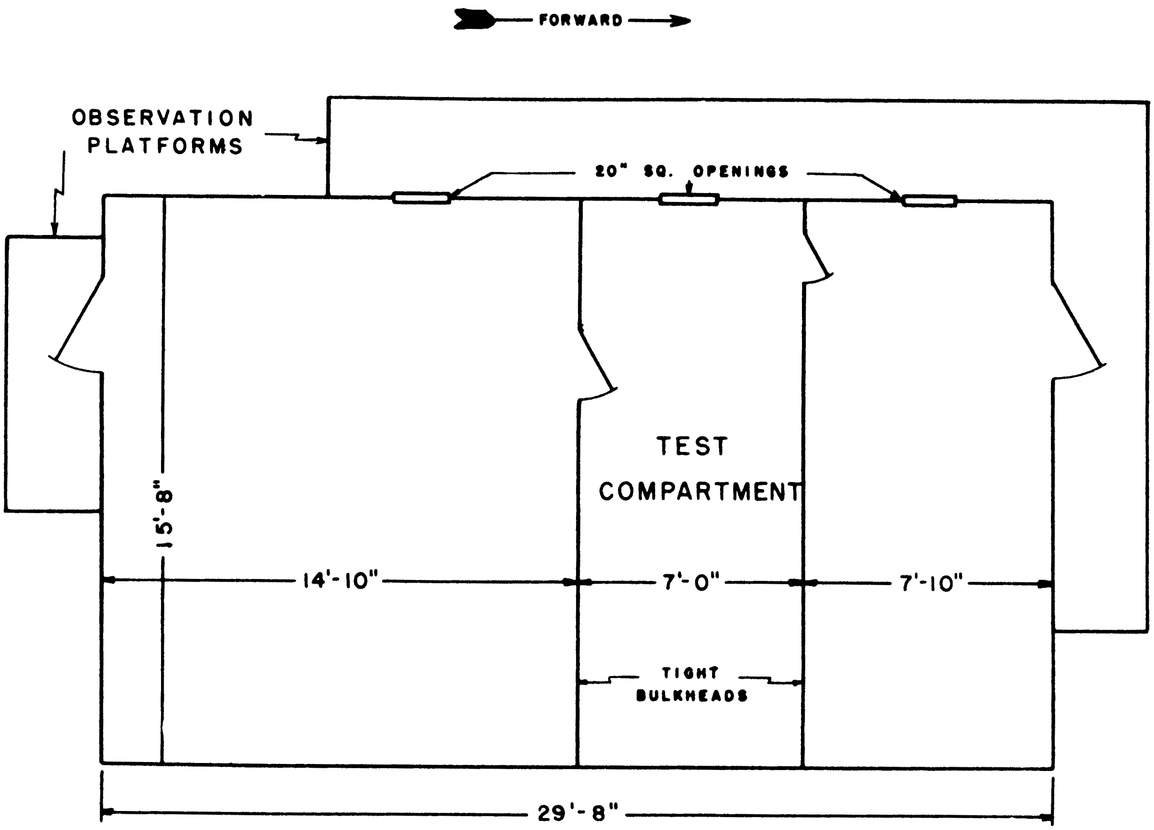

Figure 1. Plan at Main Deck of Forecastle

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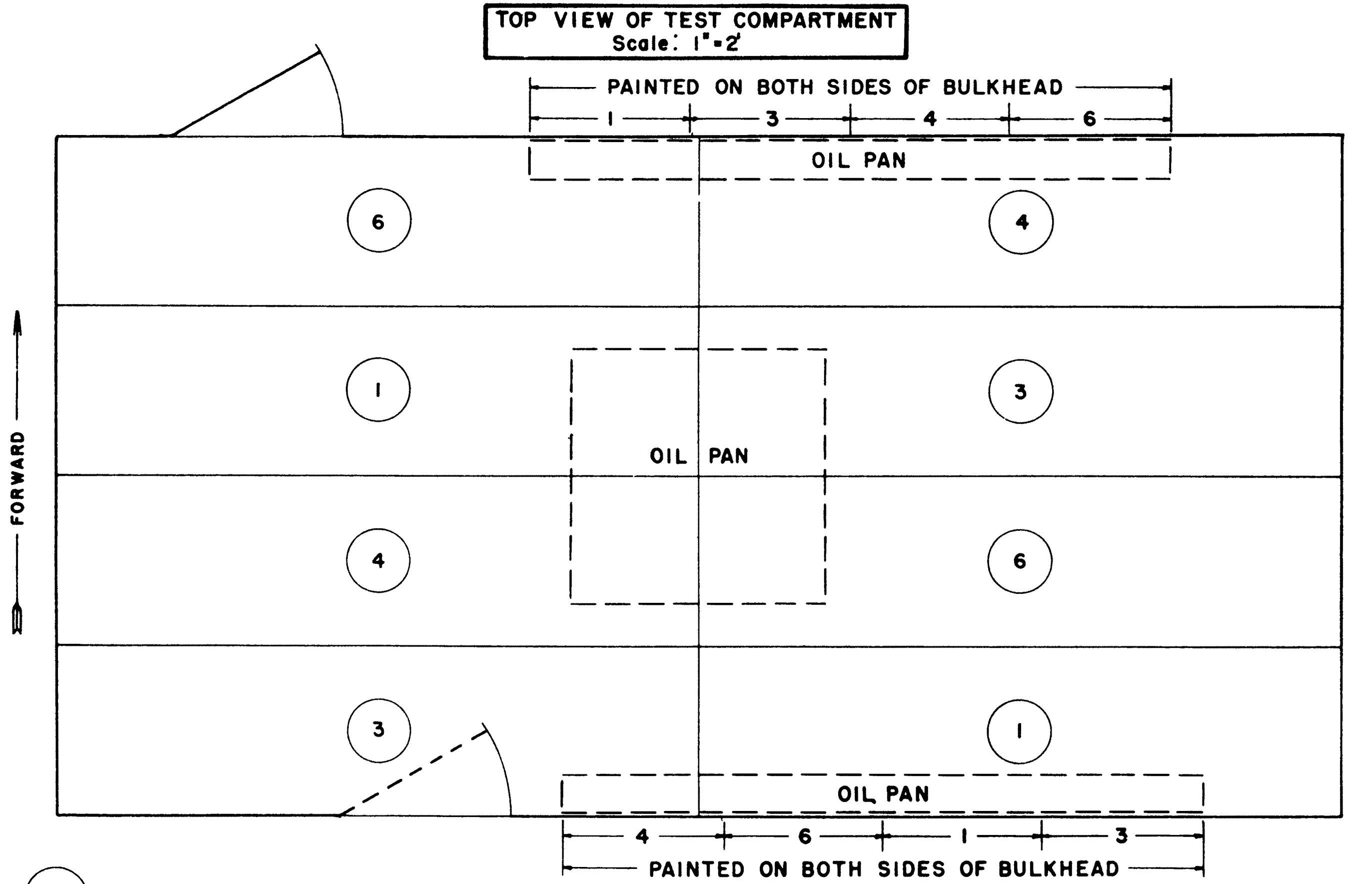
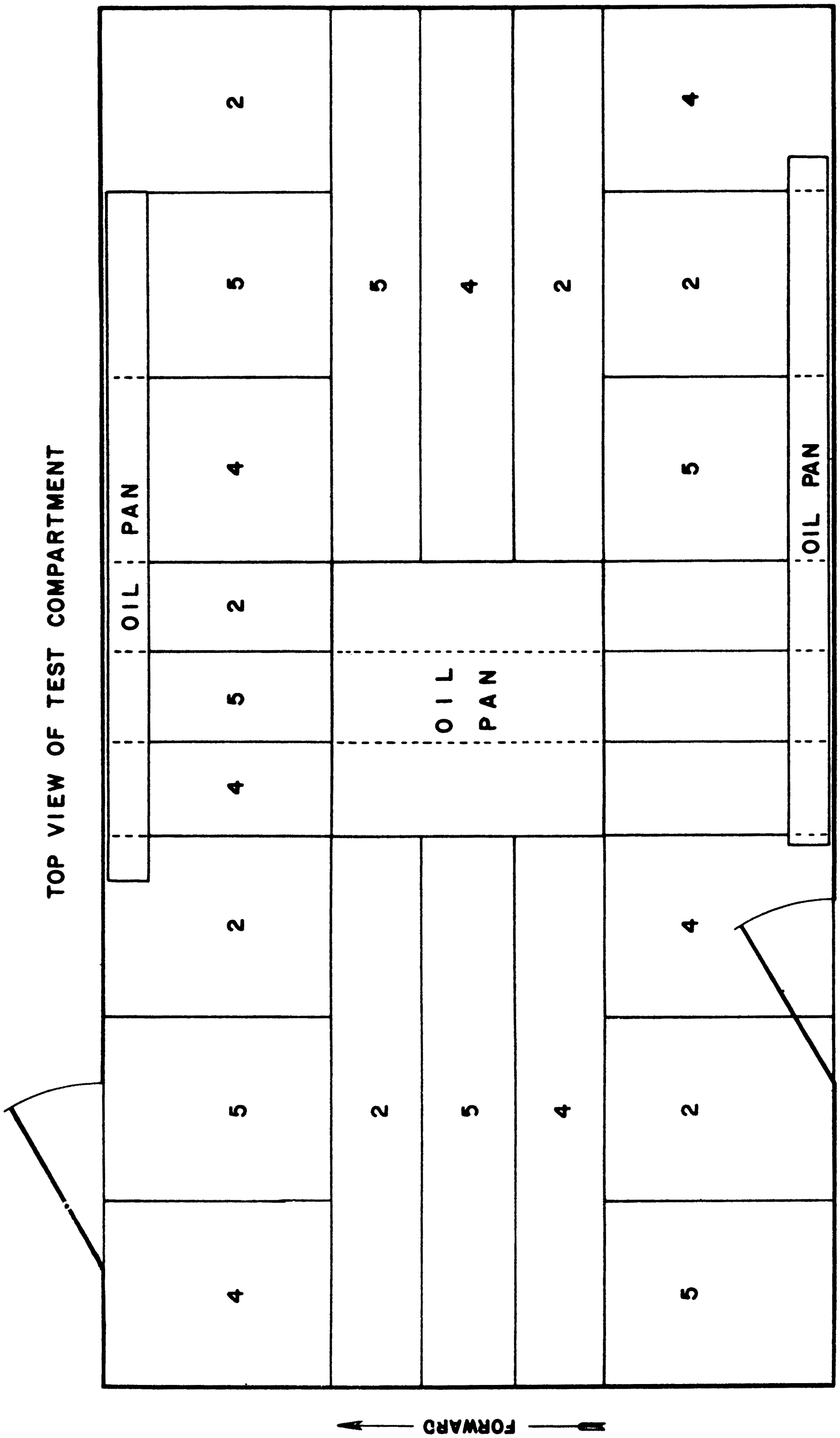


Figure 2. Identification of Bulkhead and Overhead Paint Systems

TOP VIEW OF TEST COMPARTMENT



NOTE: SIMILAR LAYOUT ON TOPSIDE DECK DIRECTLY ABOVE THE TEST COMPARTMENT

Figure 3. Identification of Paint Systems on Deck

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Table I. Identification of Paint Systems

System No.	Description
1	One coat of primer, formula 84-47, followed by fire-retardant white, formula 27. The primer, a zinc chromate alkyd type, intended for use by the Departments of the Army, Navy, and Air Force as a corrosion inhibitor for metal surfaces, conforms with the requirements of specification JAN-P-735 (4). It is not formulated to be fire-resistant. The top coat, a semigloss inside fire-retardant paint intended primarily as a finish for interior bulkheads and overheads aboard ship, conforms with the requirements of specification JAN-P-702 (3).
2	One coat of primer, formula 84-47, followed by light gray deck paint, formula 20L. The top coat approved by the Departments of the Army, Navy, and Air Force primarily for painting decks on the interior of military vessels, conforms with the requirements of specification JAN-P-700 (2). It is not formulated to be fire-retardant.
3	One coat of primer, formula 84-47, followed by white enamel, formula 30. The top coat, approved by the Departments of the Army, Navy, and Air Force for general-purpose interior or exterior shipboard use, conforms with the requirements of specification MIL-E-1115A (6). It is not formulated to be fire-retardant.
4	One coat of formula 117, followed by two coats of formula 120, and then a vinyl-alkyd gray, formula 122-27. Formula 117, approved by the Departments of the Army, Navy, and Air Force as a primer pretreatment coating for use on clean metal surfaces of all types, conforms with specification MIL-C-15328A (5). Its purpose is to increase the adhesion of the coating system; it is not a permanent protective coating in itself. Formula 120, conforming with the requirements of specification MIL-P-15930 (8), is a vinyl-zinc chromate type of primer for use over formula 117. Formula 122-27, conforming with the requirements of specification (9), is an outside gray vinyl-alkyd combination for use over a system consisting of a pretreatment wash primer, formula 117, and zinc chromate primer, formula 120. This system is considered to be fire-retardant.
5	One coat of primer, formula 84-47, followed by an experimental red deck paint similar to that specified in specification (7), formula 23, except that sufficient chlorinated paraffin was substituted for the alkyd resin solid to yield a chlorine content of 35% in the nonvolatile vehicle without altering the pigment volume. This paint was formulated by the Paint Research Section; it has not been accepted for naval use.
6	One coat of formula 117, followed by two coats of formula 84-47 and then formula 127, an alkyd-chlorinated rubber fire-retardant gray paint intended to supersede formula 27 for naval use.
7	These paints, submitted by exhibitor A, consisted of one coat of a fire-retardant chromate primer, followed by application of a fire-retardant white paint.
8	This system, also submitted by exhibitor A, consisted of one coat of a fire-retardant red lead primer, followed by application of a fire-retardant white paint.
9	These paints, submitted by exhibitor B, consisted of one coat of a fire-retardand zinc chromate primer, followed by application of a fire-retardant flat white.
10	This system, also submitted by exhibitor B, consisted of one coat of fire-retardand zinc chromate primer, followed by application of a fire-retardant semigloss white.

5 were brushed on the deck. The selection of the locations was in accordance with the intended service use of the paints. The sections were prepared so as to achieve a dry film thickness of approximately 3 mils (representative of two top coats).

Ignition Source. Fire was provided by use of three oil pans. One, centrally located measured 3 x 3 feet x 5 inches and contained 4 gallons of No. 2 burner oil. The other two, located directly adjacent to the bulkhead paint panels, measured 7 feet 8 inches x 4 inches x 5 inches and contained 1 3/4 gallons of oil each. The containers were each primed with 1 quart of gasoline, ignited, and permitted to burn to extinction.

Temperature Measurements. Prior to application of the paint, a thermocouple was welded to the center of the exterior surface of each bulkhead panel approximately 6 feet above the deck and three thermocouples were welded along the lateral axis of the test panel on the weather deck. One thermocouple also was suspended within the test compartment over the midpoint of the space approximately 2 inches below the overhead. Temperature measurements were recorded throughout the test by two General Electric potentiometer recorders connected through two rotary selector switches. Following ignition, the hatches were bolted and personnel were stationed in the adjacent compartments to observe flaming or glowing of the paint films.

Results. None of the observers reported flaming, flashing, or glowing of any portion of the exposure deck or outboard bulkhead paint films during the test, although following test, it was noted that all the paint systems were discolored or blistered and peeling, particularly the experimental red deck paint (system 5). The temperature recorded showed a maximum of 436° F. on the bulkheads, 480° F. on the weather deck, and 888° F. ambient over the center of the fire. As the bulkhead thermocouples were 6 feet above the deck, it is possible that the temperatures of the lower portions of the panels in direct contact with the flames were much higher than those recorded. However, it is believed the exposure was much less severe than would be experienced in most fires that occur in service. Since the intensity of the exposure could not be increased without endangering the security of the structure, these tests were terminated.

Tests in the Hangar Deck

Test Site. The second phase of this investigation was conducted in the hangar deck structure. The walls and floor of the compartment are of brick, the roof is of steel. The front is designed with ten equidistantly spaced 3-foot-square portholes, arbitrarily numbered from 1 to 10, from left to right, when facing the structure. Tests were conducted on painted 1/8 inch thick steel panels which were fitted over the ports flush with the inner wall, painted surface toward the outside. The initial series of tests was conducted on panels with a dry film thickness of 3 to 5 mils (representative of two top coats); the second series of tests was determined on panels with a dry film thickness of over 5 mils (representative of four top coats).

Ignition Source. Fire was provided by flooding the compartment with No. 2 burner oil, which was then primed with gasoline and ignited. The duration of test varied with the intensity of the fire and its effect on the security of the structure.

Test Measurements. A 20-gage Chromel-Alumel thermocouple was welded to the center of the exterior surface of each test panel and three were freely suspended 5 feet above the surface of the oil in separate sections within the structure. Temperature measurements were recorded by the two General Electric potentiometer recorders, connected by means of rotary selector switches. As the switches were rotated,

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contact was made with the various thermocouples, using a 5-second interval per stop. Details of the structure, arrangement of samples, and the temperature-recording equipment are shown in Figure 4. Photographs also were taken of paint films which actively flamed. In addition, groups of observers were employed to note and record the nature and extent of degradation of the paint film. Systems 1, 3, 6, 7, 8, 9, and 10 were evaluated according to the above procedure.

Results. Figures 5 and 6 illustrate the intensity of the fires to which the samples were subjected. In the initial series, the maximum ambient temperature recorded was 1680° F.; the maximum temperatures on the test panels ranged from 546° to 1057° F. In the second trial, the maximum ambient temperature was 1731° F.; the maximum temperatures from 568° to 951° F. The temperature data obtained on each individual panel are given in Table II. Only the stock white enamel flamed in the determination conducted on paint films less than 5 mils thick (two top coats). In the second evaluation, conducted on paint films whose thicknesses exceeded 5 mils (four top coats), four samples showed flaming. The stock white enamel flamed the most vigorously, the entire surface being involved. Figure 7, panel 3A, taken during the test, shows the intensity of the burning. System 7 (a commercial fire-retardant paint) flamed vigorously along the upper portion of the panel. Figure 8, panel 7A, likewise shows the intensity of the flaming. The entire area of system 9 (a commercial fire-retardant paint) was completely enveloped in flames. However, the flames were weak and flickering and they endured only for 15 seconds. System 1 (standard fire-retardant paint), as represented by panel 2, did not flame continuously, but flashed intermittently following the initial 5 minutes of exposure. Panel 9, likewise painted with system 1, did not flame or flash during this evaluation.

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Thermoelectric Fire Test

Limited use was made of the thermoelectric fire test to check the resistance to burning of the navy paint formulations (systems 1 to 6). The details of the test method are described by Birnbaum and Markowitz (1). This method subjects painted panels to an intense electrical short circuit by passage of a current of 78 volts and 300 amperes for 30 seconds. The panels are closely watched for flaming or flashing of the paint film during this ignition period. The maximum temperature of the panel is approximately 2300° F. The results of tests given in Table III indicate the gray deck (system 2), white enamel (system 3), vinyl (system 4), and chlorinated rubber (system 6) paint films when used with the undercoats employed in this test may flame and thus contribute to the spread of combustion from one compartment to another. System 4 appeared to be much less of a fire hazard than the other three which burned. The remaining systems (1 and 5), respectively standard fire-retardant white and experimental red deck, did not flame and therefore, based on this test, are considered safe for use aboard ship.

Discussion

In the preliminary studies and test determinations conducted within the hanger deck, the temperature on the test panels varied considerably in regard to the maxima recorded and the time at which these values were noted. There was considerable variation also in the ambient temperatures recorded in different parts of the compartment. This variability might have been reduced somewhat if the temperatures of all thermocouples

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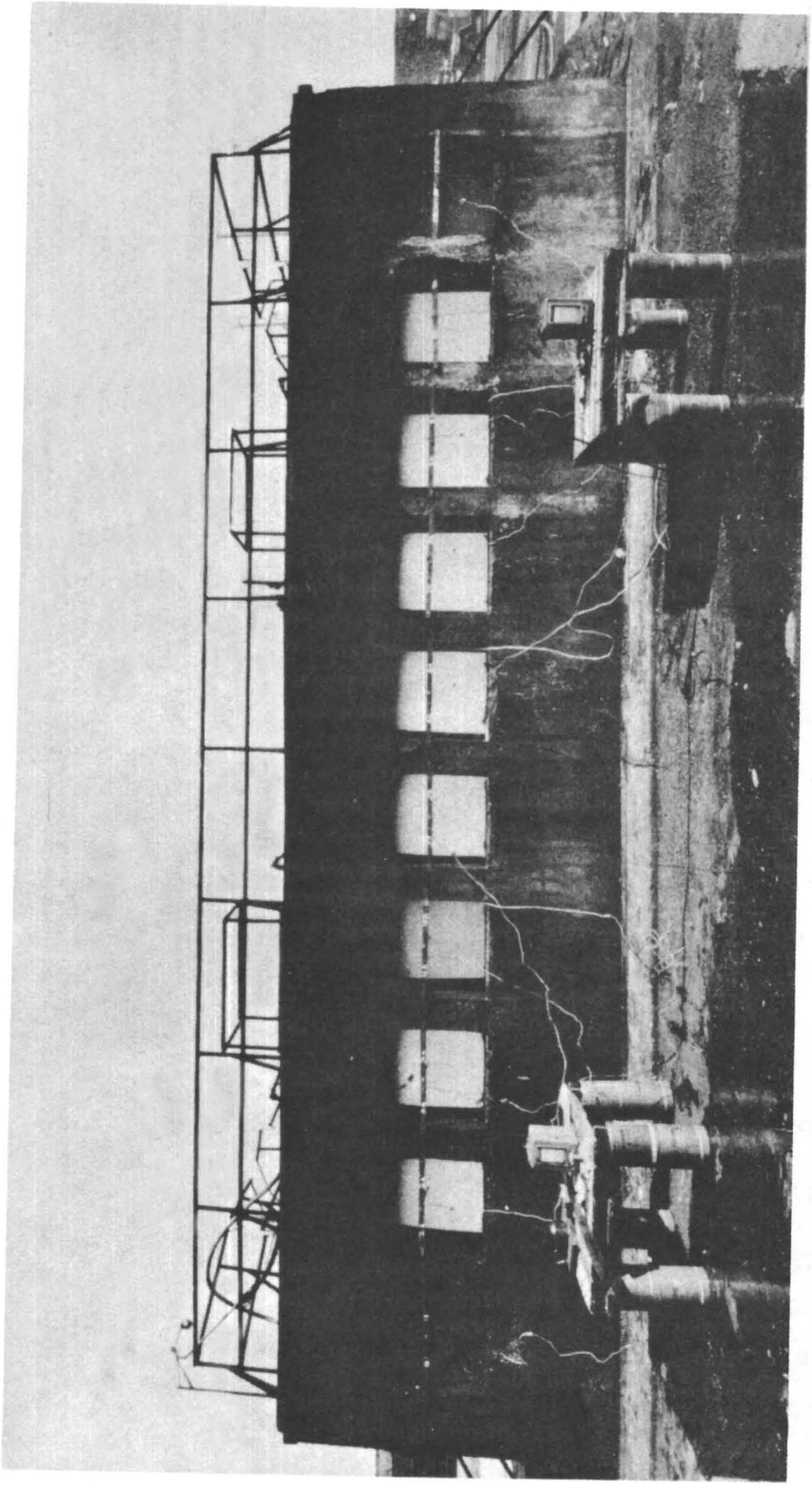

Figure 4. Structure, Arrangement of Samples, and Temperature-Recording Equipment for Tests on Hangar Deck

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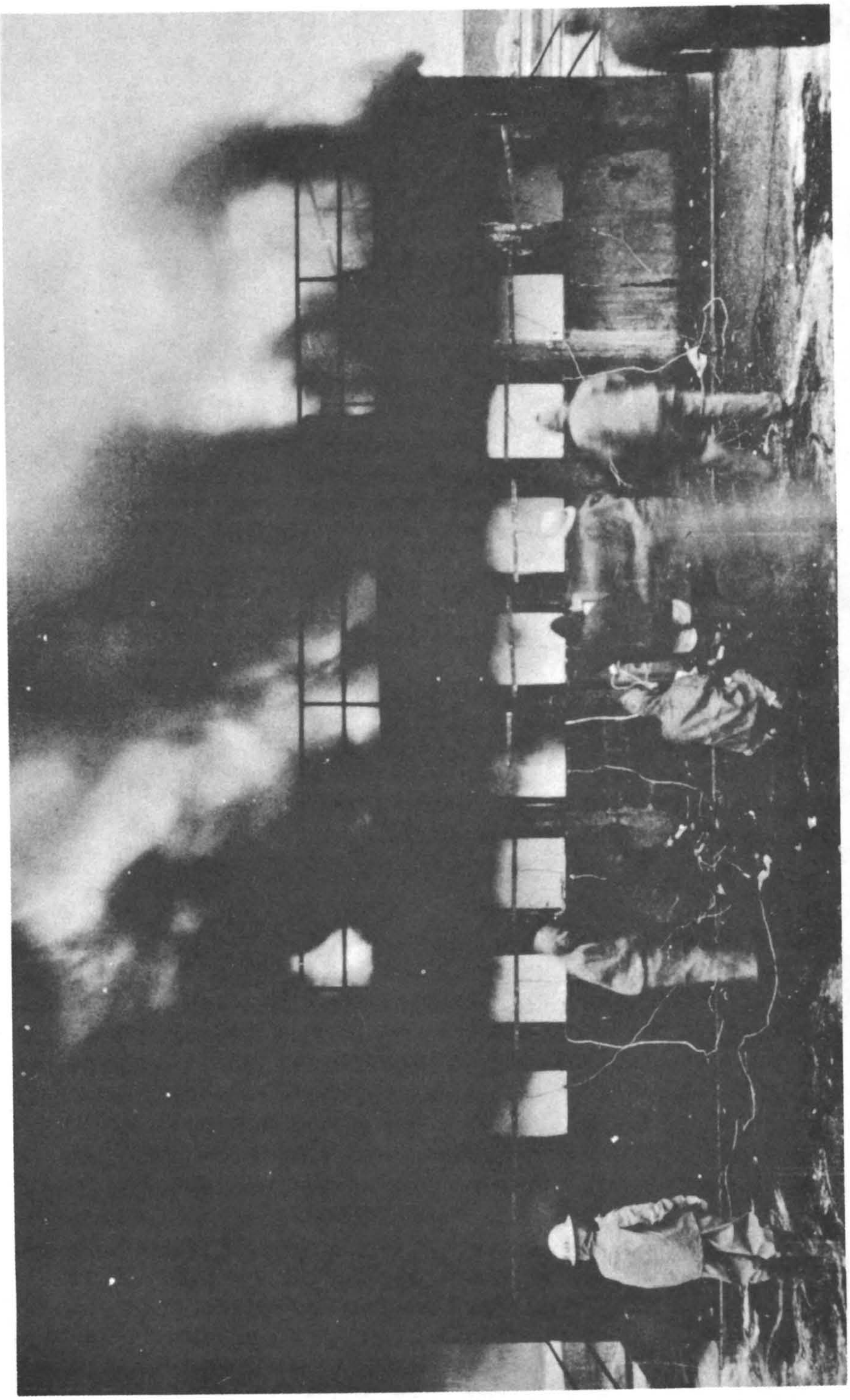

Figure 5. Intensity of Test Fires

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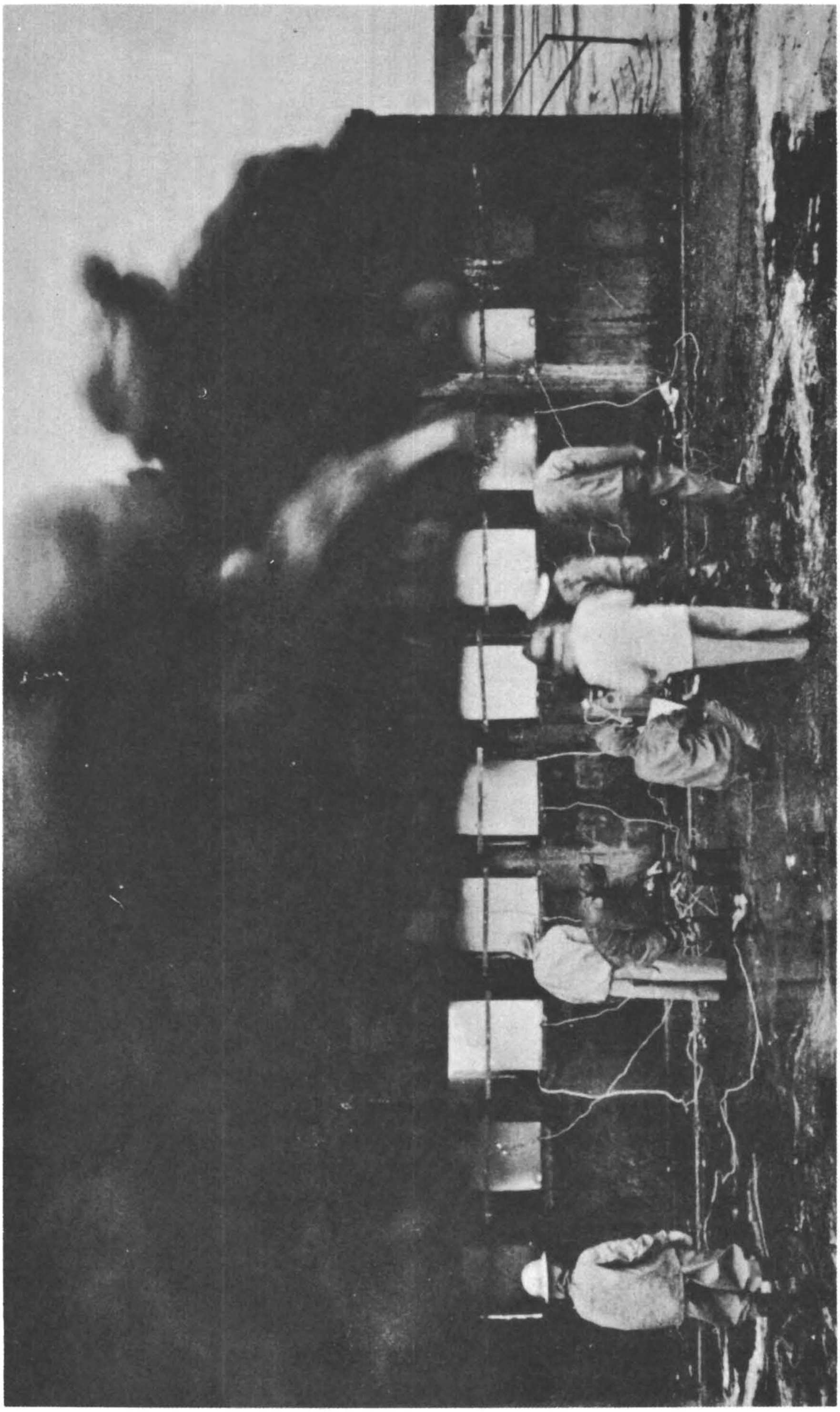

Figure 6. Intensity of Test Fires

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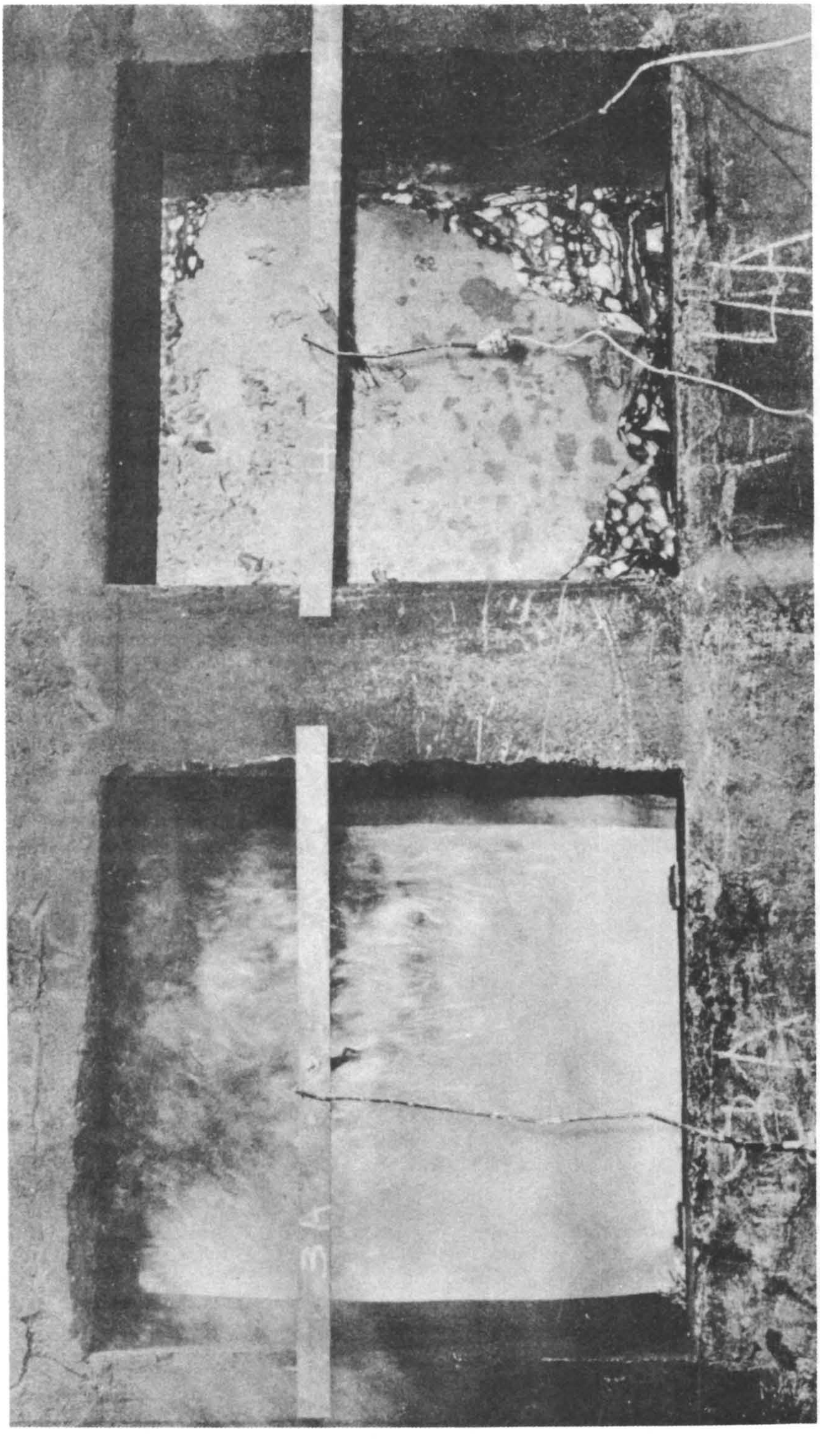

Figure 7. Panel Tests, Showing Intensity of Burning

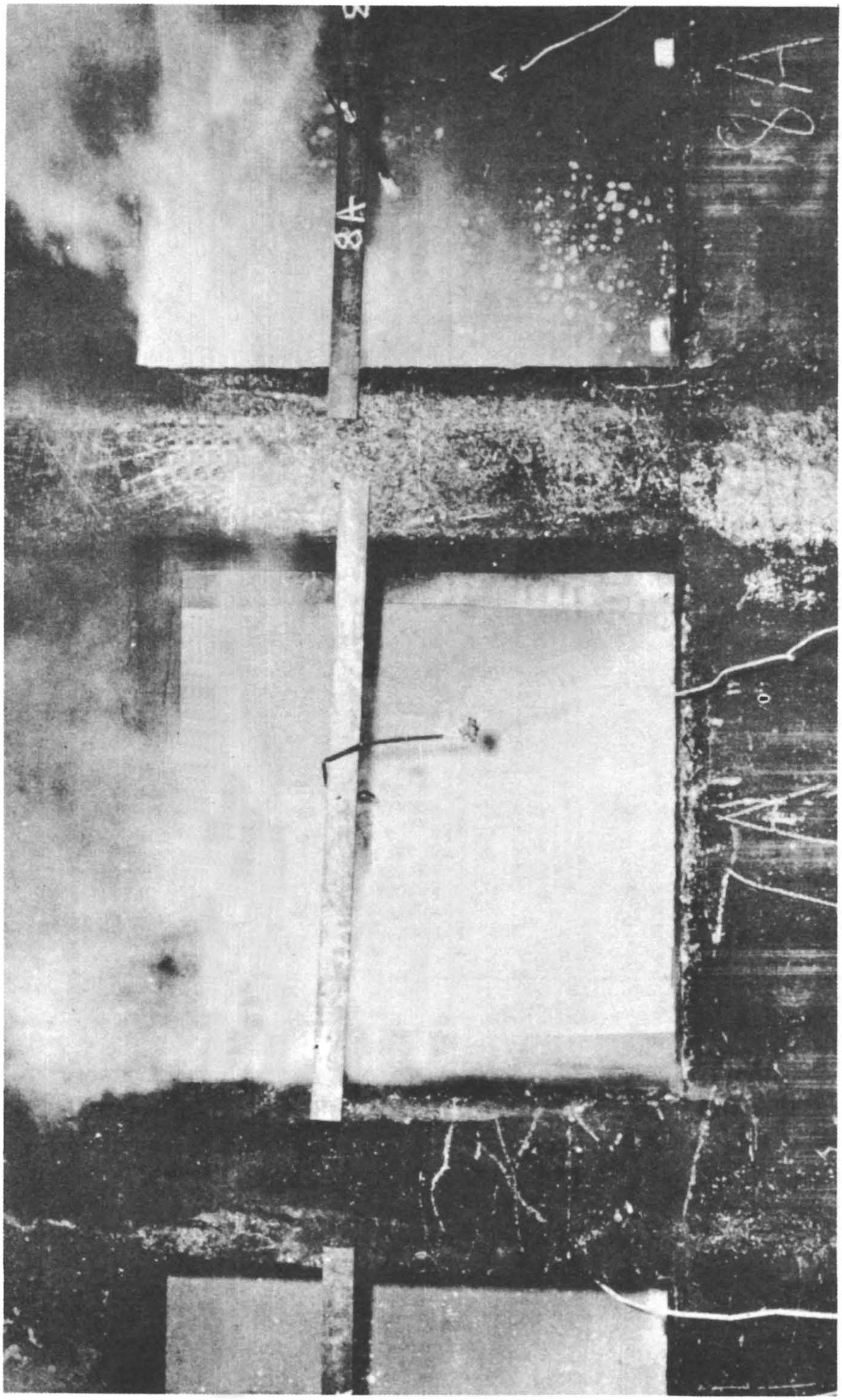

Figure 8. Panel Tests, Showing Intensity of Burning

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Table II. Summary of Tests

Paint System	Blank Plate		1 Stock Fire-Retardant White		3 Stock White Enamel		6 Stock Chlorinated Rubber		7 Comml. Fire-Retardant White	
Porthole Number[a]	1		2		3		4		5	
Determination 1										
Film thickness, mils	----		4.3		4.8		4.1		3.2	
Max. temp. recorded and corresponding time	°F.	Sec.	°F.	Sec.	°F.	Sec.	°F.	Sec.	°F.	Sec.
	256	425	740	430	[c]		589	470	546	445
Observations	----		Paint film blistered. No flaming or flashing observed.		General burning of paint film noted 6.5 minutes after start of exposure.		Paint film blistered and peeled from panel 4.5 minutes after start of exposure. No flaming or flashing noted.		Discoloration but no flaming, flashing, or blistering of paint film.	
Determination 2										
Film thickness, mils	----		7.0		9.1		6.4		5.6	
Max. temp. recorded and corresponding time	°F.	Sec.	°F.	Sec.	°F.	Sec.	°F.	Sec.	°F.	Sec.
	740	395	761	400	632	285	568	410	825	295
Observations	----		Paint film flashed intermittently following exposure of 5 minutes. Film blistered and cracked.		Entire film burned after exposure of 4.75 minutes.		Paint film blistered and peeled 3.5 minutes after start of exposure. No flashing or flaming noted.		Flaming at upper right-hand portion following exposure of 4.5 minutes.	

[a] Numbered from 1 to 10 starting on left facing structure.

[b] Thermocouple wire was torn loose

could have been recorded simultaneously. However, the scope of the test and the limitations of the recording equipment made this impossible. The only remaining assignable reasons for these temperature variations are the uncontrollable draft and burning conditions existing within the structure at the time of the test. These factors are responsible not only for the variations within my one exposure, but also for the difficulty of exactly reproducing a fire or the test results recorded during the fire.

In the trials within the hangar deck, a general decrease in fire-retardancy was noted as the thickness of the paint films increased from 2 to 4 top coats. This was true for all the systems tried, except for No. 8 which retained its fire-retardancy even at a film thickness of 5.5 mils. This general decrease in fire-retardancy with increase in film thickness is in line with normal expectations. System 1, the standard fire-retardant

Conducted within Hangar Deck

8 Comml. Fire-Retardant White 6	9 Comml. Fire-Retardant White 7	10 Comml. Fire-Retardant White 8	1 Stock Fire-Retardant White 9	Blank Plate 10	---- 4[b]	---- 6[b]	---- 8[b]
3.3	3.1	3.1	4.3	----	----	----	----
°F. Sec.	°F. Sec.	°F. Sec.	°F. Sec.	°F. Sec.	°F. Sec.	°F. Sec.	°F. Sec.
867 390	888 325	1057 295	568 335	888 305	1680 270	1663 310	1640 140
No flaming or flashing noted. Film cracked, blistered and peeled.	No flaming, flashing or blistering noted.	Film blistered. No flaming or flashing noted.	Film cracked. No flaming or flashing noted.	----	----	----	----
5.6	5.3	5.5	7.0	----	----	----	----
°F. Sec.	°F. Sec.	°F. Sec.	°F. Sec.	°F. Sec.	°F. Sec.	°F. Sec.	°F. Sec.
825 355	888 325	951 330	888 370	654 305	1376 360	1398 345	1731 280
No flaming or glowing noted. Film blistered, cracked, and peeled.	Weak flickering flames over entire panel lasting for approximately 15 seconds. Film did not peel.	No flaming or glowing noted. Film chipped and cracked.	No flaming or glowing noted.	----	----	----	----

during installation of panel.

[c] Thermocouples measuring ambient temperature within structure in locations behind indicated ports.

white, at a 4-topcoat level, reached the point at which its fire-retardancy was questionable; the fire-resistance of any film thickness over and above that tested (7 mils) would probably be unsatisfactory. Another result to be given particular attention is that obtained with the white enamel, system 2. The thought has been advanced that a fair degree of fire retardancy could be obtained with paints not specifically formulated for that property merely by keeping the film thickness low. The white enamel, system 2, tested at a 2-top-coat level (4.8 mils), exhibited general burning which would have made possible transmission of a fire to an adjacent compartment.

Fire-retardant white paint (system 1), which flashed and flamed intermittently during the second determination, also burned for 20 to 30 seconds during one of the preliminary evaluations. This confirms previous laboratory thermoelectric fire test re-

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Table III. Results of Thermoelectric Fire Test

Paint System No.	Constituents	Specimen No.	Thickness, Mils	Time to Initial Flame, Sec.	Period of Flaming, Sec. During ignition period	Period of Flaming, Sec. Following ignition period	Height of Flames, Inches	Remarks
1	Zinc chromate followed by fire-retardant white	1	3.2	0.0	0.0	0.0	0.0	Surface glowed brightly during test, but no active flaming of the paint film
		2	3.1	0.0	0.0	0.0	0.0	
		3	3.1	0.0	0.0	0.0	0.0	
		4	3.1	0.0	0.0	0.0	0.0	
2	Zinc chromate followed by light gray deck	1	3.0	15.0	15.0	00.0	2.0	Entire center section of paint film lifted off 15 seconds following ignition
		2	3.1	16.0	13.0	0.0	3.0	
		3	3.2	16.0	14.0	2.0	2.0	
		4	3.0	17.0	8.0	0.0	2.0	
3	Zinc chromate followed by white enamel	1	2.7	16.0	14.0	0.0	4.0	Blistered extensively
		2	2.8	16.0	14.0	0.0	3.0	
		3	2.9	15.0	15.0	0.0	3.0	
		4	3.0	16.0	14.0	0.0	3.0	
4	Formula 117 followed by formula P-21 and then formula P-145	1	3.0	0.0[a]	2.0	1.0[a]	1.0	Blistered extensively
		2	3.0	25.0	5.0		1.0	
		3	2.9	0.0[a]	0.0	0.0	0.0	
		4	2.8	0.0	0.0	0.0	0.0	
5	Zinc chromate followed by experimental red deck	1	3.2	0.0	0.0	0.0	0.0	- - - - - - - -
		2	3.3	0.0	0.0	0.0	0.0	
		3	2.3	0.0	0.0	0.0	0.0	
		4	3.3	0.0	0.0	0.0	0.0	
6	Formula 117 followed by formula 84-47 and then chlorinated rubber deck gray shade	1	3.2	17.0	13.0	3.0	4.0	Blistered extensively
		2	3.2	21.0	9.0	2.0	4.0	
		3	2.9	18.0	12.0	2.0	4.0	
		4	3.2	17.0	13.0	2.0	4.0	

---

[a] Momentary flashing

sults, which demonstrated that a film consisting of one coat of chromate primer and five top coats of fire-retardant white will flame following approximately 20 seconds of exposure. However, the important fact to remember and that which justifies consideration of this system as a standard for fire-retardant paint, is that the recommended application of only one top coat over one coat of primer produces a film which, from a practical viewpoint, will not burn. Reports of fires aboard ship in which fire-retardant white as well as other navy paints were exposed have borne out this contention. It is reasonable, therefore, to continue to consider this system as suitably fire-retardant.

A paint technologist who witnessed these tests suggested that the burning of system 1 may have been caused by flaming of the primer, which was not a fire-retardant type. The commercial paint systems which demonstrated fire-resistance superior to system 1 made use of fire-resistant primers.

The desirability of conducting large scale fire tests to demonstrate practical differences among materials, and eventually to set practical limits for standard requirements, cannot be questioned. However, the results of such tests are obviously more variable than the results of laboratory tests, such as the thermoelectric test, where the test conditions can be closely controlled. For example, a given paint film at the same thickness will give the same result when tested again and again in the thermoelectric fire test. This is not true of the large scale fire tests. As demonstrated, one fire-retardant white panel at a thickness of 7.0 mils, when exposed to a temperature of 761° F. at 400 seconds, showed intermittent flashing after being 5 minutes in test (Table III); whereas a second fire-retardant white panel, at a thickness of 7.0 mils, when exposed to a temperature of 888° F. at 370 seconds, showed no flaming or flashing during the entire test period. Large differences in flammability, as between fire-retardant white and white enamel, do not offer the same difficulty in the large scale tests, and it may be assumed that single tests are conclusive. To be strictly conclusive, where minor differences in flammability are concerned, would require some replication of each test. The required degree of replication is unknown at present. Because the present test could not allow sufficient replication, no conclusive evidence can be presented as to whether the present fire-retardant requirement, based on the thermoelectric test, is established at a proper level. There is some evidence that it may be too severe, as the chlorinated rubber paint system failed the thermoelectric test but was free from any flaming in the large scale test.

The chlorinated rubber paint is far superior to the present fire-retardant white in important properties, such as case of cleaning, resistance to staining, corrosion resistance, and retention of original appearance. Since the large scale test gives evidence of satisfactory fire-resistance, some consideration is being given to a sufficient lowering of the thermoelectric test to permit acceptance of the chlorinated rubber paint with careful restriction of number of coats allowed.

Conclusions

The thermoelectric fire tests confirmed the fire-resistance of the navy stock fire-retardant interior white and experimental red deck paints (systems 1 and 5) and demonstrated the flammability of the navy deck gray, white enamel, vinyl-alkyd, and alkyd-chlorinated rubber paints, systems 2, 3, 4 and 6.

The exposures conducted within the hangar deck demonstrated that:

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Even thin films (5 mils) of inherently flammable paints can be ignited by heat transmitted through a bulkhead or deck and thus could serve as a means by which fire may spread from one compartment to those adjacent.

In general, the fire-retardancy of any paint film decreases as its thickness is increased.

The use of one or two top coats of the navy interior fire-retardant white paint over one coat of primer produces a film which from a practical viewpoint will not burn.

Certain commercial formulations approach or exceed the Navy's standard paint in regard to fire-retardancy.

Summation

One means of eliminating fire hazards aboard ship is the replacement wherever possible of combustible materials with those less flammable. Work along these lines has led to the development of fire-resistant paints and appropriate tests to evaluate their fire-retardancy. However, the present performance standards for paints were selected as a matter of necessity with an insufficient background as to what level of performance was actually needed. Currently, the navy fire-retardant interior paint is required to pass a vigorous thermoelectric test. While practical tests and battle-damage reports have shown the paint is in fact fire-retardant, it is not known whether a less vigorous specification requirement might be equally suitable. If this could be shown to be true, an improvement in other paint qualities might be possible without any practical loss of fire-retardancy.

Accordingly, five formulations conforming with existing government specifications, one experimental laboratory fire-retardant paint, and four commercially prepared experimental fire-retardant formulations, were selected for evaluation in large-scale fires conducted in the simulated forecastle and hangar deck sections of the Philadelphia Naval Damage Control Training Center. The paints also were evaluated in a limited series of thermoelectric fire tests. The maximum temperatures attainable in the forecastle without endangering the security of the structure were not sufficient to evaluate realistically the relative flammability of the paints. On the other hand, single exposures within the hangar deck were sufficiently severe to demonstrate conclusively large differences in flammability, such as between the fire-retardant interior white and white enamel. Where minor differences in flammability are concerned, some replication is required, the degree of which is not known at the present.

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Fire-Retardant Coatings for Aircraft Use

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Development of a fire-retardant coating for aircraft use was undertaken by the Wright Air Development Center of the U. S. Air Force for several reasons. A suitable coating could protect valuable personnel by retarding a fire long enough to enable fire-fighting crews to extinguish it. Insulating vital areas of the aircraft from excessive temperatures would make it possible to land safely an aircraft that caught fire while in flight. Equipment used for aircraft maintenance and accessories could be protected to prevent or localize fires originating near the aircraft. This coating could be used on engine nacelles, fuselages, fire walls, fuel cells, vital lines and wires, instruments, and equipment. The fire-retardant-coating should protect aluminum from deleterious effects when exposed to a flame at a temperature of 2000° F. for at least 30 minutes. If of the intumescent or "blanket-forming" type, the critical reaction or decomposition temperature should be not less than 350° F. The coating system should have good adhesion to metal (aluminum, magnesium, and steel). Weight per 100 square feet should be less than 12 pounds. The coating should be flexible and water-resistant and exhibit other good paint properties, and should be suitable for use under flight conditions.

The words "fire-retardant coatings" usually imply paints or coating materials that will slow down or impede the progress of fire. The term as used here refers to a coating system that will not only prevent the progression of fire but also insulate and protect from heat the base to which the coating is applied. The base material is metal, usually aluminum.

The Air Force is interested in the development of a fire-retardant coating suitable for aircraft use. The problem of fire control is ever present on aircraft, which are essentially flying power plants surrounded by tanks of highly flammable fuel, and carrying personnel and cargo.

A suitable fire-retardant coating system could conceivably protect valuable personnel by retarding a fire long enough to enable the fliers to bail out if the plane were in flight. It could enable fire-fighting crews to extinguish a fire before it got out of con-

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trol if the plane were on the ground. By insulating vital areas of aircraft from excessive temperatures, it would be possible, in many instances, to land an aircraft that caught fire while in flight. When an airplane crashes, present fuselage construction provides only a relatively short period of protection to personnel from oil and fuel fires likely to develop from the crash. An aircraft is completely lost after 2 minutes of an uncontrollable fire. The coating system might be used on engine nacelles, fuselages, fire walls, fuel cells, instruments, equipment, vital lines, and wires.

The importance of this development work, although a coating would not eliminate all hazards, is shown by the fact that 80% of the aircraft losses of World War II were due to fire. The fires originated in varied areas of the airplane and were due to varied reasons (usually gun fire and involving fuel). Measures such as self-sealing and purging of fuel tanks aid immeasurably to reduce explosions and fire in fuel-containing compartments. Bomber-type aircraft are most likely to catch fire, and therefore, should receive primary consideration. At present metal fire walls to seal off areas of the aircraft and extensive fire-extinguishing systems are provided; however, fire-retardant coatings are needed to supplement these controls.

Light metal alloys are used in aircraft fabrication and of necessity the minimum quantities are used to meet the designed strength requirements, to conserve on weight. Figure 1 indicates the loss in strength when metals are subjected to indicated temperatures for 0.5 hour. It shows that 75 S-T6 aluminum alloy loses structural strength above 300° F., 24 S-T3 aluminum alloy above 350° F., and FS-1H magnesium above 300° F. The 24 S-T3 aluminum alloy is the metal usually used for structural. members in aircraft construction. For comparison, load-bearing steel will collapse at 1100° F. in less than 10 minutes.

Previous Work

A literature survey,.although very useful, presented no indication of a satisfactory material suitable for aircraft use. Tests at the Bureau of Standards (3) indicate that of paints and materials evaluated in burn-out tests on aircraft fuselage construction, the intumescent coating gave variable performance and in several tests caused more rapid failure than bare metal, due to greater emissivity of the unpainted aluminum metal. In relation to complete failure and the melting of a hole through the aluminum, however, the intumescent paint was the best of the materials used in these tests, although failing at 215 second.

The Forest Products Laboratories (6, 7), utilizing the porosity principle of insulation with a carbonaceous structure, are to be highly commended for their work on fire-retardant coatings for interior use on wood.

The Engineer Research and Development Laboratory (2) has done extensive work on the use of silicones in paint formulations. The insulative qualities of intumescent water-soluble inorganics are maintained with water resistivity (scrub resistance) improved by the use of water-repellent type silicones.

Stilbert and Cummings (10) describe very ably the status of fire-retardant coatings known to industry at the present time. Dow Latex 744B plasticized with Santicizer B-16 was added to a typical intumescent formulation to produce a decided improvement in the scrub resistance of the coatings, if less than 15% latex was used.

A patent (5) describes the basic formulation and theory used in the best fire-retardant coatings developed to date; however, it finds greatest use on wood for interior use.

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No fire-retardant coating has been developed to date by industry suitable for Air Force use on the metal of aircraft.

Kreidl (6) discusses foam glasses and how they may be prepared.

Wood, Houldsworth, and Cobb (11) showed that stable nonvolatile inorganic acids such as boric acid will dissolve silica and enable it to recrystallize in a different allotropic form.

Figure 2, illustrating the relationship of pore size to thermal conductivity at various temperatures, indicates that larger air spaces give better insulation at low temperatures. This principle of porosity should be considered when puffing mechanisms are being investigated.

Requirements

The desired properties of the fire-retardant coating system are:

It should protect metal, especially aluminum, from any deleterious effects when exposed to a flame at a temperature of 2000° F. for at least 30 minutes. Thus, for 24S-T3 aluminum alloy the maximum metal temperature should be 350° F.

If of the intumescent type, the critical reaction temperature should be not less than 350° F; otherwise the material might puff under normal operation conditions.

The coating system should have good adhesion to metal (aluminum, magnesium, and steel).

Weight per 100 square feet should be less than 12 pounds.

Coating should be flexible, water-resistant and noncorrosive and exhibit other satisfactory paint properties to enable its use on aircraft.

The crux of testing will be suitability of the coating system under actual flight conditions. The coating system when applied to a vertical surface must maintain its integrity under operating vibration in the puffed or insulating form.

Tests

The first consideration given to the project of developing a fire-retardant coating was testing methods for screening evaluation purposes. The procedure of Specifications SS-A-118 and TT-P-26 are not adequate for measuring fire-retardancy of coatings for metal surfaces, and therefore, the following test procedures were adopted.

Panels of 24-ST alclad aluminum, 6 x 6 inch 0.032 gage, are coated with the fire-retardant system (only one surface) and placed in the vibrating test rig.

A thermocouple and pyrometer indicate the temperature on the uncoated back of the specimen.

Another thermocouple and pyrometer indicate the flame temperature at the coating surface. The burner setup is designed to apply the desired temperature for the given period of time. For example, a temperature of 1750° F. can be reached in 1 minute and then held constant for 0.5 hour. Figure 3 is a photograph of a typical fire-retardant test setup.

Two types of procedures are followed:

1. A temperature of 1750° F. (or 2000° F.) is reached in 1 minute on the coating surface and maintained for 0.5 hour. The pyrometers indicate the temperature differential (insulative ability of the fire-retardant coating) between the flame temperature and the bare metal temperature. Results should be recorded on a graph indicating time vs. temperature and evaluated on a relative basis.

2. A temperature of 350° F. is maintained on the bare surface of the panel for 30 minutes and the flame temperature regulated. This test indicates the usable limits of the coating system.

Vibration is applied to the more promising test specimens.

Standard tests of water immersion, humidity resistance, corrosion, flexibility, adhesion, and weight are conducted on other specimens of the same coating system.

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Discussion

Air Force contract 33(600)8225 with the American Latex Products Corp. under J. Meyn and G. Morris (8) is designed to aid in the development of a suitable fire-retardant coating. The initial approach involved work on toluene diisocyanate (1); however, emphasis has recently been on ceramic-type coating systems. The contract work indicated that although the isocyanates when puffed gave excellent insulation, other factors restricted their use. Hydroxy ions used as the mechanism to cure the puffed isocyanate resins are very difficult to control and the reaction is sensitive. This plus the cyanide toxicity factor indicated that the material could not be satisfactorily used for aircraft application. Epoxy resins puffed and then cured with ammonia (from amines or urea) should be investigated along with ceramics. A puffed epoxy resin produces the same type of closed pore structure that was developed in the isocyanate reaction and the reaction is controllable. Even though the puffed epoxy melts at between 300° and 400° F., when used under the ceramic top coat insulation is still maintained. The ceramic materials now being investigated should also puff and give the extreme insulation and high temperature resistance required.

Although only a small number of experiments are reported here, hundreds of materials have been used both individually and collectively. The desired fire-retardant coating for aircraft use has not been developed, and extensive work must yet be accomplished. The basic variables to be considered are:

Inorganics for insulation and high temperature resistivity, such as oxides, silicates, borates, phosphates, and sulfates.

Binders or organic vehicles to hold ingredients together and offer the paint properties required, such as resins and latexes.

Puffing agents or materials which decompose at elevated temperatures to gi off water, ammonia, carbon dioxide, or similar gas.

Data

A typical intumescent coating formulation which gives fire-retardancy is as follows:

	Parts
Monoammonium phosphate	61.6
Boric acid	1.8
Starch	7.3
Gum tragacanth	0.9
Titanium-barium pigment	3.6
Urea	13.7
Paraformaldehyde	11.1

Figure 4 shows the insulative ability of the above formulation. Three coats were applied over a primer to a total dry film thickness of 20 mils, allowing 24 hours' dry time between coats. This graph indicates complete failure in 8 minutes. When subjected to other tests the coating lacked adhesion to metal, moisture resistance, and flexibility. After, puffing, the coating disintegrated under vibration.

Figure 5 illustrates the same system and indicates the insulation of 650° F. for the next 15 minutes.

Figure 6 indicates the time vs. temperature of an uncoated panel using a thicker gage of 24-ST aluminum.

Upon studying the preceding formulation with the many possible modifications it becomes evident that several approaches for improvement should be undertaken simultaneously: Silicones should be introduced into the formulation; a new binder must be used; and a new system based on ceramics should be undertaken.

Various silicone-type dispersions were introduced into the formulation in varied amounts with only limited improvements. In general, the silicones decreased the puffing ability, increased water resistance, and embrittled upon high heat when used in beneficial amounts.

Experimentation on a new binder led to the development of the following formulation:

	Parts
Monoammonium phosphate	35.5
Boric acid	35.5
Starch	9.0
Magnesium silicate	9.0
Specification MIL-R-3043 phenolic resin (solids)	11.0

This formulation offered good adhesion and flexibility with fair water resistivity. Figure 7 indicates 1450° F. insulation for 0.5 hour by a 1/8 inch coating. When 22 parts of Dow Corning silicone resin 801 were added to the preceding formulation, a 1/8 inch coating (Figure 8) indicated insulation of 1480° F. for 0.5 hour. The coating withstood vibration in the puffed condition.

A formulation involving Epon resin 1009 was similar to the Figure 7 coating; however, a bake of 140° F. for 48 hours was required.

The ceramic approach which appears the best to date because of versatility of composition as well as fire-retardancy is illustrated by the formulation which follows. In future modifications of the recipe, the sodium silicate will be replaced by an insoluble constituent, such as a silicone.

	Parts
Zinc orthosilicate	10
Feldspar	10
Aluminum powder	3
Alumina hydrate	3
Wetting agent (Prosol 180)	5
Asbestos, finely ground	10
Silicate of soda (to enamel consistency)	
Lead carbonate	50
Wetting agent (Prosol 180)	3
Silicate of soda to (enamel consistency)	

Four coats of the above were applied, with the second coat consisting of the lead carbonate portion. Figure 9 indicates that a 3/64 inch film will give 1000° F. insulation. The adhesion of the coating was good, but the silicate of soda caused poor flexibility and water resistance.

Summary

No fire-retardant coating now available is suitable for use on the metal of aircraft. Much work is still required to perfect the coatings described. Throughout this development work industry will be kept informed of Air Force developments. The Air Force would appreciate receiving samples and factual data of newly developed coatings that might be suitable for aircraft use. Contact concerning this project can be made at Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

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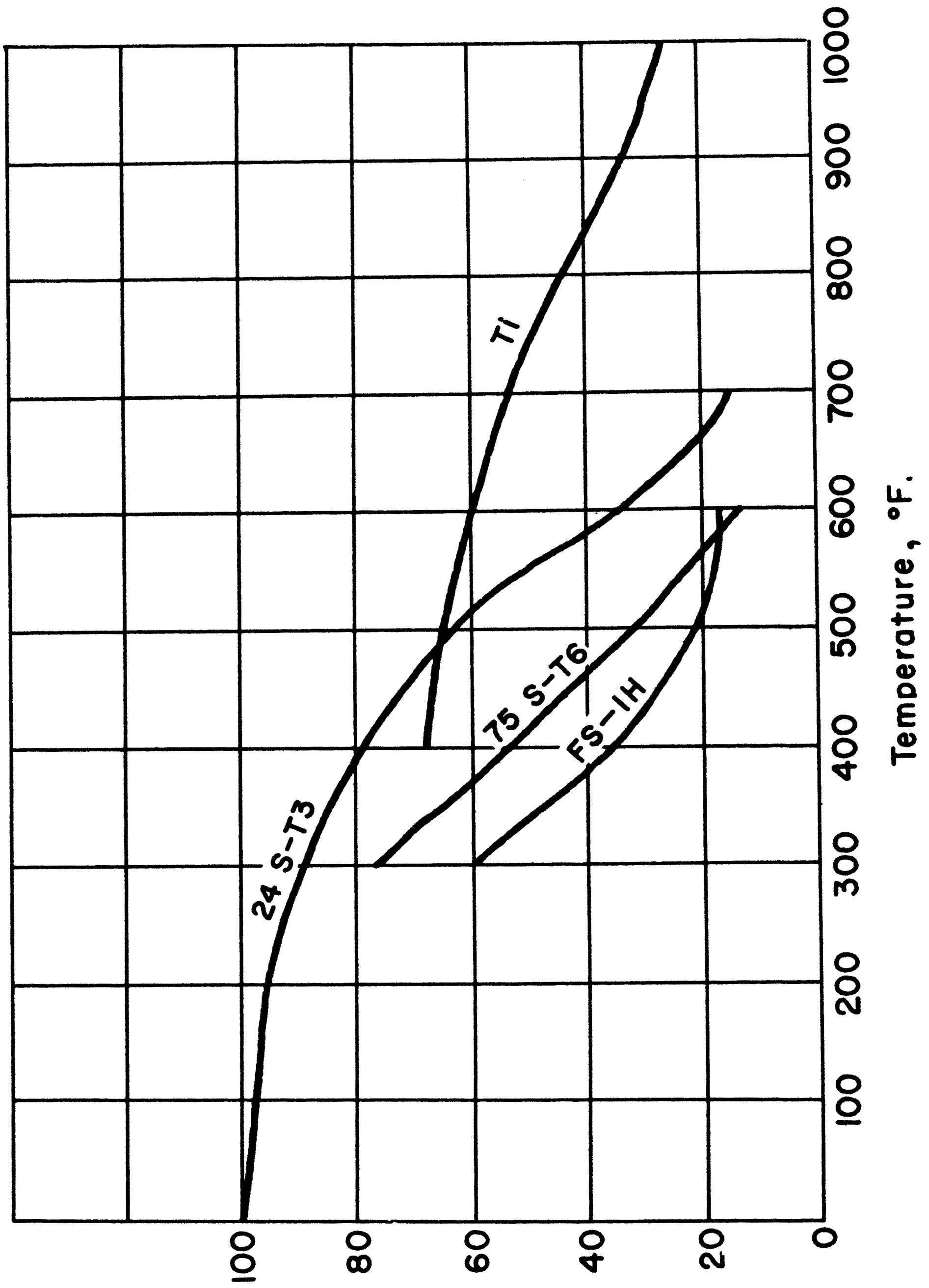

Figure 1. Per Cent of Initial Ultimate Tensile Strength Held at Temperature for 0.5 Hour

Ultimate Tensile Strength at Room Temperature, Lb./Square Inch

Aluminum	24S-T3	62,300
	75S-T6	72,200
Magnesium	FS-1H	41,200
Titanium		102,700

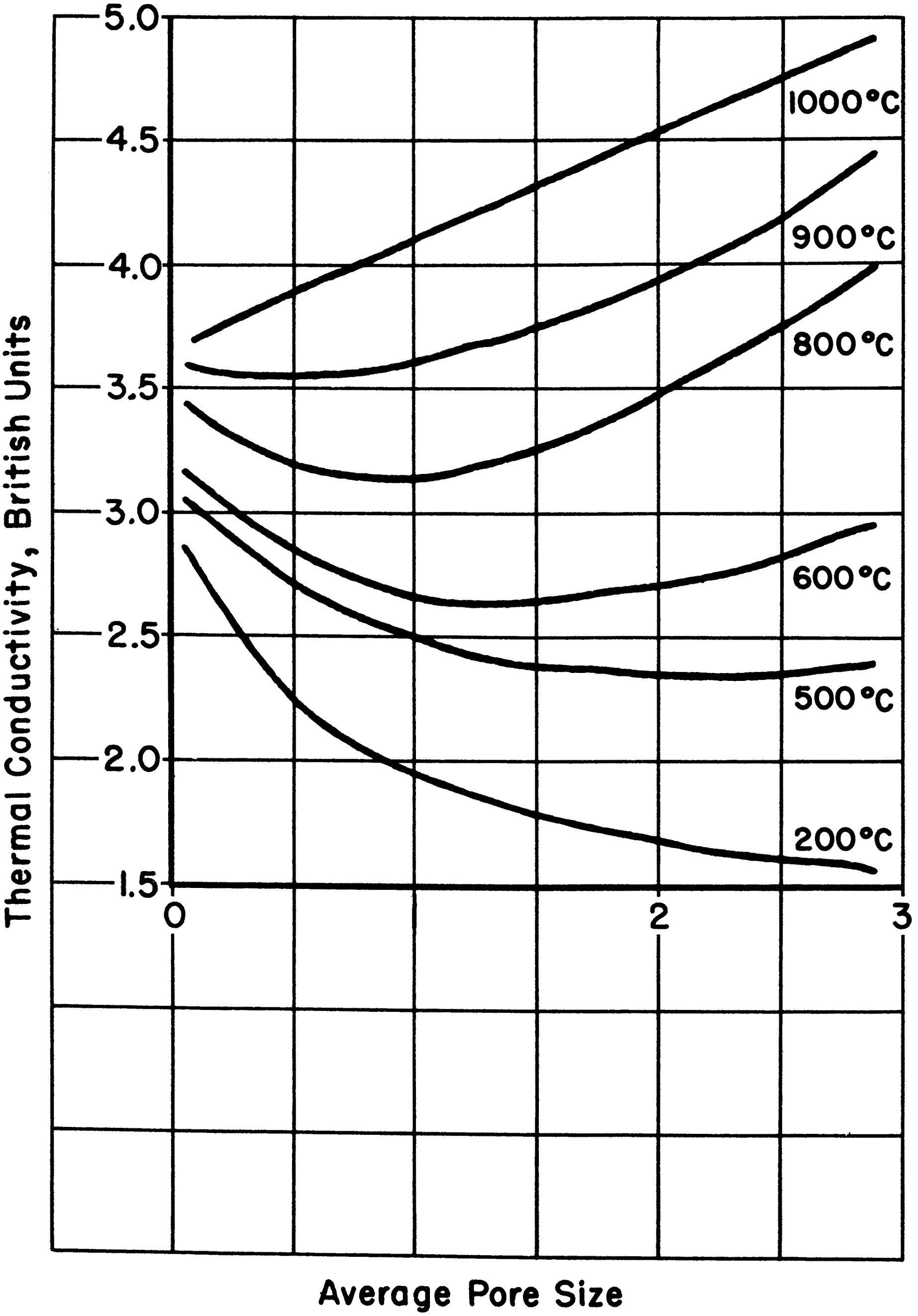

Figure 2. Pore Size vs. Thermal Conductivity

Minimum conductivity attainable with pore of different size according to Clements, Vyse, Rigby

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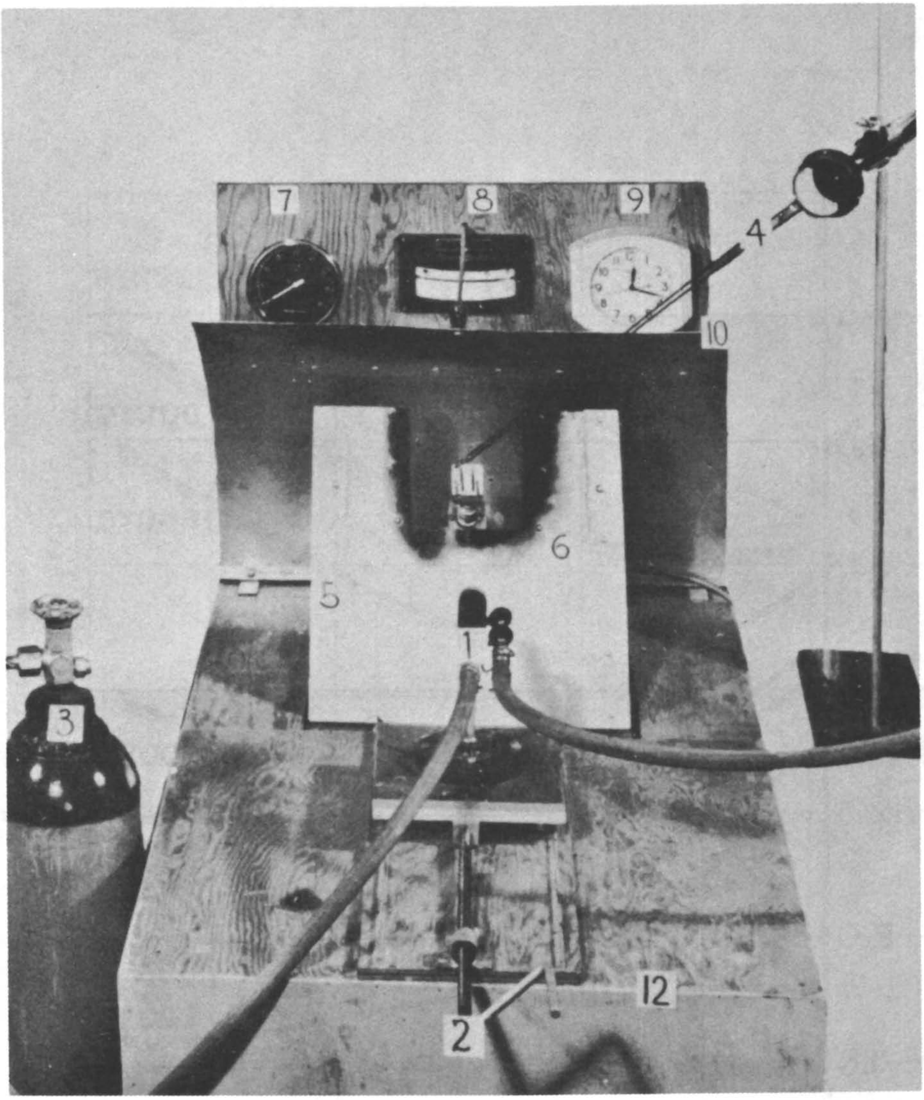

Figure 3. Typical Fire-Retardant Test Setup

1. Burner on slide
2. Slide
3. Oxygen
4. High temperature pyrometer with thermocouple
5. Vibrating rig for holding panels
6. Space for 12 x 12 inch panel if desired
7. Tachometer indicates vibration frequency
8. Pyrometer for bare surface (thermocouple in contact with test specimen)
9. Clock
10. Flame shield

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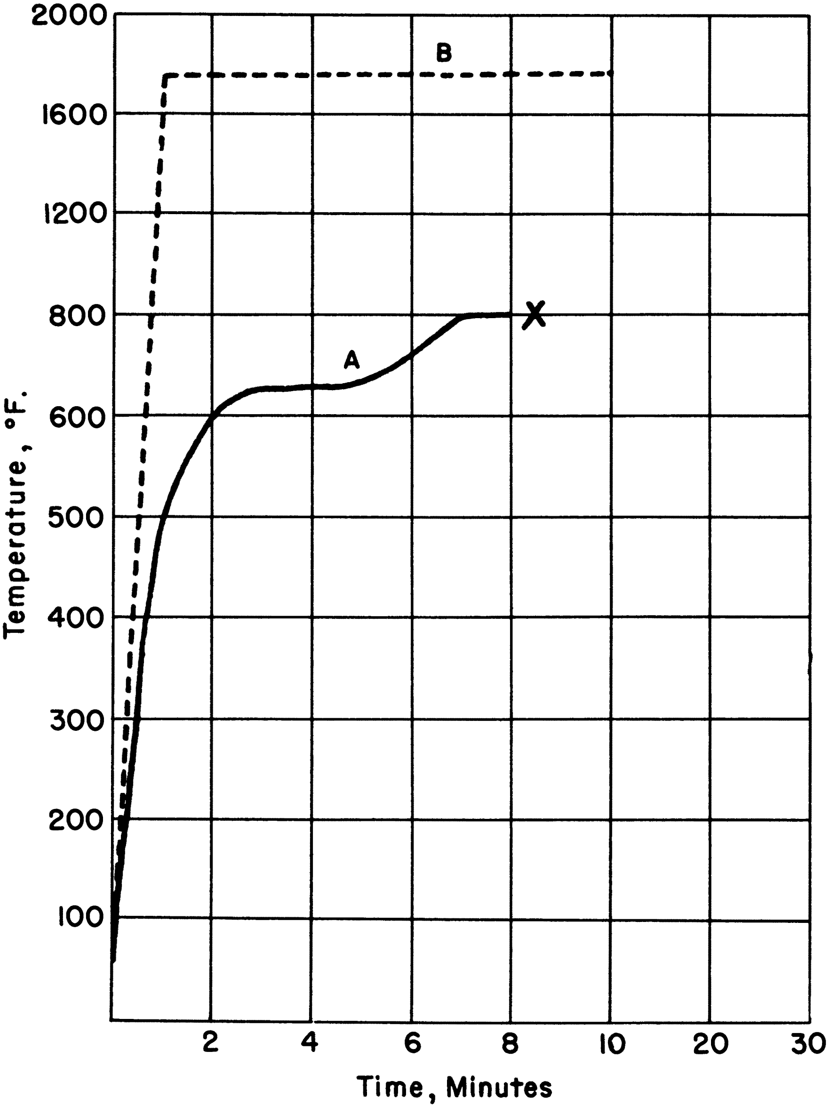

Figure 4. Insulative Ability of Typical Intumescent Coating

A. Temperature of bare side of panel
B. Temperature of flame on coated side of panel

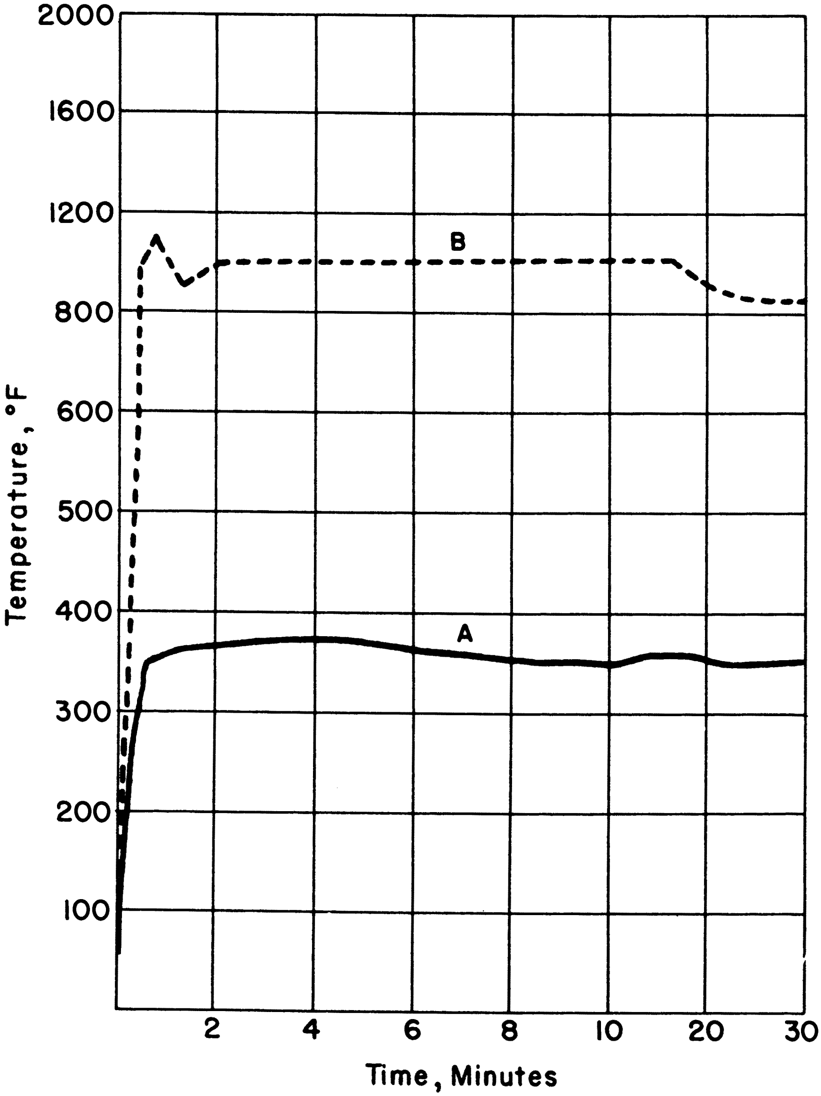

Figure 5. Insulative Ability of Typical Intumescent Coating

A. Temperature of bare side of panel
B. Temperature of flame on coated side of panel

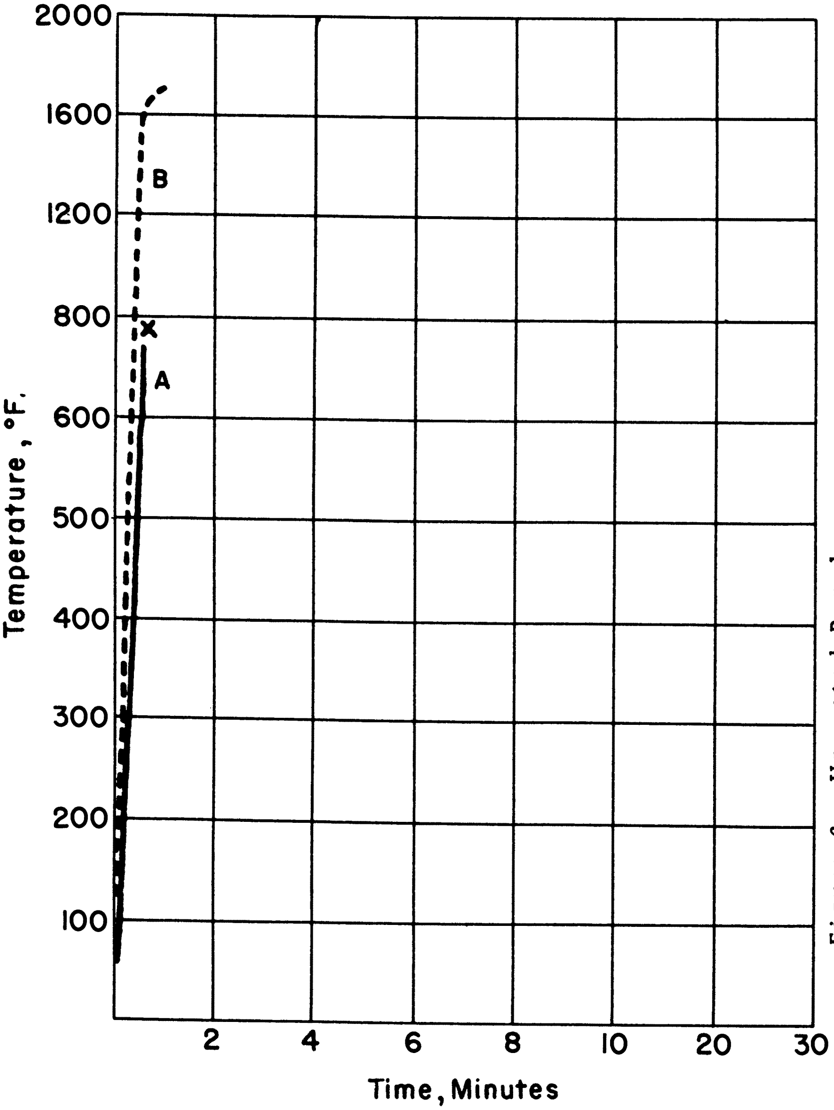

Figure 6. Uncoated Panel

Panel 0.051 inch, unable to graph 0.032 inch

A. Temperature of bare side of panel
B. Temperature of flame on coated side of panel

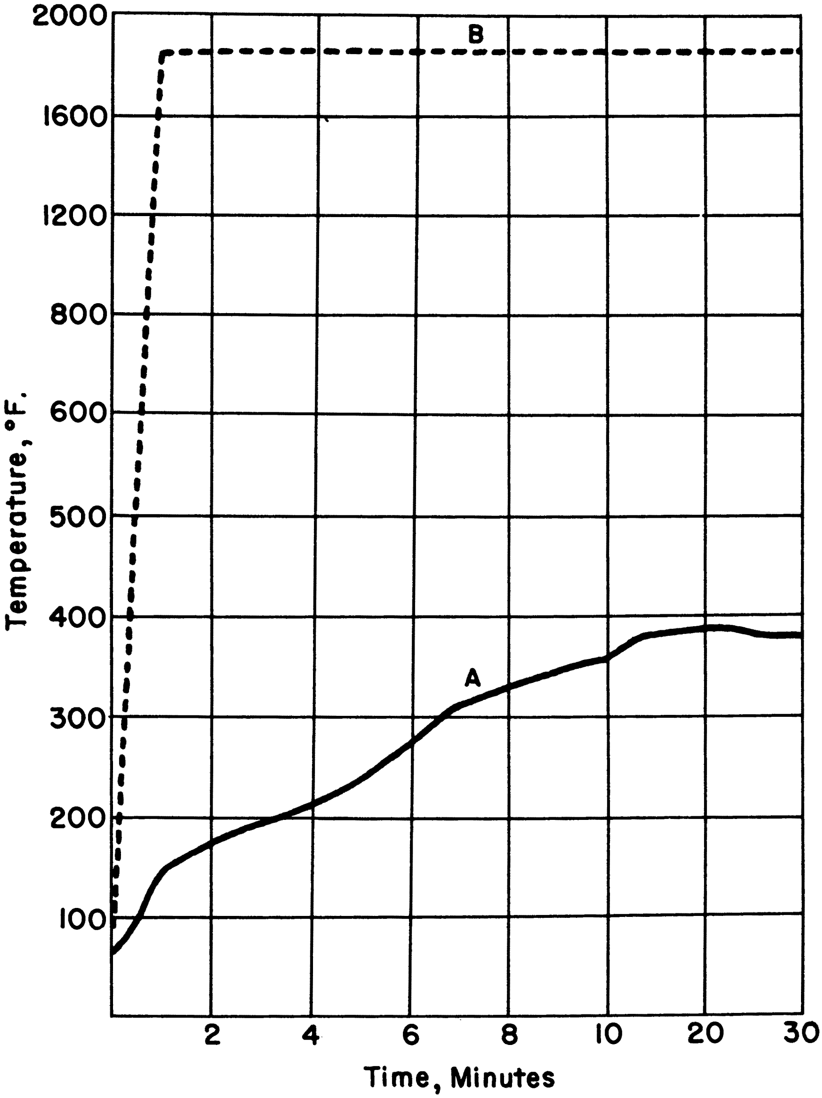

Figure 7. Insulative Ability of Coating with New Binder

A. Temperature of bare side of panel
B. Temperature of flame on coated side of panel

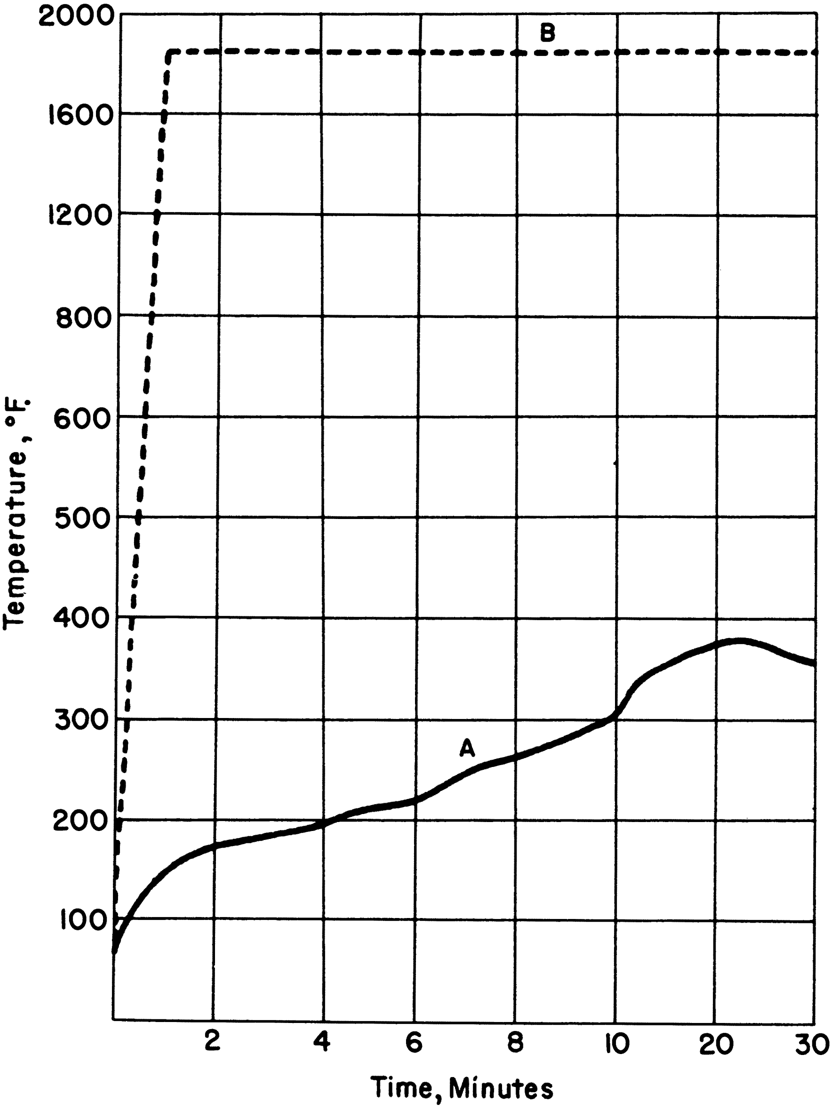

Figure 8. Insulative Ability of Coating with Silicone Resin

A. Temperature of bare side of panel
B. Temperature of flame on coated side of panel

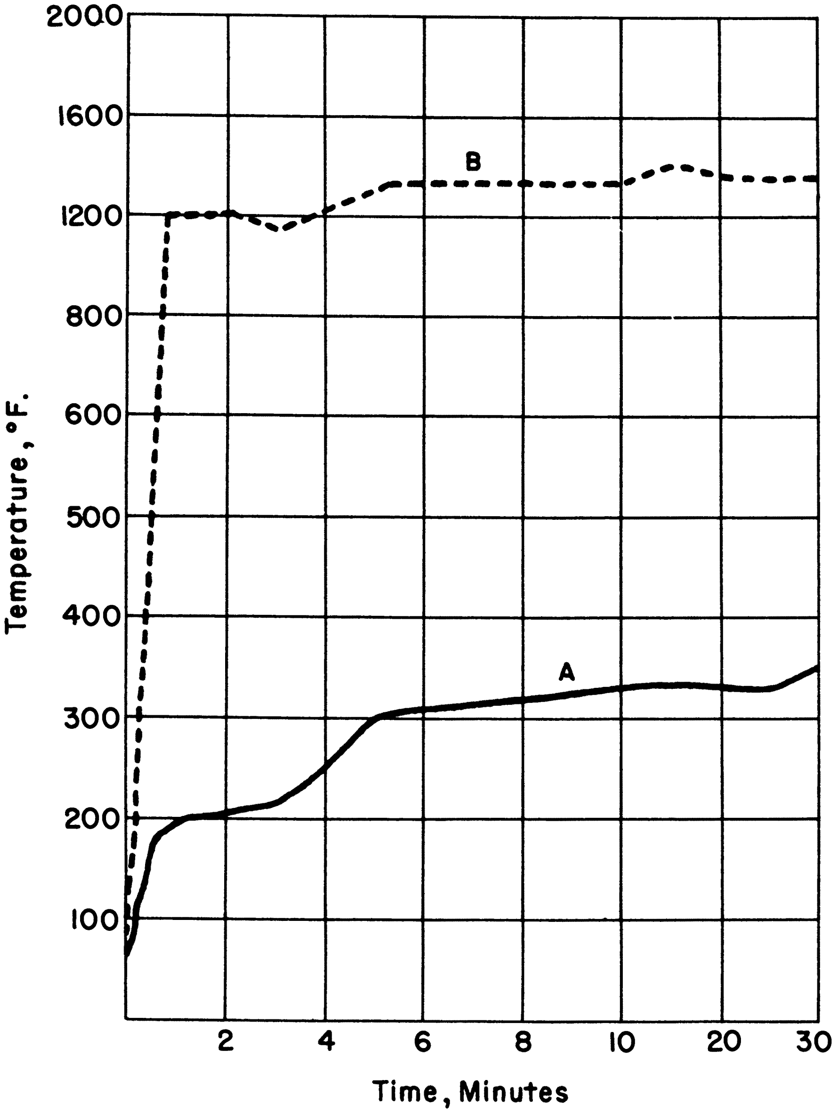

Figure 9. Insulative Ability of Coating (Ceramic Approach)

A. Temperature of bare side of panel
B. Temperature of flame on coated side of panel

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Advances in Chemistry; American Chemical Society: Washington, DC, 1954.

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High Heat- and Flame-Resistant Mastics

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Resinous mastics of low thermal conductivity and high temperature flame resistance may be used in contact with direct flame temperatures as high as 5400° F. to prevent metal from losing structural strength. Formulations are influenced by the nature of the substrate, their function, and the degree of protection not only against fire but also the elements to which the coatings may be exposed. Supplementary materials such as fiber glass mats, woven glass fabrics, or expanded metal may be used.

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Uncontrolled fire is one of the most destructive forces which man must combat. In 1951, direct losses from fire reached an all-time level of $730,000,000. Indirect losses in business, taxes, and revenue would be at least three times this amount. Fire killed over 12,500 people and injured many thousands more. In time of war the losses are inestimable. In spire of these extraordinary losses to life and property, very little advancement has been made in reducing fire through the application of fire-resistant coatings. In view of the fact that World War II was termed by some a war of fire, and the impending one would be even more so, a well-organized program for the study of fire-resistant coatings is logical and imperative. The present available knowledge is meager and the intensity of pursuit very small in relation to the potential market and its benefit to man.

Fire

Fire may be defined as a chemical process called oxidization. When the oxidization is so rapid that it is accompanied by a flame, it is call combustion. To start combustion, heat is required. The degree of temperature at which any substance will catch fire is called the ignition point, which, of course, varies with the condition of the substance, the pressure of the air, and the movement of the air. A fire will be self-supporting only when the temperature created by the combustion of the burning substance is as high as or higher than its ignition point. The heat of a fire depends upon the speed with which the chemicals combine with the oxidizing agent.

There are two kinds of fire, with and without flame. The presence of a flame always indicates that the heat has forced a flammable gas from the burning substance, and that this gas in turn combines with oxygen in the air. A substance is called flammable when it can be ignited in the air under ordinary circumstances. The luminos-

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ity of the flame is due to the presence of carbonaceous particles heated to incandescence, usually associated with incomplete combustion. A fire without flame is illustrated by the glow of the paper of a burning cigarette. The oxygen combines directly with the carbon.

Terminology

"Flame-retardant" conveys the meaning of slowing up of combustion, whereas "flame-resistant" means that some change in physical state takes place, but no self-combustion or spread occurs once the igniting source is removed. This paper is concerned not only with preventing fire of combustible materials, but also preventing physical changes in incombustible matter due to high temperatures resulting from the fire. Thus, at a temperature about 750° F. structural steel becomes progressively a weak material. At 950° F. ordinary steel has only 40% of its strength at 70° F. Buildings constructed of such steel can collapse from the heat of the fire. The word "heat-resistant" is used in this relation. Heat-resistant, therefore, as used here refers to the thermal conductivity of the fire-protective medium, the mastic.

The protective medium against fire discussed here is a water-insoluble mastic. Mastic is defined as a material of heavy paste consistency which can be applied with a putty knife, trowel, brush, or heavy duty spray equipment to yield a coating from 1/32 inch to one inch or more. These mastics are of mineral composition, bound by an organic resinous medium, and dry to ultimate hardness by the volatilization of an organic solvent. They are further characterized by high impact strength, and assistance to abrasion, water, and many chemicals.

Theories Underlying High Temperature Flame Resistance

A number of theories may be considered to explain the phenomena which occur to the fire-resistant coating during the course of the fire. The following theories are considered in this paper: gas theory, thermal conductivity, "breathing" or gas permeability, endothermic changes, and fusion. In actual practice, more than one of these theories is involved. All may occur if the fire is of long duration, accompanied by high temperatures.

What are the temperatures attained by a fire? According to the National Fire Protection Association(4):

> The acceleration of combustion with increase in temperature produces progressively higher temperatures, but then there are practical limits to the temperatures produced in fires, due to a combination of several factors. As temperatures increase, heat is dissipated by radiation, which increases as the 4th power of absolute temperature, a greater proportion of the heat goes into heating up of the nitrogen in the air and other inert materials in the fire area, and there is a theoretical limit to flame temperature. Flame temperature in fire may range between 3000° and 5000° F. but the effective temperatures as measured by the melting points of metals and other heat effects have a practical upper limit of around 3000° F. and are usually lower.

Gas Theory

A fire can exist only when all of the three factors that cause a fire are present at the same time -- fuel, an oxidizing agent, and a temperature sufficiently high to maintain combustion. The oxidizing agent with which this discussion is concerned

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is oxygen as supplied by the air. Removal of any one of these three factors will extinguish a fire.

The objective of this postulate is to dilute the oxygen in the area of the fire with inert gases to such an extent that the ratio of this mixture with flammable gases emanating from the combustible substrate (fuel) is below the limits of combustion. Oxygen may be diluted by the evolution of nonflammable gases which result from the decomposition of the ingredients of the fire-resistant mastic under fire conditions.

Effective gases which can be generated from the fire-resistant mastic are hydrogen chloride, ammonia, carbon dioxide, sulfur dioxide, and steam. The first two gases are generally obtainable in effective quantities from the decomposition of resinous binders, for example, the chlorinated polymers and the amide resins. The last three gases are normally obtained from mineral fillers in the mastic. thus the carbonates of calcium, magnesium, zinc, and zirconium are a source of carbon dioxide; the sulfates of these metals yield sulfur dioxide; while the water other than that resulting from combustion is derived from the water of crystallization of such hydrated minerals as asbestos and vermiculite. The components for the fire-resistant mastic are selected on the basis of quantity of available gas, decomposition temperature, and ease of rate of gas release. A rapid gas evolution should take place at the temperature in the vicinity at which the combustible materials yield the greatest quantity of flammable gases. For cellulosic products this is estimated to be at about 400° to 700° F.; therefore, the gases for dilution should logically come from the organic binders.

There are some facts to support a theory that effective quenching gases can be formed from the high temperature reaction products of the mastic, as, for example, hydrochloric acid and antimony oxide to form antimony oxychloride. The Department of the Army, Office of Quartermaster General (*1*), reports that combination of antimony oxide and hydrochloric acid at flame temperatures is more efficient in extinguishing a fire than either component alone.

Thermal Conductivity Theory

The objective of this theory is to insulate the combustible substrate (fuel) from attaining igniting temperature. The mastic becomes the thermal barrier for conductivity of heat of fire. It can accomplish this in two ways: through rapid conductivity of the heat away from the fire, as illustrated by the wire gauze over the Bunsen burner, through very slow thermal conductivity as exemplified by a fire-insulating brick.

High heat conductivity works well if the area over which the fire is impinged is a small part of the total. The low heat-conductive mastic has proved more feasible on a fire over the total area. In order to accomplish low heat conductivity the mastic binder itself must be a poor conductor of heat and preferably nonflowing at high temperatures. The mineral components are selected on the basis of their low k value, the coefficient of thermal conductivity as derived from the following equation:

$$\text{Rate of flow, B.t.u. per hour} = \frac{k(t_1 - t_2)}{d} \times \text{area in square feet}$$

where t_1 is the high temperature and t_2 is the low temperature in degrees Fahrenheit and d is the thickness in inches of the material. Thermally expanded minerals such as perlite and vermiculite, or naturally porous minerals such as diatomaceous earth

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and asbestos, may be employed as components of the mastic. Their efficiency is determined by their k constant, apparent bulk, specific gravity, and other properties which may be necessary to form a good mastic.

Theory of Breathing or Gas Permeability

The objective of this postulate is to control the expulsion of the fuel gases, so that the ratio of fuel gas to oxygen is below the limits of combustion. This is accomplished by formulating fire-resistant mastics through which the fuel gases will permeate or breathe. A "breathing" mastic can be attained by keeping the binder to the minimum. The porosity can be further increased during the course of the fire by the decomposition or phase changes. A breathing mastic is desirable to prevent blister formation or separation of coating from the protected surface.

Endothermic Theory

The objective of this theory in relation to fire is to dissipate the heat of the fire and retard the combustible substrate (fuel) from reaching the ignition point.

This concept presumes that the calorific input of the fire may be partly absorbed by the endothermic changes of the mineral substances employed in the formulation of the mastic. Thus, for example, such latent heat as the heat of fusion, heat of vaporization, heat of sublimation, and heat of transition (the heat required to change a unit mass of a given substance from one crystalline structure to another) all can absorb considerable energy which would otherwise be used to raise the combustible substrate to an ignition point. The efficiency of these fire-resistant minerals can also be adjudged by their specific heat values.

Fusion Theory

The objective of this postulate is to prevent the combustible substrate (fuel) from attaining the temperature of ignition. This would be accomplished by the gradual formation of a new inorganic thermal barrier of low heat conductivity to replace the original resinous mastic. The new thermal barrier would be on the order of a sintered or bloated structure, as exemplified by coke or pumice. The bloating effect can be attained through the use of minerals which tend to expand with heat, as, for example, unexpanded vermiculite. The sintering effect is attainable through the use of low fusion components, as, for example, glass fibers, "frits" as used in the ceramic industry, and other low-melting-point chemicals which may also assist in bloating. In a composition which is based on a utilization of many theories as well as on obtaining a balance of properties, both sintering and bloating may be possible.

Composition Materials of Fire-Resistant Mastics

The binder of a mastic is an organic resin dissolved in an organic solvent. A desirable resin is one which is fire-resistant and decomposes by evolution of gases which are preferably inert and nontoxic, and of maximum heat resistance. Some classifications of fire-resistant resins are:

1. Vinyl halogen polymers and copolymers
2. Halogenated natural rubber
3. Halogenated synthetic rubber

4. Halogenated naphthalene
5. Halogenated diphenyls
6. Halogenated hydrocarbons
7. Polymerized chloroprene (2-chloro-1,3-butadiene)
8. Amide-aldehyde resins

The plasticizers for these materials would be:

1. Esters of phosphoric acid
2. Halogenated mineral oils

The efficiency of halogenated materials depends upon their volatility at flame temperatures, halogen content, and the ease and rate of decomposition of the quenching gas. Gas releases can be regulated to a degree through the use of stabilizers for the product. Generally the straight-chain hydrocarbon resins release the halogen acid more readily than the aryl type. The commercially available halogenated products are principally of the chlorine family and a few of the fluorine group.

The filler composition of the mastic is generally a mixture of many materials, each one employed with a definite objective. The compositions of these materials vary with the source of supply; therefore, physical constants are difficult to compare. All materials are classified in this paper with respect to the properties in attaining a fire-resistant coating based on the theories disclosed.

Some of the minerals which are endothermic, chiefly because of their water of crystallization or by decomposition and evolution of gases, are:

A. Gas-evolving material
   Calcium carbonate (whiting or chalk)
   Magnesium carbonate
   Dolomite
   Zinc carbonate
   Barium sulfate
B. Water of crystallization materials
   Asbestos
   Vermiculite
   China clay

Some of the minerals which are of low thermal conductivity are illustrated by the following table.

Material	Density, Lb./Cu. Foot	Mean Temp., °F.	K[a]	Authority
Asbestos	23.			
Fiber	23.9	122	0.798	Groeber
Long fiber	18.3	50	0.499	Randolph
Diatomaceous earth-powder	10.6	86	0.30	Bureau of Standards
Mineral wool	8.6	103	0.27	Bureau of Standards
Glass wool	1.5	75	0.27	J.C.Peebles
Vermiculite	5-10	70	0.48	Heating and Ventilating Handbook

[a] K = B.t.u. /hr./sq.ft.(°F./ft.)

Illustrations of vitreous types of materials for the fusion theory are:

Glass fibers of various compositions
Frits of various compositions
Lead silicates
Borate compounds

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Examples of useful flame-resistant pigments are:

- Antimony oxides
- Antimony sulfide
- Arsenic oxide
- Bismuth oxide

Antimony oxide is commonly used because of its commercial availability and low cost.

Formulation of Fire-Retardant Mastic Coatings and Application Methods

Each fire hazard must be fully analyzed, and then the fire-resistant mastic is formulated accordingly. Important points which must be considered are the fire classification, the nature of the substrate, the conditions surrounding the fire hazard, and other protective properties it must possess in order that its fire-resistant properties will not be destroyed by chemical factors such as water or weathering, or by physical factors before or during the fire. In some instances, an extra demand is placed on the formulator, that the coating should not be removed by the pressure of the water used in extinguishing the fire.

When the desired properties are not attainable through the composition of the mastic alone, it becomes necessary to supplement the mastic with other fire-resistant materials and engineering knowledge. Supplementary materials which can be used in conjunction with the mastic are (1) products of fiber glass such as fabric, mat, and fiberboard, (2) expanded metal wires of various kinds, and (3) stud welding of rods, split rods, etc. The fiberglass products may serve as supplementary thermal barriers or used as laminates to reinforce the mastic. The mastic can be anchored to the substrate by means of stud welding of rods, split rods, or expanded wire. This procedure assures the adherence of the coating during the course of the fire and against the impact of the pressure of the water used in extinguishing the fire.

Flame-Resistant Tests

The nature of the flame tests is of the utmost importance in the evaluation of the properties of the fire-resistant mastics. The proper tests are based on careful consideration of the type of combustile or incombustible substrate, the nature of the flame exposure to which these substrates may be subjected in the course of the service, and other requirements which may be needed to meet the desired specifications.

The combustible materials with which this paper is concerned are those used in building construction, such as wood and other compressed cellulosic derivative materials. The incombustible materials are metals which must be protected from reaching critical points when exposed to the heat of the fire. The critical points are the temperatures at which the metals soften and lose their structural strength under fire exposure.

The National Board of Fire Underwriters defines the ignition temperature of any solid material as the lowest temperature to which any part of it must be raised to cause the material to ignite (3). The ignition temperature of wood varies from 380° to 870° F. depending on the kind of wood and the size, shape and condition of the sample; the method, rate, and conditions of heating; the method of measuring the temperatures; and the condition of glow or flame considered as constituting ignition. Tests by National Bureau of Standards show that ignition temperature of the same wood may vary from 440° F. when it is in the form of thin shavings to 750° F. when it is in a larger piece.

The Forest Products Laboratory illustrated the chemical changes which wood undergoes when it is subjected to temperatures below that necessary to produce quick ignition. The test was conducted with wood blocks 1 1/4 x 1 1/4 x 4 inches in size, placed in a quartz tube held vertically. The source of heat was a heating element surrounding the tube. A free, natural draft occurred. Under these conditions, distillation of the wood took place and the liberated vapors were ignited. The ignition by flame was possible when the wood was held at 600° F. for about 2 minutes, at 500° F. for about 5 minutes, at 400° F. for 20 minutes, or at 340° F. for 40 minutes.

The charring temperature of wood is lower than the ignition temperature. Forest Products Laboratory tests show that charring of the wood can take place at oven temperatures of 225° F. with long periods of heating, and field experience shows that wood in long contact with low-pressure steam pipe becomes charred, and under favorable circumstances ignition may occur.

There are many laboratory methods of evaluating the protection offered by flame-resistant coatings to combustible materials. All differ in their techniques. Flame impingements on the test panel may be made while the test panel is resting in the horizontal or vertical position, or at an angle of 45°. The observations are noted for a given period, but differ for each test. Degradations of the combustible materials are also noted in various ways: flame spread and rate of spread, fuel contributed, smoke produced, degree of charring in terms of area or volume, and loss of weight.

The Underwriters' Laboratories evaluate building materials of fire hazard nature in their own devised equipment on a scale much larger than that followed in the industrial laboratories, and record the results by rate of flame spread, fuel contributed, and smoke produced. The evaluations are recorded numerically in relation to the data recorded during the burning of select red oak under standardized conditions as producing the 100-point on a classification scale, while the data recorded during similar exposure of an incombustible material (asbestos-cement board) produced the 0-point. Some commonly practiced laboratory methods developed for determining the flame-resistance of combustible materials are: Federal Specification SS-A-118a, Schlyter test or its modifications, and British Standard Specification 476a or its modifications.

The Federal Specification SS-A-118a, which is designed for slow-burning combustibles in the horizontal position, measures the flame spread within a 20 or 40 minute period under a prescribed flame temperature curve. A mild Schlyter test measures the flame when the test panel is in the vertical position, whereas a modification of the fire test of British Standard Specification 476a measures char area on an inclined test panel. Reasonably good correlation trends between results of these three test methods were found by the Forest Products Laboratory (2). A good flame-resistant coating will effectively check flame spread by all three tests. A coating which will perform effectively with one material will not necessarily be satisfactory for another. While reasonably good correlation trends between the results of the three test methods were found, the accumulated data indicated the difficulty of predicting infallibly, on the basis of performance in one test method, what the performance would be in another test method.

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The heat-insulating properties of the mastic applied over metals is measured in the laboratory by impinging a fire on the mastic side and measuring the heat transfer to the opposite side by thermocouple readings. To qualify in the building construction field it is desirable to conform to American Standard A2.1-1942, which Underwriters' Laboratories use to grant approval of fire-resistant coatings. This test prescribes a standard exposing fire of controlled extent and severity, and the performance is defined as the period of resistance to standard exposure elapsing before the first critical point in behavior is observed. The performance is expressed as "2-hour," "1-hour," etc.

The most effective and convincing tests are those which are made to reproduce the true conditions to which the materials of fire hazard nature may be exposed. Thus, the railroads evaluate a fire-resistant coating for the protection of their creosote-impregnated wood trestles by reproducing a fire on a section of a replica trestle built to scale and treated with the fire-resistant coating.

In all evaluation it is necessary to remember that the results of any test are influenced by the thickness of the coating, the period allowed for complete drying of these coatings, and the method of application. Because of the difference in the ignition points of various combustibles or the yield points of metals, every satisfactory test must be qualified as to application method and full description of substrate given.

Some Properties of Fire-Resistant Mastics

Some of the unique properties which can be attained by fire-resistant mastics are exemplified by a commercial formula of a composition which cannot be disclosed. The high temperature flame-resistance and low heat transfer are illustrated through the use of Thermit, a mixture of powdered aluminum and iron oxide, which on ignition develops a heat of 5400° F. in 60 seconds. The test panel consists of a slab of steel 3/8 inch thick and 18 inches square, over which a coating of 1/2 inch of flame-resistant mastic has been imposed. On this panel a sand mold 3 inches in diameter is formed, and paper cup containing 1/4 pound of Thermit is placed within the ring of sand, and then it is surrounded with 1/2 pound of magnesium shavings. A gasoline torch is used to ignite this mass of fuel. The intense heat and flame last about 3 minutes. Immediately after the exhaustion of the Thermit, a hand placed on the metal opposite where the reaction occurred does not feel an appreciable change in temperature. The same Thermit test on 1/8-inch steel burns a hole 2 inches in diameter within 20 seconds. As a result of the Thermit test, the mastic shows a black, sintered crust approximately 3 inches in diameter and about 1/8 inch deep.

The heat transfer through the same composition mastic by flame temperature of 2000° F. directed against it is illustrated by three test panels of steel 3/16 inch thick and 12 inches square. One panel was soated with 9/16 inch of mastic, and the second bad steel wire lath welded on a five points and then covered with 1/2 inch of mastic; the third panel was left bare. The source of fire for the tests was a large gas burner with forced air feed. Temperatures of the heat source and heat transfer on the uninsulated side were made with the thermocouple. The results of the fire test were as follows.

Test Panel	Temperatures on Bare Side of Steel, ° F. 5 min.	15 min.	25 min.	40 min.
No mastic	850	---	---	---
9/16 inch mastic	176	386	522	604
Wire lath and 1/2 inch mastic	176	496	658	---

At the conclusion of the test, the unanchored mastic exhibited the loss of appreciable initial adhesion to the metal. The lath-anchored panel was subjected to the fire only 25 minutes because the extreme heat fused the jets of the burner, necessitating cessation of the test. After cooling, the mastic layer from this panel could not be removed even with application of considerable force. Whenever excellent bondage under fire is desirable, anchorage of the mastic is desirable.

Another illustration of the low heat transfer of the mastic at moderate temperatures was demonstrated in connection with a test for spraying the underside of vehicles used for carrying explosives. A steel panel 1/16 inch in thickness was coated on one side with 3/8 inch of mastic. The panel was suspended horizontally with the insulation side down. A pine box wood block, 3/8 x 3/4 x 1 1/2 inches, was placed in the center of the panel. The block rested on the 3/8 x 1 1/2 inch side. A Fischer burner was placed under the block. It was set to develop a temperature of 800° F. It required 8 minutes before any sign of charring showed on the wood and 30 minutes before approximately 1/8 inch charring occurred. Under similar circumstances a block of this wood placed over the bare steel showed charring in 10 seconds and burst into flame in 65 seconds. Similarly, a 1/4-inch millboard and 1/16 inch sheet in place of the mastic would delay the charring of the wood for 9 minutes and produce 1/32 inch of charring of the wood in 30 minutes.

Thermal conductivity, $\underline{k}$, of the mastic under illustration was determined to be 1.03 at 10° F. mean temperature as measured by apparatus designed by the National Bureau of Standards. $\underline{k}$ equalsthermal conductivity in terms of B.t.u. per hour, per hour, per degree Fahrenheit temperature difference, for a specimen 1 foot square and 1 inch thick. This value of $\underline{k}$ compares with the following values obtained from the "Heating, Ventilating and Air-Conditioning Guide":

Light-weight concrete	2.50
Sand and gravel concrete	12.00
Mineral wool insulation	0.27
Expanded vermiculite insulation	0.48
Expanded vermiculite concrete	0.86 - 1.10

The impact resistance of the mastic applied on 16-gage steel, 4 x 6 inches, as a layer of less than 1/8 inch was determined by dropping weights from various heights. A 100-gram brass weight dropped on a panel placed at a 45° angle at varying heights up to 10 feet results only in dents in the mastic, but no removal. A 5-kg. weight dropped from a height of 2 feet onto the center of a panel placed at a 45° angle, bent the panel to an angle of 22° and removed enough mastic to expose 1/32 sq. inch of bare metal. The force exerted by a 5-kg. weight falling 2 feet is approximately equivalent to that of a 1-lb. rock traveling at 35 miles per hour.

The Taber abrader test for abrasion resistance of the mastic shows that the mastic has an abrasion resistance of rubber tile and unprinted linoleum.

The salt-fog corrosion resistance of the mastic appears excellent. Incipient corrosion of a mastic-coated steel panel of 1/16 inch thickness appears only after 1 mont. This compares to complete failure of red lead primer in 4 to 5 days.

Application of Fire-Resistant Mastic

The resinous mastics have opened, through the medium of thickness of application

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and accordingly a wider scope in formulation, new usages which have not been possible to attain by thin coatings. The resinous mastics also overcome the shortcomings of the inorganic matrixes: chiefly, the lack of adequate and retained adhesion, insufficient flexibility under various temperatures, absorption of flammable oils, water, and corrosive agents, and the lack of sufficient expansion with thermal changes of the substrate.

The resinous mastics have also shown their superior characteristics against various finishes in shock resistance under extremely rapid changes in temperature, such as -60° to 4123° F.

In the building field, as fire-resistant coating for wood, fiberboard, and metals, they have numerous applications. Unusual usage of the fire-resistant mastics is their application against brush fires on railway trestles constructed of wood which had been impregnated with as much as 3 gallons of creosote-petroleum oils per cubic foot.

Another new application of the mastic is on the underside of motor vehicles used for transportation of explosives and other dangerous flammables. Experiences of the past few years indicate that motor vehicles equipped with dual tires are likely to be involved in serious fire should one of the dual tires become deflated. In this case, the mastic must not only exhibit fire-resistance and low thermal conductivity, but must have good impact and good abrasion resistance as well as weatherability.

The inherent properties of the fire-resistant mastic may be exploited for many other applications. On the basis of low thermal conductivity, the mastic forms a suitable coating on metal sheet buildings which prevents condensation, reduces noise coefficient, and retards radiated heat. Another property which is sometimes important is that the mastic does not support mildew. For this and other reasons, the mastic has been applied on the interior of concrete storage granaries to prevent the grain from mildewing in the area adjacent to the concrete walls.

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