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FIRE RETARDANT PAINTS

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ABSTRACT

The mechanism involved in the flame-proofing of cellulose is explained on modern electronic concepts. Some recent developments on intumescent paint and mastic compositions with the scope of their further improvement are discussed.

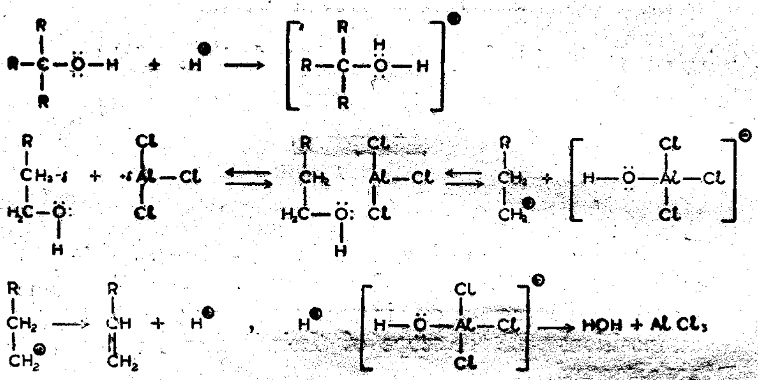
Fire retardation implies the prevention of damage to the substrate by checking the propagation of combustion from the spot which is in the direct vicinity of the flame. The use of paint coatings to retard or prevent the spread of fire on combustible materials and metals has attracted much interest in the past and more so in the recent years. [1, 2, 3, 4].

Cellulose is the common type of fuel for a fire. This on thermal degradation above 300°C, in the first stage yields inflammable, gaseous, liquid, tarry and solid products, belonging to aliphatic, aromatic and heterocyclic series. These while burning generate heat and help further combustion. The flaming process leaves a carbonised residue that does not burn so readily. In the second stage, this carbonaceous matter oxidises and glows. The function of an effective fire retardant is to direct the reaction towards the second stage.

An ideal fire retardant paint should be nonflammable or of low order of flammability, smooth out the surface of the substrate to reduce the surface area exposed to air, retain insulation as long as possible under direct fire attack and possess sufficient decorative and protective properties of the usual paints. Intumescent paints and mastics are quite close to these characteristics.

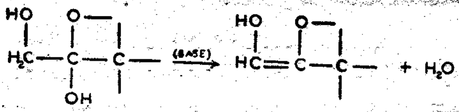
Mechanism of flame proofing

Cellulose, being a polyhydric alcohol, on thermal decomposition in the presence of acidic or basic catalysts, like $AlCl_3$, Al_2O_3, H_3PO_4, $NaOH$ is supposed to undergo dehydration through carbonium or carbonion mechanism.[5] The interpretation depends upon the reactions performed by Lewis acids and bases [6, 7] which are either present as such or produced at the flaming temperature. For example, when an acid reacts with a compound that can give a pair of electrons, a carbonium ion is formed. These reactions are due to the complex formation of the electron poor atoms of the acid with the electron-rich atoms of the base through the lone pairs of the latter. This addition of proton disturbs the electronic system by drawing the pair of electrons between carbon and oxygen toward the oxygen, and results in the elimination of a molecule of water. In turn, a carbonium ion is formed that being unstable, if not stabilized

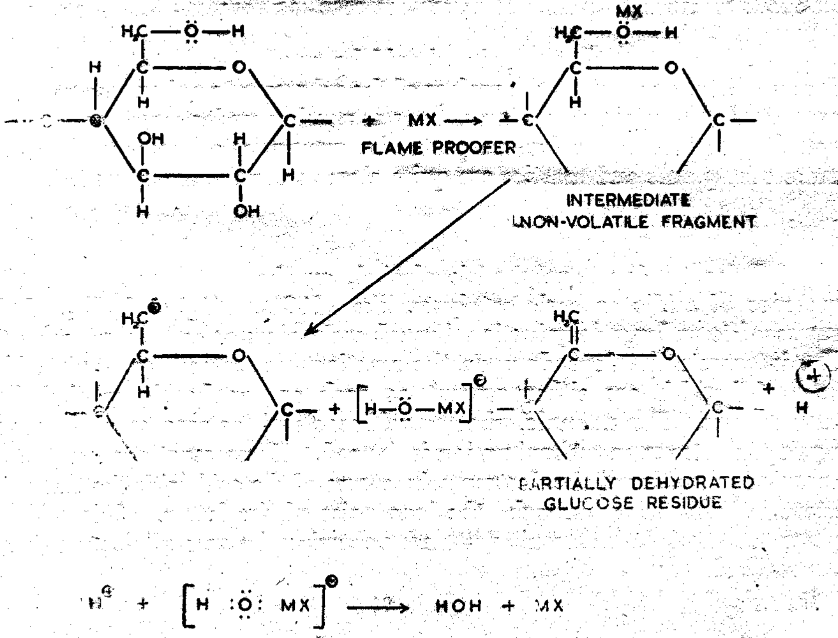


by resonance or hyperconjugation, rearranges and splits out a proton. This proton reacts at another electron-rich point, and the process is repeated.

The base catalysed dehydration involves the formation of transitory carbon ion, usually at a β—carbon atom, with the simultaneous displacement of the ion or molecule being eliminated.



Flame proofed cellulose consists of a heterogeneous solid solid system. Considering one of the glucose units in a cellulose chain the dehydration mechanism involved in the flame proofing can be presented as under:



The whole process continues until all available -OH groups are eliminated and a difficult combustible carbonaceous residue is left.

Intumescent paints

These paints, when subjected to heat puff out and form foams that exclude the air, and thus behave as much thicker and better insulators in protecting the fibre or metal. Sodium silicate[8], sodium borate and mono-ammonium phosphate are effective fire retardants known for wood [2, 3, 9, 10, 11, 12].

For example, a preferred composition [13] contains Na-water glass (30-5° Be') 23-5, talcum 26, lithophone 7-11, water 15-21, and starchy binder 15-19. Another paint composition[14] is made by heating linseed oil 250 g. and Mn-resinate 100 g. to form a solution and slowly adding 600 g, of Na-silicate (35-7° Be '), and finally 50 g. sodium bicarbonate.

A typical intumescent coating[15] comprises 10-30 per cent. water-soluble amino plast resin (such as urea-formaldehyde or melamine-formaldehyde), 30-50 per cent. mono and (or) diammonium phosphates and sufficient pigments to make a total of 100 per cent. The pigments should consist of at least one from each of the following groups : (*i*) barytes, gypsum, lithophone, ZnS, $Ti0_2$, $Ti0_2$—$BaSO_4$, $Ti0_2$-$CaSO_4$; (*ii*) silica, clay, pyrophyllite, talc, mica. The addition of casein to the paint gives a good foamstabilising effect[26]. Insulating properties when exposed to flame are effective for 5-10 minutes.

The treatment of phosphorous oxychloride with anhydrous ammonia yields a water-insoluble, chlorine-free product[17] that consists of a mixture of phosphoryl-triamide, phosphoryl-imido-amide and polyphosphoryl amides. This is an effective fire retardant when incorporated in a paint or emulsified resin binder.

Alkyd resins give the best non-intumescent interior paints. A good interior paint of this type consists of : TiO_2 144 lbs, starch 57·5 lbs, ammonium phosphate 330 lbs, amino acetic acid 61·5 lbs., 10 cps chlorinated rubber 119 lbs, 50% alkyd resin solution 115 lbs, Hi Flash Naphtha 206 lbs, 60% silicone resin solution 8·2 lbs ; and the whole lot is mixed with Hi Flash Naphtha 82·5 lbs ; and PVC 67%, wt/Gal. 11·2 lbs.

Unfortunately, the good intumescent agents are water soluble and their paints have poor resistance to water and scrub.

Mastics

The protection of non-combustible substrates like metals, from the change in their physical characteristics as a result of fire is no less significant. The maximum damage to an aircraft is due to fire, and is taken to be totally lost after two minutes of fire. Figure I shows the loss in strength when aircraft metals are subjected to the various temperatures for 30 minutes. For comparison, load bearing steel will collapse at 1100°F in less than 10 minutes.

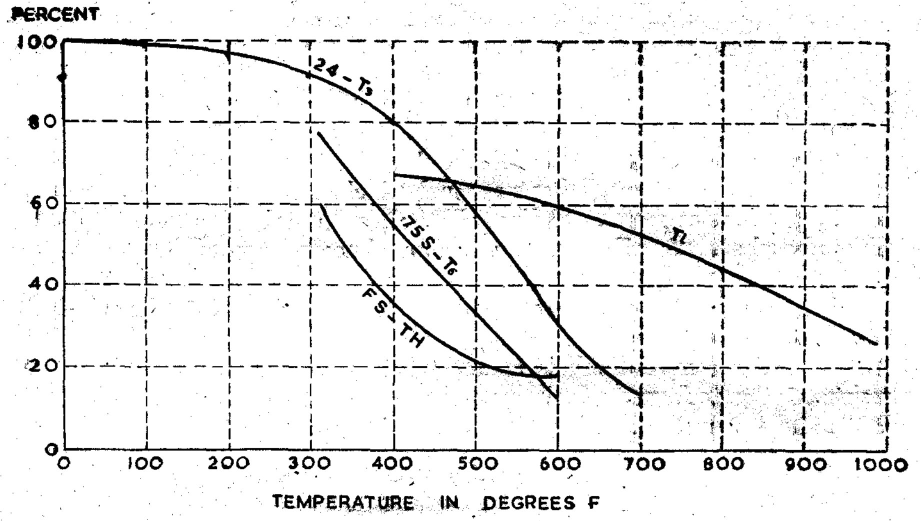


FIG 1—Ultimate tensile strength expressed as percentage of initial ultimate tensile strength at °F when held at different temperatures for 1/2 hour.

U. T. S. at room temperature :—

Aluminium	24S—T3	62,300 p.s.i
Aluminium	75S—T6	72,220
Magnesium	FS—TH	41,200
Titanium	Ti	102,700

A mastic is both a paint and an heat insulator. It is prepared as a thick paste, and in most of the cases is of mineral composition with a resin binder and an organic solvent. It is applied to give a coating of 1/32″ to 1″ in thickness, that subsequently dries up to give a hard coat. It has high impact strength and is resistant to abrasion, water and most of the chemicals.

The nonflammable gases, like hydrochloric acid, ammonia, carbon dioxide, sulphur dioxide and water, evolved from the mastic as a result of heat, dilute the oxygen in the vicinity of fire and help in the retardation of combustion. Thus the choice of its ingredients depends upon : (*i*) quantity of available gas, (*ii*) decomposition temperature, and (*iii*) ease in rate of gas release. The important sources of these gases are fire resistant resins that are also binding materials *e.g.* halogenated rubber, 2-chlorobutadiene-1 : 3, halogenated hydrocarbons, halogenated diphenyls, vinyl halogen and amide-aldehyde polymers ; the filler materials such as carbonates and sulphates of Ca, Mg, Zn, Zr, and hydrated minerals like vermiculite, asbestos etc. The gas release can be regulated with the incorporation of stabilisers. By having suitable compositions of the fillers and the binders, the mastics can be obtained for various specific functions.

It has been observed that the adhesion of lath anchor mastic on steel is more than in the case of unanchored mastic. The following are the results of a gas burner test on mastic :

Type of test	Temperature in °F on bare side of steel at :			
	5 min.	15 min.	25 min.	40 min.
No mastic	850°	..	..	..
9/16" mastic	176°	386°	522°	604°
Wire lath and ½" mastic	176°	496°	658°	..

Mastics are effective in protecting steel perfectly up to 5400°F. Recently they have found many applications in the building field in making wood, fibreboard and metals as fire-resistant. These can be applied by the military on the underside of the motor vehicles used for carrying explosives and highly inflammable materials.

Scope for further research

Upto the present day no suitable fire retardant paint is available to the Air Force for the metal of the aircraft. Any coating prepared for this purpose should be able to protect the metal, particularly aluminium at 2000°F for at least half an hour. It should have good adhesion to metal and an applied weight less than 12 lbs./100 square feet. Besides, it should be flexible, water resistant and suitable under actual flight conditions.

The modern paint used on the bulkheads and overheads of surface ships is fire retardant by virtue of its high pigment volume, and by incorporation of antimony oxide as part of the pigment. The paint vehicle is medium-long oil alkyd resin. In actual experience the paint has been found to be an effective fire retardant coating, but due to high pigment concentration produces an uneven surface, and consequently suffers from the ease in cleaning.

The organo siloxane systems provide unlimited opportunity for designing new flame resistant polymers. The possibilities of utilizing alkyl halosilanes as water repellants in the paints, and the use of fluorophenyl silicones and chlorinated phenoxy phenyl silocones as stable flame proof resins for service at elevated temperatures are of particular interest.

The ortho-silicic esters can be incorporated in paints to provide a harder and more insulating film. These compounds undergo slow hydrolysis to give a film of silica. Ethyl-ortho-silicate, now produced on a large scale, is being used for this purpose.[18]

More intensive work has to be carried out on epoxy resins, puffed and then cured with ammonia (from amines or urea), and on ceramics. The ceramic material should swell and give high insulation and temperature resistance. Further, new and better binders are to be investigated for silicone.

During recent years the U. S. Air Force has been conducting investigations on fluorine-containing materials for application in aircraft. The development and incorporation with paints of polymers like that of monochlorotrifluoroethylene and tetrafluoroethylene that would combine thermal stability with chemical inertness is an highly fruitful field. Possibly the most promising class of new fluorine-containing polymers is represented by poly-1 1-dihydroperfluorobutyl acrylate[19] [—CH_2 CH ($COOCH_2CF_2CF_2CF_3$)—]$_n$; and is at present intensely studied by U. S. Air Force. Flouroelastomers have to be further developed and their application in fire retardant paints remains to be investigated.

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