

by periodate-permanganate oxidation of the cyclopropene ring (18) seen in the cleavage products. It is concluded that little or no malvalic and stercolic acid are present in the unsaturated fractions isolated from cottonseed oil by mercury derivative chromatography. Furthermore, because of the 10 ppm lower limit of the Halphen test (16), there is some doubt in this author's mind whether refined cottonseed oil, even before methyl ester preparation, etc., contains more than a few tenths per cent of these acids.

The monoenoic acids found in abundance in nature can be considered related to oleic acid in that two-carbon units have been consecutively added to the carboxyl end of the molecule. Rapeseed oil is a good example of this series, since it contains major amt of 9-octadecenoic (oleic), 11-eicosenoic and 13-docosenoic (erucic) acid and a small amt of 15-tetracosenoic acid. *Cis*-9-hexadecenoic (palmitoleic) acid, found in most vegetable and animal fats, is an obvious exception to this rule. The present finding of additional monoenoic acid isomers in vegetable oils indicates a new series, which can be considered related to palmitoleic by the same two-carbon addition rule (i.e., 9-hexadecenoic, 11-octadecenoic, 13-eicosenoic and 15-docosenoic acid). The fatty acid composition of milkweed seed oil lends supports to the existence of this

new series, since in this oil a high palmitoleic acid content was accompanied by a high 11-octadecenoic acid level. Other materials rich in palmitoleic acid (such as animal fats and marine oils) would be expected to contain significant amt of the related higher mol wt isomers.

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Water-Resistant, Oil-Based, Intumescent Fire-Retardant Coatings. I. Developmental Formulations¹

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Abstract

Water-resistant, intumescent fire-retardant paints have been formulated from different types of chemically modified oil-based vehicles, carbonific polyurethanes, spumific melamine phosphates, spumific organohalophosphorus compounds, additives, pigments, driers and solvent. The synthesis of their three major components—the vehicle itself, the spumific melamine phosphates and the carbonific polyurethanes—is described. As a result of evaluation in the standard fire-test cabinet and in the Underwriters' Laboratories' 25-ft tunnel furnace, the formulation whose vehicle has a higher content of tung oil and whose carbonific components are less thermoplastic appear to be most promising. However, these research results have again manifested the importance of the contribution of *each* component in achieving effective fire retardance.

Introduction

SINCE THERE HAS BEEN A significant increase in fire losses, the development and proper application of good fire-retardant coatings have been strongly recommended by coating technologists, fire marshals and

industrial and government officials to reduce loss of life and property (1,3,4,13,21,22,26,30,31). In fact, the National Fire Protective Assoc. reported that 11,800 lives and \$1,590,000,000 worth of property were lost through fires in the U.S. in 1962 (5).

However, there have been misconceptions about the purposes of fire-retardant coatings. Although they do not prevent fires, they do temporarily suppress the spreading of flames. By permitting fire fighters to arrive at the scene before the building is engulfed by flames, this temporary delay could help save many lives and buildings. Since there are millions of non-fire-retardant buildings throughout the country (1, 13,22,26,31), effective fire-retardant coatings would have unlimited military and industrial potential.

In addition to being fire-retardant, these coatings should have the serviceable, protective and esthetic properties of conventional coatings: can stability, spreadability, drying and bonding characteristics, color and tint retention, serviceability, and water and weather resistance (4,13,15,17,24,25,31). However, none of the fire-retardant coatings presently available possess all of these desired characteristics (2,19,24).

Fire-retardant coatings vary in performance; but, generally speaking, there are two types: intumescent and nonintumescent. The former are more common and appear to be more effective, since their foamy expansion insulates the substrate from the effects of heat and flames and reduces their spread (1,3,4,19,

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TABLE I
 Water-Resistant, Oil-Based, Fire-Retardant Coatings

Components (nonvolatiles) ^a	Formulations								
	A %	B %	C %	D %	E %	F %	G %	H %	I %
Titanium dioxide (rutile)	2.86	2.86	2.86	2.86	2.86	4.89	4.89	5.86	7.03
Zinc borate	8.42	8.42	8.42	8.42	8.42	14.38	14.38	17.19	20.70
Magnesium silicate	0.42	0.42	0.42	0.42	0.42	0.72	0.72	0.85	1.02
Lead sulfate	4.80	4.80	4.80	4.80	4.80	8.20	8.20	9.80	11.80
Lead carbonate	4.80	4.80	4.80	4.80	4.80	8.20	8.20	9.80	11.80
Zinc oxide	2.70	2.70	2.70	2.70	2.70	4.61	4.61	5.51	6.65
Tris(2,3-dibromopropyl) phosphate	8.00	5.00	5.00	10.00	10.00			10.00	
.....	12.00	10.00	10.00						
.....	20.00 ^b	20.00 ^b	20.00 ^c	25.00 ^d	25.00 ^d	18.00 ^d
.....	25.00 ^e	30.00 ^e	30.00 ^e	30.00 ^f	30.00 ^f	30.00 ^f	30.00 ^f	30.00 ^f	30.00 ^f
Chlorinated paraffin	5.60	5.60	5.60	5.60	5.50	5.62	5.62	5.60	5.60
Polyamide resin	4.09	4.54	4.54	4.54	4.54	4.58	4.58	4.54	4.54
Cobalt naphthenate solution	0.11	0.06	0.06	0.11	0.11	0.10	0.10	0.10	0.11
Lead naphthenate solution	0.90	0.55	0.55	0.45	0.50	0.40	0.40	0.45	0.45
Anti-skinning agent	0.15	0.10	0.10	0.15	0.20	0.15	0.15	0.15	0.15
Ultraviolet screening agent	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15

^a The viscosity was adjusted to ca. 90 Krebs Units with mineral spirits or Hi-flash naphtha.

^b The pentaerythritol polyurethane was synthesized from 3 moles of pentaerythritol and 2 moles of tolylene diisocyanates.

^c The pentaerythritol polyurethane was synthesized from 2 moles of pentaerythritol, one mole of tolylene diisocyanates and 2 moles of phenyl isocyanate.

^d The pentaerythritol polyurethane was synthesized from 2 moles of pentaerythritol, one mole of tolylene diisocyanates and 5 moles of phenyl isocyanate.

^e Oil-based vehicle "b."

^f Oil-based vehicle "a."

^g Oil-based vehicle "a" and air-blown tung oil mixture (2:1 ratio).

21,24,25,26). Two types of components promote this protective action: spumifics, which foam, and carbonifics, which produce a carbon matrix; their combined response creates layer after layer of spongelike insulating mats of cellular carbonaceous material (4, 15,25). The components that produce the best spumific and carbonific action, however, appear to be too water sensitive to be used in reliable fire-retardant coatings (2,19,25,31).

Since commercially available intumescent fire-retardant coatings did not meet all military requirements, the So. Reg. Res. Lab. undertook a cooperative research program with the U.S. Army Engineer Res. & Dev. Laboratories to develop water-resistant, oil-based, intumescent fire-retardant coatings from domestic vegetable oils. Fairly good water-resistant, intumescent fire-retardant coatings had previously been prepared from isano oil, linseed oil, additives, pigments, driers and solvent (2,6,14). However, since isano oil is obtained from the nut of the *Onguekoa gore* (Engler), native to Central Africa (3,4), it must be imported and is classified as a strategic raw material. This tree is considered unsuited for vegetative propagation or economic production under domestic climatic conditions, and it takes about 20 years for this tree to produce oil-bearing nuts from seeds.

Isano oil is an unusual seed oil since its mixed triglycerides contain major percentages of C₁₈ diacetylenic acid (51%), such as isanic (17-octadecene-9,11-dienoic) acid (12,27), and of their 8-hydroxy derivatives (22%), in addition to minor percentages of dihydroxystearic acid and the usual saturated and unsaturated fatty acids, such as myristic, palmitic, stearic, oleic and linoleic (11,18,20,23). One of the outstanding characteristics of isano oil is that it explodes and then carbonizes when heated above 200°C. This property makes it suitable for the formulation of intumescent fire-retardant coatings (2,6).

Since the intumescent properties of isano oil are attributed to its conjugated diacetylenic and hydroxy-diacetylenic moieties, research efforts were directed toward synthesizing conjugated diacetylenic glycols (32) by oxidative coupling (9). However, although the paints formulated from the polyesters of these diacetylenic glycols were superior to those formulated from isano oil or chemically modified isano oil vehicles (2,6), even better coatings were developed from chemi-

cally modified oil-based vehicles and water-resistant spumific and carbonific materials, additives, pigments, driers and solvent.

This paper reports the synthesis of chemically modified oil-based vehicles, water-resistant carbonific pentaerythritol polyurethanes and water-resistant spumific melamine phosphates. In addition, it summarizes the progress toward the development of water-resistant, intumescent, fire-retardant coatings from different types of chemically modified oil-based vehicles, carbonific pentaerythritol polyurethanes, spumific melamine phosphates, spumific organohaloalkyl phosphates, additives, pigments, driers and solvent. Such formulations will be referred to as "experimental coatings."

Experimental

Materials

Practical grade phenyl isocyanate (97% minimum strength), practical grade tolylene diisocyanates (99% minimum strength, 80/20 ratio of 2,4/2,6 isomer mixture) reagent grade triphenyl phosphite, reagent grade *N,N*-diethylaminoethanol and reagent grade melamine (Eastman Organic Chemicals), technical grade pentaerythritol and abietylamine (Rosin amine D, Hercules Powder Co.), reagent grade phosphoric acid and reagent grade benzene (J. T. Baker Chemical Co.), tris(2,3-dibromopropyl) phosphate (Firemaster T23P, Michigan Chemical Corp.), technical grade tris(hydroxymethyl)ethane (Trojan Powder Co.), chlorendic (1,4,5,6,7,7-hexachlorobicyclo(2.2.1)-5-heptene-2,3-dicarboxylic) acid (HET acid, Hooker Chemical Corp.), chlorinated paraffin (Diamond Alkali Co., Chlorowax 70), polyamide of dimerized linoleic acid and ethylenediamine (General Mills, Versamid 930), dehydrated castor oil "H-J" (Pacific Vegetable Oil Corp.), raw tung oil, air-blown tung oil "Z₄-Z₅" [Pan American Tung Res. & Dev. League (10)], linseed fatty acids (Archer-Daniels-Midland Co, Vegetable acid 520), Hi-flash naphtha (Humble Oil and Refining Co., Solvesso 100), reagent grade absolute ethanol (U.S. Industrial Chemicals Co.), anti-skinning agent (National Aniline, ASA and Troy Chemical Co., Troykyd Special), UV absorber (Antara Chemicals, UVINUL-490), cobalt naphthenate and lead naphthenate (The Harshaw Chemical Co., Uversol cobalt liquid 6% and Uversol lead liquid 24%), zinc oxide AZO-11 (American Zinc Sales Co.),

TABLE II
Fire-Retardant Performance of Paint Films in the Standard Fire-Test Cabinet^a

Formulation	Dry paint on panel ^b				Panel wt loss after burning ^c		
	Coats			Total (g)	Thick-ness (mils)	Non-leached (g)	Leached (g)
	1st (g)	2nd (g)	3rd (g)				
A	16.2	13.3		29.5	7.4	10.9	12.1
	14.4	12.7		27.1	6.8		
	15.0	12.4	13.3	40.7	10.2		
	15.5	12.4	12.6	40.5	10.1		
B	13.4	11.8	12.5	37.7	9.4	6.6	7.0
	14.4	12.5	12.9	39.8	10.0		
C	17.1	14.3		31.4	7.9	5.8	6.2
	16.2	13.9		30.7	7.7		
	15.6	12.5	11.6	39.5	9.9		
	16.4	13.9	12.4	42.7	10.7		
D	15.2	13.7		28.9	7.2	4.0	4.3
	14.2	14.0		28.2	7.1		
	14.3	14.2	14.7	43.2	10.8		
	16.1	13.8	14.2	44.1	11.0		
E	10.9	11.7	10.5	33.1	8.3	9.0	6.9
	12.3	12.0	8.0	32.3	8.1		
	14.8	15.9	14.5	45.2	10.8		
	15.7	16.5	12.4	44.6	11.2		
F	18.1	13.8		31.9	8.0	6.5	6.5
	15.8	13.0		38.8	9.7		
	16.8	12.5	13.0	42.3	10.6		
	15.5	13.2	12.9	41.6	10.9		
G	16.2	13.8		30.0	7.5	8.7	10.5
	16.0	14.1		30.1	7.5		
	16.0	14.4	13.2	43.6	10.9		
	16.3	13.4	14.2	43.9	11.0		
H	16.4	13.8		30.2	7.6	8.8	8.7
	14.6	14.1		28.7	7.2		
	16.8	15.8	11.8	44.4	11.1		
	16.3	13.2	13.1	42.6	10.7		
I	18.0	15.0		33.0	8.3	10.3	10.1
	17.6	14.3		31.9	8.0		
	19.6	14.5	11.6	45.7	11.4		
	19.5	14.4	11.3	45.2	11.3		
J ^d	14.3	14.2		28.5	7.1	12.8	
K ^e	18.1	15.2		33.3		18.3	19.0
	18.1	14.7		32.8			
	17.2	15.0	14.7	46.9			
	18.3	14.0	14.3	46.6			
L ^e	21.2	22.0		43.2		12.8	17.0
	24.0	19.5		43.5			
	23.3	20.9	18.4	62.6			
	21.2	20.2	19.9	61.3			
M ^f	16.5	14.1		30.6		5.6	22.1
	16.8	13.3		30.1			
	16.5	14.3	17.0	47.8			
N ^f	12.4	12.8		25.2		4.0	20.5
	12.4	12.6		25.0			
	12.2	20.6	14.1	46.9			

^a The procedure described in Federal Specification TT-P-34a was employed to evaluate the fire-retardant performance of the paint films prepared from the experimental and commercial coatings. The standard fire-test cabinet is also illustrated in ASTM D 1360-58.

^b The thickness is an approximation based on g/sq ft of the paint applied to each test specimen.

^c Wt loss is a measure of fire-retardant performance: the lower the value the better the performance.

^d A water-resistant fire-retardant coating formulated with isano oil (U.S. Patent 2,754,217).

^e A commercial, exterior, non-fire-retardant coating.

^f A commercial, interior, fire-retardant coating.

zinc borate (Maryland Pigment and Research Corp.), rutile titanium dioxide (E. I. du Pont de Nemours and Co., Ti-Pure R-610), fine-grade magnesium silicate (Sierra Tale Co., Mistron Tale), basic lead sulfate (white), basic lead carbonate (high tinting strength), and TT-T-291a mineral spirits (28) were used.

Synthesis

Oil-Based Vehicles. Vehicles containing tung oil were synthesized by the procedure of Goldblatt et al. (16) with slight modifications.

a) In a 5-liter round-bottom flask equipped with thermometer, stirrer, inert gas inlet, Dean-Stark apparatus and Glas-Col heating mantle, 500 g tung oil, 500 g dehydrated castor oil and 175 g (1.46 moles) *tris*(hydroxymethyl)ethane were alcoholized and gas-

proofed in a nitrogen atmosphere and in the presence of 0.03% sublimed litharge at 300C for 8 min. After the temp was reduced to 280C, 1000 g (3.57 moles) linseed acids and 175 g (1.46 moles) *tris*(hydroxymethyl)ethane were added, and the reaction mixture was esterified at 250C for about one hr until ca. 80-90% of the theoretical amt of water of esterification was evolved. The temp of the reaction mixture was reduced to 150C, and 433 g (1.11 moles) chlorendic acid and several ml of benzene were added to facilitate the removal of the water azeotropically. The reaction mixture was esterified at 180C for ca. three hr, to an acid value of ca. eight, until practically all the water of esterification was removed. The temp of the reaction mixture was reduced to 100C, and 195 g (1.12 moles) of tolylene diisocyanates, one liter of Hi-flash naphtha and 0.01% diethylaminoethanol catalyst were added. Heating was continued at 100C for two hr. Several ml of absolute ethanol were added to prevent excessive crosslinking upon aging.

b) A more viscous and faster-drying vehicle was prepared by a similar technique, except that the amt of tung oil was increased from 500 to 800 g and the amt of dehydrated castor oil was decreased from 500 to 200 g.

When tung oil is heated at high temp, caution should be exercised to prevent gelation; i.e., heating in excess of recommended procedure should be avoided. Even though the reaction products begin to adhere around the stirrer under abnormal conditions, gelation can be retarded or prevented by the immediate addition of ca. 1% abietylamine.

Pentaerythritol Polyurethanes.

a) In a 2-liter stainless steel beaker equipped with stirrer, thermometer and Glas-Col heating mantle, 272 g (2 moles) of pentaerythritol, 595 g (5 moles) of phenyl isocyanate, 174 g (one mole) of tolylene diisocyanates and 0.01% diethylaminoethanol catalyst were vigorously stirred for ca. four hr while the temp was maintained between 50 and 60C. Then the temp was increased gradually to 120C within two hr. (*Caution* should be exercised at all times to prevent an uncontrollable exothermic reaction.) The viscous reaction mixture was cured at ca. 150C in a gravity convection oven overnight.

b) A higher-melting pentaerythritol polyurethane was synthesized by a similar technique from 272 g (2 moles) of pentaerythritol, 238 g (2 moles) of phenyl isocyanate and 174 g (one mole) of tolylene diisocyanates.

c) A much higher-melting pentaerythritol polyurethane was synthesized by vigorously stirring 408 g (3 moles) of pentaerythritol and 348 g (2 moles) of tolylene diisocyanates in the presence of 0.01% diethylaminoethanol catalyst at ca. 100C for several min. The viscous reaction mixture was poured into a teflon-lined container and cured at about 150C in a gravity convection oven overnight.

Upon cooling, the first two polyurethanes were friable, whereas the third was extremely hard. However, all three pulverized to a powdery, light-colored, water-resistant material that was easily formulated into coatings with suitable vehicles, spumific components, additives, pigments, driers and solvent.

Melamine Phosphate. Seventy-five g (0.6 moles) of melamine was dispersed in 300 ml of water by rapid agitation in a Waring blender. Three hundred ml of a 20% phosphoric acid aqueous solution (0.6 mole) were quickly added. The resulting mixture coagulated momentarily, but continued vigorous stirring for ca.

TABLE III
 Fire-Retardant Performance of Paint Films in Tunnel Furnaces

Formulation	Dry paint on panel ^a				Fire-retardant performance ^b					
	Coats			Total (g)	UL tunnel furnace			UL and SU tunnel furnaces observations		
	1st (g)	2nd (g)	3rd (g)		Flame-spread	Fuel-contributed	Smoke-developed	Blistering & rupturing	Carbonaceous build-up	
A	18.4	16.0	...	34.4	Slight	Slight	
	15.2	15.2	...	30.4	Slight	Slight	
	18.4	16.0	12.8	47.2	Slight	Slight	
	15.2	15.2	15.2	45.6	Slight	Slight	
	12.8	8.8	...	21.6	54	31	170	Negligible	Slight	
	12.1	10.1	...	22.2	56	32	251	Negligible	Slight	
	11.5	14.9	12.8	39.2	46	22	316	Localized	Slight	
	10.8	12.1	13.5	36.4	45	25	311	Localized	Slight	
	D	20.9	20.9	Slight	Slight
		18.9	18.9	Slight	Slight
18.0		16.1	...	34.1	Excessive	Localized	
21.6		16.5	...	38.1	Excessive	Localized	
9.9		12.2	14.1	36.2	Excessive	Localized	
13.2		13.5	9.2	35.9	Excessive	Localized	
26.1		26.1	87	27	260	Moderate	Localized	
26.0		26.0	85	33	410	Moderate	Localized	
27.1		6.2	...	33.3	82	51	519	Excessive	Localized	
27.2		6.1	...	33.3	87	42	534	Excessive	Localized	
28.3		15.2	...	43.5	79	36	651	Excessive	Localized	
28.3		15.4	...	43.7	81	42	891	Excessive	Localized	
E		12.9	15.8	...	28.7	Negligible	Moderate
	12.9	10.5	10.0	33.4	Negligible	Moderate	
	13.3	10.0	12.9	36.2	Localized	Moderate	
	13.7	14.6	16.4	44.7	Localized	Moderate	
	18.7	13.5	...	32.2	41	22	213	Negligible	Moderate	
	18.4	13.9	...	32.3	41	22	204	Negligible	Moderate	
	17.3	13.9	13.6	44.8	39	18	250	Localized	Moderate	
	16.1	13.6	13.5	43.5	41	14	273	Localized	Moderate	

^a Coverage is given in g/sq ft. The approx thickness in mils = g/4.

^b The procedure described in ASTM E-84-61 was employed to evaluate the fire-retardant performance of the paint films in the UL tunnel. The paint films evaluated in the SU tunnel furnace (17) are those for which data on flame-spread, fuel-contributed and smoke-developed values are not given.

10 min produced a homogeneous suspension that was easily dried in a mechanical convection oven at 120C overnight. This slightly water-soluble and hygroscopic melamine phosphate was heated at 210C for ca. five hr. The resulting melamine phosphate was water-resistant and similar to the pentaerythritol polyurethanes in appearance and in other properties previously described.

Formulation of Coatings

The experimental coatings were formulated with varying percentages of chemically modified tung oil-containing vehicles, carbonific pentaerythritol polyurethanes, spumific melamine phosphates, spumific *tris*(2,3-dibromopropyl) phosphate, additives, pigments, driers and solvents, as shown in Table I. The various ingredients were ground to a number 3 grind (North Standard Scale, particle size less than 3 mils) in a steel ball mill within one hr or in a pebble mill within 40 hr.

Preparation and Evaluation of Test Specimens

Two- and three-coat (3-4 mils/coat) films were painted onto poplar heartwood panels (6 x 12 x 1/4 in.). Before and after leaching in a water bath at 50C for 48 hr, they were evaluated for their fire-retardant performance in the standard fire-test cabinet as described in Federal Specification TT-P-34a (29) or ASTM D 1360-58 (7). The wt loss of panels painted with the experimental coatings, isano oil coating or commercial coatings is reported in Table II.

One-, two- and three-coat films were painted onto Douglas fir plywood panels (19.5 x 96 x 3/8 in.) or Douglas fir 1 x 4 in. flooring panels (19.5 x 96 x 1 in.). After being cured for at least 30 days, test specimens were first screened for their fire-retardant performance—such as minimized blistering and rupturing of the paint film, adequate adherence between coats and substrate and suitable fine carbonaceous buildup—in the So. Utiliz. Res. & Dev. Div.'s (SU) elementary

8-ft tunnel furnace (17) and then evaluated in the Underwriters' Laboratories' (UL) 25-ft tunnel furnace for flame-spread, fuel-contributed and smoke-developed index values, as described in ASTM E 84-61 (8,19). The performance of experimental formulations A, D and E is reported in Table III.

Results and Discussion

This research emphasized the importance of each component in the production of practical coatings having max fire-retardant performance and serviceability. For example, the vehicle must be compatible with other components; its viscosity must promote ease of application and max fire-retardant performance; it must have good can stability, drying characteristics and water resistance and minimum flammability. The carbonific and spumific components must not adversely affect the can stability of the coating and must have good water resistance and intumescent fire-retardant properties that act synergistically with the vehicle, additives and pigments. The additives and pigments must impart fire-retardant properties to the coating and not adversely affect the fire-retardant performance of the vehicle and carbonific and spumific components.

In the synthesis of good tung oil-containing vehicles, the proportion and functionality of all components and the reactivity of the functional groups must be considered. Components with multiple functionality, such as tung oil, *tris*(hydroxymethyl)ethane, chlorogenic acid and tolylene diisocyanates, will promote the necessary crosslinking, but the reactivity of different types of functional groups may vary. The conjugated triene moieties of tung oil undergo crosslinking by Diels-Alder adduction at high temp. This desirable phenomenon decreases the concn of these moieties and helps to produce vehicles that dry and bond well, do not wrinkle and are weather-resistant. However, this reaction has to be controlled and cannot be carried to completion, because excessive cross-

linking by Diels-Alder adduction will result in gelation or poor drying and bonding.

Tris(hydroxymethyl)ethane undergoes transesterification by alcoholysis of tung oil at high temp, crosslinking by esterification with chlorendic acid at relatively high temp and crosslinking by reaction with tolylene diisocyanates at moderate temp. The crosslinking of *tris*(hydroxymethyl)ethane can be easily controlled by adding a suitable amt of monofunctional fatty acids such as linseed acids, but the crosslinking of tung oil is more difficult to control since crosslinking proceeds readily during the alcoholysis or transesterification and esterification reactions. However, unlike the Diels-Alder adduction, the esterification reaction is generally carried to completion to produce vehicles of low acidity.

Since suspensions of pentaerythritol in isocyanates in the presence of tertiary amine catalyst react slowly between temp of 50 and 60C, pentaerythritol polyurethanes can be easily prepared from pentaerythritol, phenyl isocyanate and tolylene diisocyanates. Such mixtures, however, have to be reacted at low temp for several hr to prevent uncontrollable exothermic reactions. On the other hand, the reaction of suspensions of pentaerythritol in tolylene diisocyanates are less exothermic, but they are not necessarily easier to control. Phenyl isocyanate can be used both as a diluent and as a reactant; therefore, it is much easier to prepare homogeneous pentaerythritol polyurethanes from pentaerythritol, phenyl isocyanate and tolylene diisocyanates under controlled heating conditions than from pentaerythritol and tolylene diisocyanates. The incorporation of phenyl isocyanate keeps the reaction mixture fluid enough to be stirred for several hr without difficulty. It also renders the product more friable. On the other hand, less thermoplastic pentaerythritol polyurethanes can be prepared from pentaerythritol and tolylene diisocyanates. The important observation, however, is that pentaerythritol polyurethanes with the desired properties can easily be prepared by varying the proportion of monoisocyanate and diisocyanates, as described in the experimental section.

In the preparation of highly water-resistant melamine phosphates, the heating temp after drying of the melamine phosphate slurry are critical. It has been found that the most water-resistant melamine phosphates are produced by heating the dried melamine phosphate at temperatures between 205 and 215C, preferably 210C, for several hr. Lower temp are not adequate to produce water-resistant melamine phosphates, and higher temp cause excessive pyrolysis.

Some of the two- and three-coat test specimens performed well in the standard fire-test cabinet (7,17,29) before and after leaching in a circulating water bath at 50C for 48 hr. As shown in Table II, the wt loss of test specimens of experimental formulations C and D were in the same low range before and after leaching as were the test specimens of two of the best commercial, interior, intumescent coatings (formulations M and N) before leaching. Experimental formulations A,B,E,F,G,H and I were not as fire-retardant as experimental formulations C and D in the fire-test cabinet, but they were much more fire retardant than the isano oil formulation J and the commercial non-fire-retardant formulations K and L.

As shown in Table III, however, tests in the 25-ft tunnel furnace (8) and in the elementary 8-ft tunnel furnace (17) indicate that experimental formulation E performs best. Paint films of experimental formulation D, the best performer in the simple but informa-

tive fire-test cabinet, blistered and ruptured excessively in the tunnel furnaces; consequently, its flame-spread index values were relatively high: 79-87. Paint films of experimental formulations A and E, however, blistered very little, and the migration of the flame was reduced considerably: the index values were 45-56 for A and 39-41 for E. In addition, formulations A and E produced a thin layer of carbonaceous material, which effectively insulated the substrate from the effects of the flame and heat.

These observations indicate that the chemically modified oil-based vehicles are very important in the development of intumescent fire-retardant coatings. For example, the difference between formulation D, the poor performer, and formulation E, the good performer, was attributed to the chemically modified oil-based vehicle. Thirty-three per cent of the vehicle in formulation D was substituted with highly bodied (Z_4-Z_5) air-blown tung oil (10) to produce formulation E. On the other hand, the difference between formulation D, the poor performer, and formulation A, a fairly good performer, was attributed to a higher tung oil content in the chemically modified oil-based vehicle and to lower thermoplasticity of carbonific pentaerythritol polyurethanes. A higher tung oil content imparts better drying to the paint film, and the less thermoplastic carbonific and spumific materials minimize blistering and rupturing.

As a result of these findings, research is being continued to elucidate the importance of the vehicle and of carbonific and spumific materials in the development of water-resistant, oil-based, intumescent fire-retardant coatings that will perform well in the UL tunnel furnace.

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