

A Method and Apparatus for Determining the Ignition Characteristics of Plastics

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A method for the determination of the ignition temperatures of plastics is described. It is suitable for the determination of flash-, as well as self- or autogenous-ignition temperatures. The flash temperature is that temperature at which the specimen yields combustible gases ignitable by a flame. The self-ignition temperature is the lowest temperature of supplied air, under optimum conditions of air flow, at which a reaction of the specimen, or of its decomposition products, begins and is self-accelerated to the state of combustion. The described method generally results in lower and more consistently reproducible values of the self-ignition temperature than those reported by several other investigators.

Twenty-seven different specimens of plastics, covering a wide range in characteristics, were tested by the method described.

I. Introduction

An apparatus and method for determining the ignition characteristics and behavior of plastics under well-controlled conditions have been developed at this Bureau from a consideration of the fundamental principles of ignition. Twenty-seven specimens of plastics with a wide range of physical properties and ignition characteristics were tested in order to determine the validity of the method and the adaptability of the apparatus.

It is doubtful whether methods heretofore proposed for measuring the ignition temperatures of plastics actually indicate the lowest ignition temperatures. Stokes and Weber [1]¹ measured the ignitability of plastics by bringing the specimen into contact with a heated porcelain rod just removed from a furnace, or with a molten lead bath heated in a furnace to the required temperature. The estimated temperature of the porcelain rod or of the lead, at which the specimen "instantly" ignited, was accepted by them as the ignition temperature. Delmonte and Azam [2] later substituted molten sodium hydroxide for the lead bath. In their tests, the bath temperature at which a plastic specimen ignited instantly, or within 10 sec, when in contact with the bath was considered as the ignition temperature of the material. More recently, Schoenborn and Weaver

[3] used a method in which the specimen was placed in a furnace heated to a temperature definitely above the ignition temperature of the material. The ignition temperature was defined by the estimated surface temperature of the specimen at the instant of the ignition and was called by them the "apparent ignition temperature." The estimate of this temperature was made by analytical extrapolation of temperatures measured within the specimen, to yield those at the surface at the moment of ignition.

In this method, observation of the temperatures and the extrapolation from them to the actual locus of ignition did not give consistent and reproducible results for a given material [4].

Gale, Stewart, and others [5, 6] used an electrically heated coil around the plastic specimen and observed the time lag required for gases developed from the specimen to be ignited by spark plugs. A so-called ignition temperature, (which in reality is the "flash temperature," as defined in section II) was determined by them from a "conversion curve." This curve was developed by measuring with a thermocouple the temperature at the edge of the specimen and observing the time lag for ignition. This time lag was composed of two superimposed periods; one of which was the time required to heat the coil, and the other was the time required to heat the specimen and to produce sufficient combustible gases to be ignited by the

¹ Figures in brackets indicate the literature references at the end of this paper.

spark plug. These superimposed lags are related to two entirely different phenomena, therefore the range of the ignition temperature, which indicates the accuracy of their determination (shown in table 3 of [6]), varied for a given plastic from 55° to 175° C, with an average of 127° C.

Most of the results obtained by these and similar methods differ materially in their numerical values, as well as in their consistency and reproducibility, because they were obtained under entirely different and noncomparable conditions that were unsuited for the determination of the lowest ignition temperatures. The main purpose of the studies at this Bureau was to develop a sound relation between the ignition phenomena and controllable conditions of test; and on this basis to determine the lowest values of the ignition temperatures and any other characteristics that may affect the fire hazards and therefore safety regulations.

II. Theoretical Considerations

Several years ago a constant-air-temperature method for measuring the ignition temperatures of solids, based upon the principles of ignition stated below, was developed at this Bureau. In this method, successive specimens of the material were heated in air at different constant temperatures until one of them ignited. The same method was found applicable for plastics with a wide range of thermophysical characteristics.

The following definitions of ignition characteristics of materials were employed in the development of the test method. The "flash temperature" is the initial temperature of the air passing around the specimen, at which a sufficient amount of combustible gas is developed to be ignited by an external heat source such as a flame, spark, or hot surface. The "self-ignition temperature" is the initial air temperature, at which, in the absence of an ignition source, ignition occurs of itself, as indicated by an explosion, flame, or sustained glow.

It is well known that the ignition of most combustible materials, excepting those such as cellulose nitrate that contain oxygen in an active form, can be initiated only in the presence of sufficient amounts of oxygen. Before ignition occurs, oxygen must participate in an oxidation reaction with the solid or liquid material, with the vapor, or

with gases evolved at elevated temperatures from the decomposition of the material. In order to promote this reaction, the products of oxidation must be removed continuously and fresh portions of oxygen supplied. Actual ignition, as indicated by a flame, may result either from the accelerated exothermic reaction of vaporized or gaseous components of the material with oxygen, or through the self-heating within the solid or liquid material, which eventually leads to sustained glow of some of the nongaseous components or of the carbonized residue.

On the above basis, ignition can be defined as a self-perpetuating exothermic reaction that is initiated at the temperature of incipient oxidation, and that increases the temperature of the reactants above the initial air temperature until an explosion, flame, or sustained glow occurs. Because of the temperature differences existing within the reacting masses and between them and the surrounding walls, a certain part of the generated heat is dissipated to masses at lower temperatures. Also, some heat is carried away by the passing air and by the products of oxidation. The rate of the oxidation reaction, as well as the rate of its acceleration to self-ignition, is dependent upon the rate of heat dissipation. This will be evident from the following discussion of the time-temperature curves drawn in figure 1 for different initial temperatures.

If an incombustible material be subjected to heating at the constant-air-temperature, t_0 , the temperature of the material will eventually be practically equal to that of the surrounding air, e. g. after the time lag l_0 . This lag depends upon the mass, heat conductivity, and specific heat of the material and upon the initial temperature difference between the air and the material. At relatively low air temperatures, a similar behavior will be observed with combustible materials. However, at a higher air temperature t_1 , which is higher than the observed temperature of incipient oxidation t_x , the material begins to oxidize with the generation of heat, and beyond the point t_x , the temperature of the material increases more rapidly than it would in the normal process of heating without oxidation. The temperature of the material continues to increase and eventually exceeds the air temperature, t_1 . The rate of temperature increase depends upon the difference between the rates of heat generation and of heat

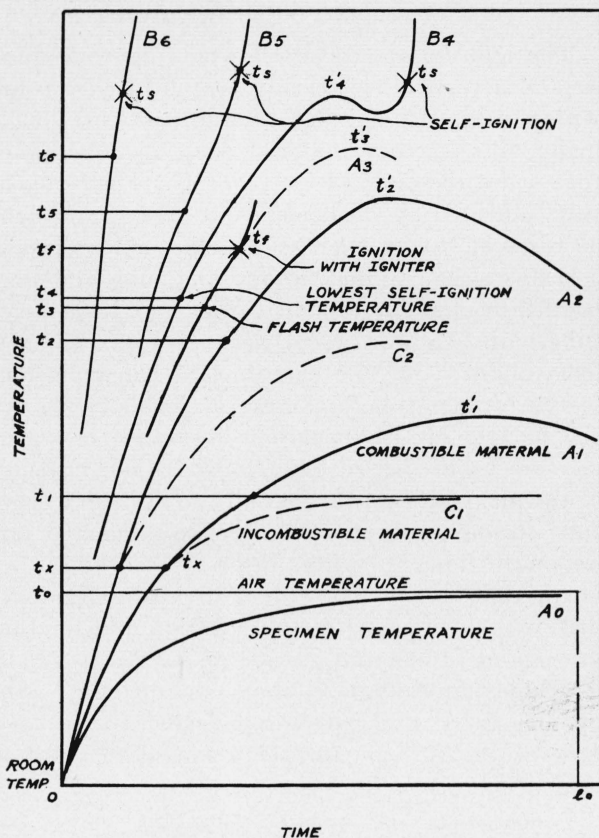


FIGURE 1. Theoretical time-temperature curves for heating and ignition of materials.

Curves A_0 , A_1 , A_2 , and A_3 for nonignition reaction at air temperatures t_0 , t_1 , t_2 , and t_3 ; curves B_4 , B_5 , and B_6 for self-ignition reaction at air temperatures t_4 , t_5 , and t_6 ; curves A_0 , C_1 , and C_2 for heating of noncombustible materials at air temperatures t_0 , t_1 , and t_2 .

dissipation. The rate of heat generation depends mainly upon the temperatures of the specimen and of the air, the supply of air, the concentration of oxygen in the reacting gases, and the chemical and physical characteristics of the material. The rate of heat dissipation depends in part upon the temperature difference between the reacting mass and their surroundings, and in part upon the rate of flow of the air. An insufficient air flow leads to contamination of the air by the products of oxidation and depletes the oxygen supply. This condition hinders oxidation and lowers or stops entirely the exothermic reaction. On the other hand, an excessive air flow carries away a large amount of the generated heat and thus lessens or interrupts the exothermic reaction. The optimum rate of air flow, at which a relatively favorable rate of reaction is reached, must be estab-

lished experimentally for each type of material. The temperature of the material usually continues to rise until the rate of heat generation equals the rate of heat dissipation, e. g. at a point corresponding to the maximum temperature t'_1 , indicated by a thermocouple Th_3 (fig. 2) in or on the specimen. This process is often accompanied by the evolution of vapor gas, which at this particular stage may not be ignitable, either by itself or by an igniter, because of its low rate of evolution and consequent dilution with air.

At some other constant-air-temperature such as t_2 , the material may self-heat by oxidation to a higher temperature such as t'_2 . However, during self-heating, starting at an air temperature of t_3 , the concentration of evolved combustible gases or vapors may become favorable to their ignition by the pilot flame at a particular temperature t_f , which is often below the maximum temperature t'_2 of the previous case, where the ignition could not have occurred. The air temperature t_3 in this case is called the flash temperature. In the absence of the ignition flame, self-heating may proceed to the corresponding maximum temperature t'_3 without self-ignition. Owing to these factors, regularly observed with many materials, the instantaneous temperature t_f has no important significance, even if it could be determined accurately, because this temperature, as well as the rate of heat generation and the rate of gas development and dilution, depend mainly upon the initial temperature and velocity of the air passing around the specimen.

In many cases, it was observed that the rate of the exothermic reaction was reduced beyond a temperature peak such as t'_4 by excessive contamination of the air with the decomposition products, by cooling caused by a high rate of air flow, by some endothermic reaction, or by reduction of the available reactive material. With proper adjustment of air flow (which reduces the rate of temperature rise near the point t'_4), it is possible for the rate of oxidation to be accelerated again to the self-ignition of gases at a higher temperature, such as t_s . This temperature, t_s , like the temperature t_f , has no important significance in relation to the ignition characteristics, because it depends upon both the initial air temperature t_4 and the rate of air flow. Therefore, the temperature t_4 of the air, at which with the optimum air flow and in the absence of an igni-

tion source, ignition occurs is called the self-ignition temperature of the material.

At higher initial air temperatures such as t_5 and t_6 , self-ignition occurs more readily, and the ignition lag rapidly diminishes to a fraction of a second with continued increase in the initial temperature. The ignition lag for the lowest self-ignition temperature (t_4) may vary from a few minutes to a few hours, depending upon the difference between the rates of heat generation and heat dissipation, which is affected by the size of the specimen, as well as by the thermo-chemical and physical properties of the material.

The evidence of self-ignition is usually observed in the form of an explosion, flame, or sustained glow. In some plastic materials the ignition temperatures corresponding to the various types of behavior differ appreciably. The self-ignition accompanied by explosion or flame usually occurs at comparatively high initial air temperatures; however, slow decomposition and carbonization of some plastics leads to glow of the corners and edges at lower temperatures. Therefore, a secondary term, "self-ignition by glow", is proposed. The self-sustained glow may in some cases, with proper air flow, lead to ignition of the combustible gases.

The foregoing considerations indicate that "instant" ignition of the material in contact with a hot surface, as specified by some of the early methods, occurs at much higher temperatures than are observed with the constant-air-temperature method. Therefore, as explained in section V, 5 this hot-surface ignition temperature does not represent the true fire hazard of the materials.

III. Ignition Apparatus

The apparatus for the determination of the ignition characteristics of plastics was developed on the basis of the fundamentals of ignition phenomena discussed above. In the construction of the apparatus, particular attention was given to the following major requirements:

(a) The temperature of the air passing the specimen should be uniform and constant. (b) The air flow should be steady and controllable. (c) The specimen should be in a stream of air of known temperature; be visible from the outside; and be easily removable.

1. Construction of the Apparatus

The ignition apparatus shown in figure 2 consists of a vertical electrically heated furnace tube with a 4-in. (10 cm) bore, 8¾ in. (22 cm) long, made of refractory material such as a ceramic that will withstand at least 1,000° C. The furnace tube is heated by electric current passing through 50 turns of No. 16 B&S gage nichrome wire in an asbestos sleeve wound around the tube and imbedded in alundum cement. The inner refractory tube with a 3-in. (7.6-cm) bore, 8¾ in. (22 cm) long, about ⅛ in. (0.3 cm) thick is placed inside of the furnace tube and rests on small blocks in the bottom of the furnace. The space between the two tubes is used for circulation and heating of the air, admitted tangentially to the refractory tube through a copper tube. The preheated air enters the inner tube from below. The top of the latter tube is covered with a divided refractory disk with an opening for observation and for the passage of smoke and gases. If desired, a small gas flame can be lighted above the opening. An opening fitted with disk is provided at the bottom of the furnace for the removal of residue that accumulates during the tests.

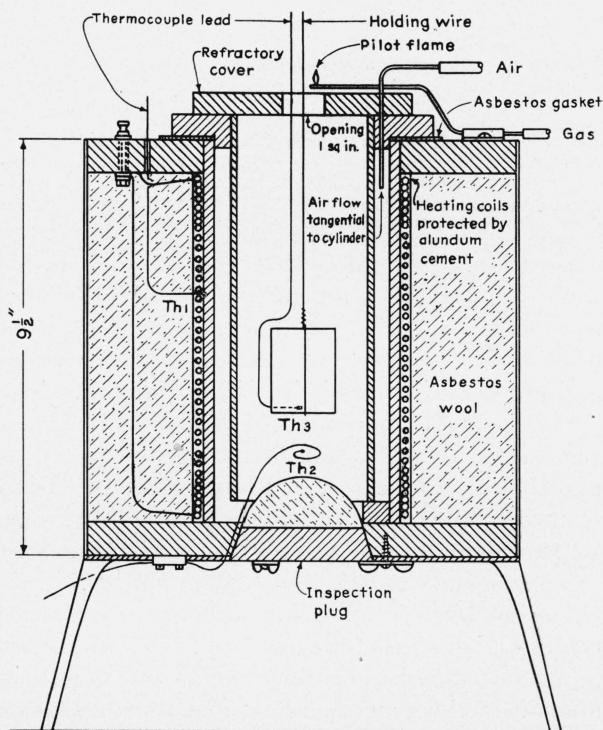


FIGURE 2. Ignition apparatus for solids.

Th_1 —thermocouple on outer wall, Th_2 —thermocouple in air stream, Th_3 —thermocouple in or on the specimen.

2. Thermocouples

The temperature of air rising in the inner tube is indicated by thermocouple Th_2 placed below the specimen. It is advisable to shield this thermocouple against heat radiated from the specimen during intense oxidation reactions, especially if the thermocouple is near the specimen. However, since the temperature of the air supplied to the chamber remains substantially constant, any momentary increase of temperature shown by thermocouple Th_2 during intense oxidation reactions is not important. The temperature of the air in the inner tube is maintained constant by current supplied through a variac connected in series with the heating coils. Adjustments of the current are preferably made by reference to the readings of thermocouple Th_1 behind the coils, rather than by reference to thermocouple Th_2 (below the specimen), which always has a somewhat delayed response to current changes.

A third thermocouple, Th_3 , is either attached to the surface or inserted within the lower part of the specimen. The rate of temperature rise in the specimen, indicated by this thermocouple is generally related to the rate of the oxidation reaction. The exact location of thermocouple Th_3 in the specimen is of minor importance because of the uncertainty as to the locus of ignition, but since ignition is usually initiated at the surface of the lower part of the specimen, it is desirable to locate the thermocouple junction in this region. A small bare thermocouple junction is used because of its sensitivity to small variations in temperature.

3. Size of Specimen

The size of specimen is varied with type and availability of the material. The standard size usually specified for incombustibility tests [7] is 1½ in. (3.8 cm) wide by 2 in. (5 cm) long, by the thickness of specimen, which should not exceed 1½ in. (3.8 cm). However, for determining the ignition characteristics of plastics, the preferred size of specimen is ¾ in. (1.9 cm) by ¾ in. (1.9 cm) by ¾ in. (1.9 cm) by about ½ in. (1.3 cm) thick. For materials made in thin plates, the specimen consists of a few plates with a total thickness of about ½ in. (1.3 cm) tightly bound together by wire. For materials submitted in the form of small pieces, chips, filings or powder, and for those

that melt or bubble at temperatures below ignition, a wire screen basket or a porcelain crucible with a capacity of about 0.5 in.³ (8 ml) is used. Within these limits the ignition temperature is not appreciably affected by the size; however, the ignition time-lag varies perceptibly with the size. Small specimens of those materials that develop insignificant amounts of combustible gases, yield less consistent results for the lowest ignition temperature than do those of larger size.

4. Suspension of Specimen

The arrangement for holding the specimen is important, especially for materials whose physical state changes at temperatures below the ignition point. Materials that remain rigid during the test can be suspended on a wire; those which melt to a viscous mass and which bubble can be held in a wire-screen basket; and those which melt to a liquid state, like methyl methacrylate, polystyrene, and others; or those which foam like cellulose acetate, can be placed in a preheated porcelain crucible. Owing to a large gradient in the temperature of the air in the upper portion of the inner tube, the specimen should be placed in the region 4½ to 6½ in. (11 to 16 cm) from the top, where the air temperature around the specimen is uniform within ±3 deg. C.

IV. Test Procedure

1. Rising-Temperature Method

In tests conducted in accordance with the rising-temperature method [7, 8], the specimen is placed in the apparatus at a comparatively low temperature. In the method described in reference [8] the temperature of the apparatus is then raised at the rate of 500 deg C per hour until ignition occurs by itself, or by an igniter, or until 750° C is reached. If at this temperature ignition has not occurred, the material is considered incombustible. Some materials heated in this manner decompose or carbonize slowly without ignition of the material of the carbonized residue at temperatures higher than those obtained with the constant-temperature method. Therefore, this method is not always suitable for exact determination of the flash and self-ignition temperatures. However, it can be used to indicate the approximate ignition temperatures by the evidence of appreciable self-heating in the region of

the ignition temperature, even though actual ignition is not observed. More precise determinations of the flash and self-ignition temperatures can be made by the constant-temperature method described below.

2. Constant-Temperature Method

When the temperature of the air passing through the inner tube with a selected rate of flow has become constant at a selected value, a specimen of the material to be subjected to test is placed in the middle of the inner tube together with a thermocouple, Th_3 , either attached to the surface or inserted within the specimen. The air temperature may fall slightly below the initial value, owing to the presence of the cold specimen, but within a few minutes it returns to the initial value. The uniformity of the air temperature around the specimen is quite sensitive to the velocity of air flow, especially when the size of the specimen is small. Fluctuations in temperature caused by excessive turbulence can be avoided by keeping the air velocity around the specimen at about 15 ft/min (5 m/min), particularly during the preliminary tests. However, a favorable rate of air flow is usually fixed in accordance with the trend of the exothermic reaction. The rate is generally varied from 3 to 40 ft/min (1 to 13 m/min), depending upon the material tested. A close selection of the optimum rate of air flow can be made with a series of tests in the region of the lowest ignition temperature, conducted with various constant rates of air flow.

V. Test Results

1. Test Materials

To aid in the development of an ignition apparatus and a suitable test method, 27 samples of plastics were employed. These plastics, with a wide range of physical and ignition characteristics, were divided into two basic groups: (a) thermoplastic, and (b) thermosetting. Most of the latter group were reinforced with paper, asbestos, cotton, or glass fabric. A general description of these plastics is given in table 1.

2. Ignition Characteristics of Thermoplastic Materials

The basic ignition characteristics of some of these thermoplastics, including results of hot-plate tests, are given in table 2. The plastics of the

thermoplastic group, with the exception of polytetrafluoroethylene, were transparent, and the appearance of small bubbles was observed at an early stage of decomposition at comparatively low temperatures. The appearance of bubbles and the swelling of the material increased rapidly with an increase in temperature, particularly with cellulose nitrate, which suddenly, without preliminary self-heating, ignited with an explosion or burst of flame. The bubbling of cellulose acetate increased during the melting to produce a foam. Methacrylate and polystyrene melted to thin liquids and boiled similarly to water, hence these materials were held in a crucible. The ~~first~~ ~~formed~~ heavy foams of vinyl chloride-acetate yielded a hollow porous carbonized shell, inside of which the glow was usually initiated. This material was held in a wire-screen cup.

Cellulose nitrate, a material containing active oxygen, can be ignited without air flow, and therefore its lowest self-ignition temperature varied considerably with the method of heating and the impurities present. Specimens of this plastic in the $\frac{1}{2}$ - by $\frac{3}{4}$ - by $\frac{3}{4}$ -in (1.3 by 1.9 by 1.9 cm) size, heated for 6 hr under selected conditions with normal air flow, about 15 ft/min, as found favorable in the preliminary tests of most of the plastics, were not ignited at an air temperature of 140° C and during this time were self-heated to only 4° C above the air temperature. During a test with an air temperature of 141° C, the temperature of the specimen after 1 hr and 54 min reached only 150° C, when sudden decomposition and ignition occurred, as shown in figure 3. The ignition lag rapidly diminished with rise in the initial air temperature, as the two curves in figure 4, drawn for different time scales, indicate. The lower curve represents the change in the ignition lag time for air temperatures from 141° to 220° C, and the upper curve, for air temperatures above 220° C. With the air temperature at about 141° C, the ignition lag decreased at the rate of about 12 min per increase of 1 deg C. On the other hand, at air temperatures above 250° C, the ignition lag was shortened to a fraction of a minute. The ignition lag curves for other plastics are shown in figure 5. In order to produce ignition within 10 sec, as specified in some methods, the air temperature had to be above 370° C, and a 1-sec lag could be obtained only at air temperatures above 550° C. Therefore, an ignition temperature de-

TABLE 1. Identification of plastics

Type	Manufacturer or source	Thick-ness	Name or description
THERMOPLASTIC MATERIALS			
Cellulose nitrate.....	Celanese Corp. of America.....	<i>in.</i> 1/16	Celluloid, transparent.
Cellulose acetate.....	Monsanto Chemical Co.....	1/8	Clear, special optical grade.
Methyl methacrylate:			
(a).....	E. I. du Pont de Nemours & Co., Inc.....	1/8	HC-202.
(b).....	Rohm & Haas Co.....	1/8	Plexiglas.
Vinyl chloride-acetate:			
(a).....	Bakelite Corp.....	1/8	Clear, VS-1310.
(b).....	do.....	1/4	Do.
Polystyrene.....	Plax Corp.....	1/4	Clear, Type M, compression molded.
Polytetrafluoroethylene.....	E. I. du Pont de Nemours & Co., Inc.....	3/8	White plate.
THERMOSETTING MATERIALS			
Phenolic group:			
Paper Laminate:			
(a).....	Consolidated Water Power and Paper Co.....	1/8	} Cross laminated Mitscherlich paper: 30 percent Bakelite phenolic resin.
(b).....	Consolidated Water Power and Paper Co. (new lot).....	1/8	
Cotton-cloth laminate.....	Synthane Corp.....	1/8	Grade L, 48 percent Bakelite, BV-1112 resin.
Asbestos-cloth laminate.....	do.....	1/2	Grade AA, 47 percent Bakelite, BV2427 resin.
(a).....	U. S. Plywood Corp.....	1/8	6050.
(b).....	do.....	1/8	5013.
Melamine group:			
Mineral-filled melamine.....	American Cyanamid Corp.....	1/4	592.
Cotton-cloth laminate.....	do.....	1/4	White plate.
Glass-cloth laminate:			
(a).....	Formica Insulation Co.....	1/8	128, FF-55.
(b).....	U. S. Plywood Corp.....	1/8	Not available.
Polyester group:			
Glass-cloth laminate:			
(a).....	Army Air Forces, Wright Field.....	1/8	ECC-11-112.
(b).....	U. S. Plywood Corp.....	1/8	4143.
(c).....	do.....	1/8	4128.
(d).....	do.....	1/8	5016.
(e).....	do.....	1/8	4128+5 percent At.
(f).....	do.....	1/8	5041.
(g).....	do.....	1/8	MR-21A.
Silicone group:			
Glass-cloth silicone:			
(a).....	Formica Insulation Co.....	1/8	ESS-12-261, grade G-6.
(b).....	U. S. Plywood Corp.....	1/8	Not available.

TABLE 2. Ignition characteristics of plastics

Type	Ignition temperature				General behavior
	Flash	Self ignition		Hot-surface	
		Glow	Flame		
THERMOPLASTIC MATERIALS					
	° C	° C	° C	° C	
Cellulose nitrate.....	141	-----	141	550	Bubbled, gas exploded.
Cellulose acetate.....	305	-----	475	600	Bubbled, melted, foamed, flamed.
Methyl methacrylate:					
(a).....	280	-----	450	600	Bubbled, melted, liquefied, boiled, flamed.
(b).....	300	-----	462	600	Do.
Vinyl chloride-acetate:					
(a).....	320	377	557	650	Flowed, foamed, carbonized, glowed, flamed.
(b).....	340	355	435	650	Do.
Polystyrene.....	345	-----	488	600	Bubbled, melted, liquefied, boiled, flamed.
Polytetrafluoroethylene.....	-----	-----	530	-----	Melted, evaporated, boiled, flamed.
REINFORCED THERMOSETTING MATERIALS					
Phenolic group:					
Paper laminate:					
(a).....	300	310	430	600	Blistered, carbonized, glow, flame.
(b).....	311	344	367	600	Do.
Cotton-cloth laminate.....	339	320	492	500	Do.
Asbestos-cloth laminate.....	382	-----	500	None below 750°	Blistered, carbonized, self-heated, flame.
Glass-cloth laminate:					
(a).....	520	-----	571	-----	Intensely self-heated, flame.
(b).....	540	-----	580	-----	Do.
Melamine group:					
Mineral-filled melamine.....	313	350	455	700	Glow, flame.
Cotton-cloth laminate.....	-----	-----	480	-----	Flame.
Glass-cloth laminate:					
(a).....	500	-----	645	None below 750°	Flame below specimen.
(b).....	475	-----	623	do.....	Do.
Polyester group:					
Glass-cloth laminate:					
(a) 900.....	346	400	462	600	Glow, flame.
(b) 4143.....	394	-----	447	-----	Audible explosion.
(c) 4128.....	358	-----	452	-----	Do.
(d) 5016.....	352	-----	433	-----	Audible explosion. Flame below specimen.
(e) 4128+5%AT.....	355	-----	453	-----	Do.
(f) 5041.....	364	-----	488	-----	Audible explosion; flame.
(g) MR-21A.....	377	-----	475	-----	Audible explosion; flame below specimen.
Silicone group:					
Glass-cloth laminate:					
(a).....	527	-----	564	None below 750°	Flame.
(b).....	490	-----	550	do.....	Do.

fined by the method that required a lag of from 1 to 10 sec was very much higher than the self-ignition temperature defined by the present method and hence did not represent the true fire hazard.

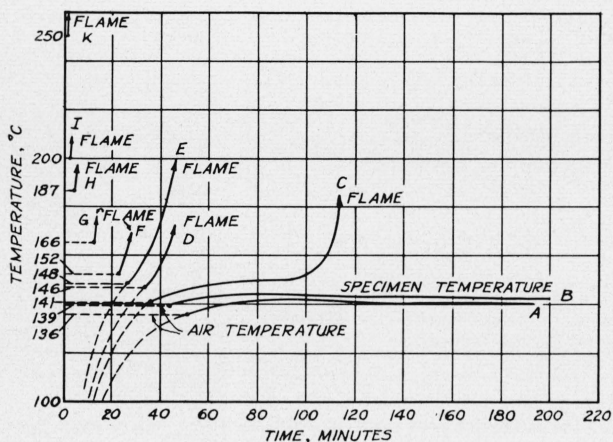


FIGURE 3. Time-temperature curves for cellulose nitrate.

Curves A and B for nonignition reaction; curves from C to K for self-ignition reaction. The lowest self-ignition temperature is 141° C.

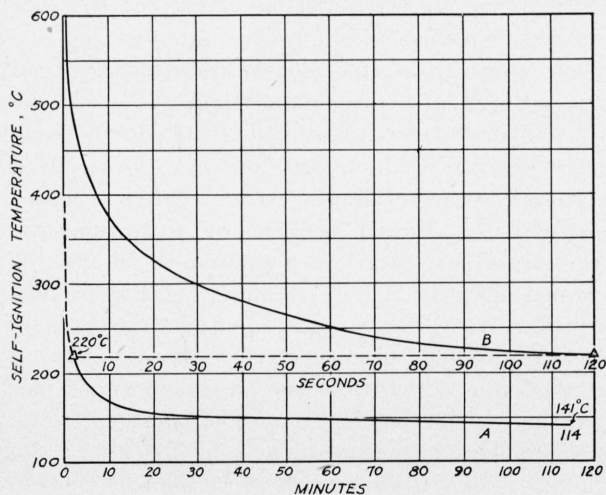


FIGURE 4. Ignition lag curves for cellulose nitrate.

Curve A at air temperatures from 141° to 220° C and curve B from 220° to 600° C.

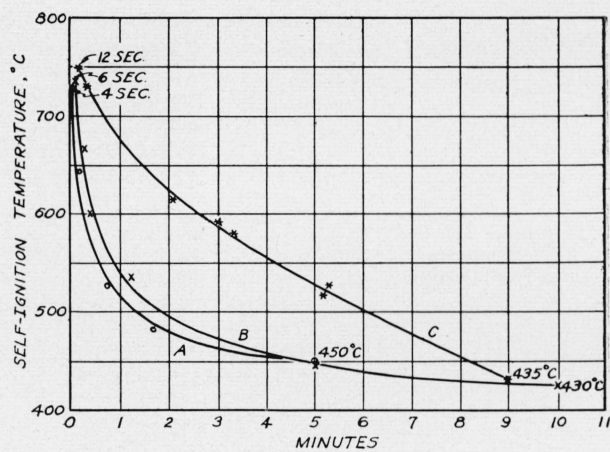


FIGURE 5. Ignition lag curves for plastics.

Curve A—methyl methacrylate (a); curve B—phenolic paper laminated; and C—vinyl chloride acetate.

A box of cellulose nitrate plastic triangles, separated by wrapping paper, was reported to have ignited after a 1-hr exposure to the sun in southern Texas. Specimens of material from the same source, about $\frac{3}{4}$ in.³ in volume, were subjected to tests in the ignition apparatus at the Bureau in a closed test tube without air circulation. During 72 hr of heating, self-heating of the specimen was observed to be about 1 deg C at 105° C, about 5 deg C at 135° C, and the rise in temperature was only 6 deg C at 141° C after 6 hr of heating. However, at a temperature of 142° C, self-heating of about 6 deg C occurred during a 32-min period, when the specimen burst into flame. These tests indicate that the temperature of incipient oxidation was about 105° C, and the self-ignition temperature was approximately 142° C. Triangles from the same lot, separated and covered by the original wrapping paper, were self-ignited after 3.5 hr of heating at a temperature of 135° C, the self-ignition temperature of the paper being about 235° C.

Physical properties of the thermosetting materials, observed at different temperatures prior to ignition, are shown in table 3.

TABLE 3. *Physical characteristics of thermosetting materials prior to ignition*

	Cellulose nitrate	Cellulose acetate	Methyl Methacrylate		Vinyl Chloride acetate	Polystyrene
			(a)	(b)		
Temperature, °C						
Appearance of bubbles...	105.....	130.....	150.....	200.....	160.....	160.
Loss of transparency....	120.....	150.....	220.....	250.....	190.....	200.
State prior to ignition...	Soft.....	Soft.....	Liquid.....	Liquid.....	Spongy mass.....	Viscous liquid.
Rise in temperature, °C						
Self-heating of material prior to ignition.	10.....	40.....	15.....	20.....	Glow.....	None.
Self-heating of gases above the molten material.	None.....	None.....	Very high.....	Very high.....	Slight.....	None.
Apparent cause of self-ignition.	Rapid decomposition.	Self-flash of gases from inflated material.	Self-heating of gases above molten metal.	Self-heating of gases above molten material.	Glow of carbonized materials.	Self-flash of gases in 2d state of decomposition.

The appearance of bubbles and loss of transparency of the plastics rapidly increased with the temperature and duration of exposure; therefore, the extents of these changes observed within the first hour have only relative significance. In cellulose acetate the bubbles increased mainly in size, in contrast with other plastics in which they increased greatly in number. The state prior to ignition varied with the type of plastic. Both cellulose nitrate and acetate plastics are soft just before ignition. However, near the ignition temperature, cellulose nitrate remains soft indefinitely, whereas cellulose acetate inflates, melts, and evaporates. Methyl methacrylate (fig.6) and polystyrene melted below their ignition temperatures and remained in a liquid state for an appreciable time until entirely evaporated without ignition. Vinyl chloride-acetate formed a spongy semi-soft shell inside of which a glow of carbonized material occurred. The self-heating of all of these materials (with the exception of vinyl chloride-acetate) prior to ignition varied from 10 to 40 deg C above the air temperature. Vinyl chloride-acetate self-heated considerably, owing apparently to oxidation and carbonization of the spongy mass. Very intense self-heating was observed only in the vapor above molten methyl methacrylate plastics, in that the wires holding the crucible became red hot. It is doubtful whether there was a catalytic effect of these heated wires to produce self-ignition, which usually occurred at an early stage of the reaction and

before the wires became red hot. However, in the nonignition zones the red hot wires did not appear to stimulate ignition. Self-ignition of cellulose nitrate, indicated by a mild audible explosion, usually occurred very suddenly, apparently owing to rapid decomposition of the soft inflated material. Cellulose acetate was ignited when gases from the inflated material escaped through a local rupture into the hot air. If the air temperature was not sufficiently high, these gases escaped without ignition and the deflated material began to melt. Methyl methacrylates (a) and (b) ignited because of an exothermic reaction of gases and hot air above the molten or foamed material. For example, methyl methacrylate (a) and (b) was ignited at air temperatures of 450° and 462° C, respectively, the liquid being at 460° and 472° C, and the foam and vapor just prior to ignition reached over 600° and 645° C, as measured by a thermocouple held just above the liquid. The self-ignition of vinyl chloride-acetate was usually indicated, as stated before, by glow of carbonized portions inside the spongy shell; however, at higher air temperatures these glowing portions ignited gases developed in the incompletely carbonized mass. At an air temperature below 340° C, polystyrene developed such an amount of incombustible gas during about the first 5 minutes that the pilot flame could not be kept lighted. However, at the next stage of decomposition this effect disappeared, and the burning of the pilot flame became normal. At an

air temperature of 345° C gases that developed during the second stage could be ignited by the pilot flame after about 13 min, and at 488° C they were self-ignited after 5.5 min. It is interesting to note that the temperature of the liquid polystyrene always was below the air temperature and when self-ignition occurred, it was only 400° C.

The ignition characteristics of polytetrafluoroethylene were determined only approximately, because of the limited size of the sample then available.

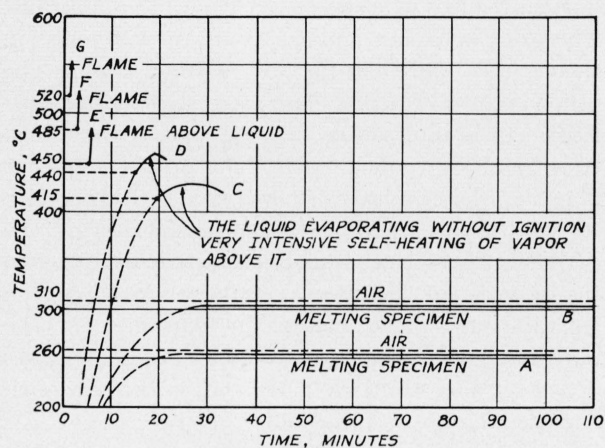


FIGURE 6. Time-temperature curves for methyl methacrylate (a).

Curves A to D for nonignition reaction, curves E to G for self-ignition reaction.

3. Ignition Characteristics of Reinforced Thermosetting Materials

The plastics of the thermosetting group usually changed their shape slightly because of a slow process of blistering and carbonization at temperatures below that of self-ignition. When these materials were heated at or near the ignition temperature for an appreciable time, the plastic resin evaporated or carbonized, but the asbestos and glass fabrics remained in layers. On the other hand, combustible fillers, such as paper or cotton fabrics, usually carbonized slowly into a more or less uniform mass with blisters on the surface. If, at comparatively high temperatures, then the glow started at the edges and corners or in the cracks. At still higher temperatures, the decomposition proceeded faster and the gases were self-ignited by the exothermic reaction with the passing air.

Method for Ignition of Plastics

The ignition characteristics of plastics of the phenolic laminate group varied considerably with the type of filler, as shown in the second part of table 2. The flash temperature varied from 300° to 540° C. Glow was observed only if paper or cotton cloth fillers were present. Glow in other phenolic materials was not sustained after removal of the specimen from the furnace, in spite of very intense self-heating, which sometimes produced a temperature of 600° C. The lowest self-ignition temperature, characterized by a flickering flame, varied from 430° to 580° C., depending upon the type of the filler. The combustion of these fillers was usually slow and not sustained after removal of the specimen from the apparatus.

The ignition characteristics of materials of the melamine group also varied with the type of filler, as shown in table 2. The rate of oxidation of mineral-filled melamine was found very sensitive to airflow and size of specimen, as shown on the curves F, G, and H in figure 7, particularly in the region of glow. The specimens of normal size did not reach the state of glow with the different rates of air flow, marked on the time-temperature curves corresponding to initial air temperature of 368° and 384° C. However, the specimens of double that size were found glowing at 350°, 355° C, and higher temperatures, with practically the same variations in the air flow. The size of the cotton-cloth melamine laminate submitted for test was sufficient for the determination of the self-ignition temperature only. Therefore, data on flash and glow temperatures were not developed for this material.

Glass-cloth melamine laminate (a) was the most heat-resistant of the plastics tested. In spite of the evolution of dense smoke, the oxidation reaction was so weak that up to a temperature of 450° C the self-heating did not exceed 15 deg C above the air temperature. In the region of 500° C, the temperature of the mass of melamine laminate increased about 100 deg C above the air temperature, and the color of the mass became a dull red. Dense smoke, in which the odor of ammonia was predominant, usually disappeared in 4 min. The oxidation reaction in the gas evolved from the specimen at that time became so intense that the wires holding the specimen were heated to a bright red color, distinctly visible against the darker specimen and

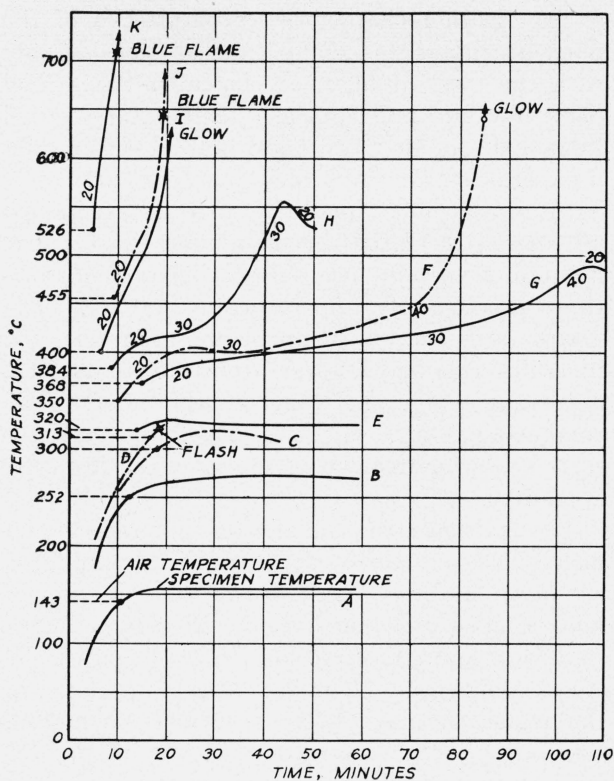


FIGURE 7. Time-temperature curves for mineral-filled melamine.

Curves A, B, C, D, E, G, and H for nonignition reaction, curves F, I, J, and K for self-ignition reaction. Figures on curves—air velocities in feet per minute, curves F, G, and H are taken during adjustment of air flow. —, specimens, single size; - - - - -, specimens, double size.

furnace wall. The intensity of self-heating in the melamine increased with air temperatures up to 660° C, at which temperature a blue flame started to flicker over the darker surface of the specimen. The red color of the self-heated mass of material did not represent a state of sustained glow, because when the specimen was moved into a cooler portion of the furnace or was removed from the furnace entirely, the mass cooled rapidly.

The self-ignition temperature of this plastic is difficult to determine exactly because of the several different types of ignition that were observed. With careful adjustment of an optimum air flow, an occasional blue or red flame was observed for type (a) at an air temperature of 645° C, a flickering of blue flame was observed at 662° C, and a continued flaming at 673° C. The lowest self-ignition temperature was 645° C. The ignition of gases by the pilot flame was obtained occasionally at 500° C and regularly at an air temperature of 544° C. For glass cloth melamine

laminates (b), self-ignition was occasionally observed at 623° C and the flash temperature at 475° C.

The ignition characteristics of the polyester plastics were substantially the same. The flash temperature varied from 346° to 394° C and the self-ignition temperature from 433° to 488° C. The self-ignition was characterized by mild explosion of gases developed from the material, or by an audible flash of gases without destructive effect. The combustion of these materials varied quite appreciably: glass-cloth laminate type (d) burned readily when removed from the apparatus, whereas types (c) and (g) burned well only in the furnace and then for only a short time. The other materials of this class were slightly combustible. It is interesting to note that the combustible gases developed from some of the polyester plastics were relatively heavy, and therefore settled to the bottom of the furnace during the early states of decomposition, particularly when the rate of air flow was very low. Self-ignition usually took place below the specimen in the bottom of the furnace, and burning of these gases in the furnace continued even after the specimen had been carefully lifted out.

Both types of glass-cloth silicone laminates had about the same ignition characteristics. These withstood heating very well up to 450° C. Appreciable self-heating (115° C) was observed at 540° C. Flammable gases were developed at a temperature of 490° C for this plastic of type (b) and at 527° C for type (a). Such high flash points for gases seemed to be caused by the development of a noncombustible gas during an early stage of the decomposition of the material. This gas extinguished the pilot flame during the first 5 min. of the reaction. The self-ignition of the gases was irregular and was first observed at air temperatures of about 564° C and then only after 5-min lag, when the contamination of the combustible gases had been sufficiently reduced. At an air temperature of about 600° C, self-ignition became more regular, and the time lags varied from 2 to 3 min. During the next 3 min the plastic burned with long orange flames.

4. Reproducibility of Test Results

The reproductivity of the ignition temperature values of plastics as determined in the present

apparatus depends upon two major factors: one is uniformity of chemical composition and physical state of the plastics from which the specimens are taken; and the other is the sensitivity of the test method and the apparatus to the ignition characteristics of the material. The first factor was substantially constant for most of the plastic materials when tested and for a long time subsequently. An exception was found in cellulose nitrate, which sometimes changes under the action of sunlight and temperature. The ignition characteristics of some plastics, such as methyl methacrylate, vinyl chloride-acetate, and a few others (bearing the same names) varied with the manufacturer's lot or with their purity.

The sensitivity of the constant-temperature test method to the ignition properties characteristics of the material is high, owing to the fact that the temperature in the whole apparatus can be stabilized in advance and kept substantially constant during the test. The temperature and rate of air flow are under good control. The reproducibility

of the results depends mainly upon the accuracy of the test procedure and the interpretation of the observed evidence of ignition, i. e., upon the following three factors: (1) The positioning of the specimen in the region of uniform temperature in the furnace tube (middle position); (2) correct selection of the optimum air flow for the most favorable rate of temperature rise in the reacting mass; and (3) careful bracketing of the temperatures that correspond to the types or stages of ignition, such as: explosion, flash, flame, glow, cold flame, or luminescence.

The bracketing of the lowest ignition temperature is usually made in the manner shown in table 4, with five or more determinations within the region of the boundary between ignition and nonignition zones in order to secure the desired temperature range, which is usually between 2 and 5 deg C. This range depends upon the required accuracy and the available time, since the time lag in this region may vary from a few minutes to a few hours.

TABLE 4. *Determination of the lowest self-ignition temperature*

Methyl methacrylate				Vinyl chloride acetate				Paper phenolic				Mineral filler melamine		Glass cloth polyester	
(a)		(b)		(a) clear		(b) yellowish		(a)		(b)		Temperature	Evidence	Temperature	Evidence
Temperature	Evidence	Temperature	Evidence	Temperature	Evidence	Temperature	Evidence	Temperature	Evidence	Temperature	Evidence				
°C		°C		°C		°C		°C		°C		°C		°C	
550	Flash	517	Flash	580	Flash	500	Flash	463	Flash	475	Flash	572	Flash	488	Flash.
510	Flame	470	Flame	564	Flame	475	Flame	442	Flame	469	do	545	Orange flame.	470	Flame.
470	do	464	do	560	do	440	do	433	do	467	Flame	532	Blue flame	466	Flame.
453	do	462	do	557	do	435	do	430	do	468	Glow	455	do	462	Do.
450	do	460	No ignition.	553	Glow	432	Glow	427	Glow	463	do	453	Glow	463	Glow.
448	No ignition	458	do	550	do	428	do	423	do	418	do	408	do	558	Do.
445	do	455	do	420	do	382	do	366	do	350	do	355	do	404	Do.
440	do	450	do	377	do	355	do	310	do	344	do	350	do	400	Do.
440	do			375	No ignition.	353	No ignition.	307	No ignition.	342	No ignition.	346	No ignition.	398	No ignition.
				370	do	350	do	303	do	338	do	344	do	392	Do.
				361	do	340	do	298	do	320	do	312	do	360	Do.

In table 4 only typical results are given, and many practically identical results observed during the tests are omitted. In some cases a non-ignition state was observed 1 or 2 deg. C above the lowest self-ignition temperature, owing to accidental variation of test conditions. When the evidence of the ignition is clearly defined (as

with cellulose nitrate and acetate, methyl methacrylate, and other thermoplastic materials) the results are closely reproducible. For example, a sample of methyl methacrylate plastic of type (a) was tested in October 1946 and retested in March and December 1947; the results were 450°, 451°, and 450° C. In contrast, methyl methacrylate

of another shipment, type (b) had an ignition temperature of 462° C. Yellowish vinyl chloride-acetate, type (b) was tested first in October 1946 and retested in February 1948, with the same value, 435° C, which differed from the value (557° C) for the clear type (a).

In those cases where the evidence is not clearly defined owing to a gradual change of intensity and color of the flame from a steady orange to a flickering blue, or to the appearance of flame at the end of the glowing period, the reproducibility of results depends upon the type of observed evidence. For example, the flash of the paper phenolic laminate was observed at 467° C after a 4-min lag; another specimen of the same sample glowed at 467° C, and a weak flickering flame appeared only after 16-min lag. This difference was caused by sudden exposure of a noncarbonized portion of the specimen to hot air through the opening of a crack or the separation of layers of the specimen. However, the change between glow and nonglow states was defined more clearly at 344° C, a value reproduced at other times.

The determination of the ignition state was more difficult with glass-cloth melamine laminate. In the absence of glow, the intensity of ignition gradually diminished from a bright flash at 673° C to a blue flame at 662° C, which did not appear at all at 650° C. However, the flame was observed in two of five specimens at 645° C, but in none of the five at 630° C. No explanation of this uncertainty of behavior is offered, but it could be caused by the presence of ammonia gas, which might have interfered with the ignition.

The reproducibility of the test results depends upon careful technique and accuracy of observation, as much as upon the apparatus and the principles involved.

5. Ignition by Hot Surface

Early determinations of the ignition temperature of plastics were often made by contact with hot surfaces. Basically, in the hot-surface methods, the surface is only a medium for the transmission of heat to the specimen, because the hot surface does not participate in the oxidation that usually causes ignition. The essential element in the ignition is the oxygen of the air, the temperature of which is usually considerably below that of the hot surface, particularly if the latter is not within a uniformly heated furnace. Moreover, in

most cases, the ignition of plastics occurs because of intense oxidation of the gaseous components evolved during the process of heating. This process requires a time lag, which varies from hours to fractions of a second, depending upon the ambient air temperature. The air-temperature gradient from a vertical hot surface exposed to the atmosphere, as our experiments showed, varies considerably with the distance from the surface. The temperature drop in the first 1/8-in. (3-mm) zone is from 150° to 200° C when the temperature of the hot surface is 600° C. These results are in agreement with Kennard Work [9]. Combustible gaseous products from plastics, turbulently moving along the surface within the zone, usually have only a few seconds in which the oxidation reaction may be accelerated to cause ignition. Therefore, for this limited time lag the average air temperature within the 1/8-in. (3-mm) zone must be much higher to cause ignition than in a uniformly heated furnace with an unrestricted time lag. Hence, ignition by contact with a hot surface occurs only at higher temperatures than are required for ignition in uniformly heated air.

The hot-surface apparatus used in these studies consisted of a 1/4-in. (0.6-cm) steel plate, heated by coiled resistance wire imbedded in the grooves of a refractory plate attached to the back of the steel plate. All sides of the assembly, except the front, were heavily insulated by asbestos wool mixed with vermiculite. The temperature of the exposed front vertical surface of the "hot plate" was indicated by a thermocouple junction imbedded in the plate. The specimen was usually held in contact with the vertical hot surface about 5 min, or until ignition took place, which might occur during the first 1 or 2 min. The temperatures of the hot plate at which different plastics were ignited are given in the fifth column of table 2. With the exception of cellulose nitrate and cotton-fabric phenolic laminate, most plastics ignited only at plate temperatures of 600° C or higher. Three thermosetting plastics, although ignited by other methods as shown in table 2, did not ignite with the maximum hot surface temperature of 750° C.

These results show that the "hot-surface-contact method" is not as suitable for indicating the lowest temperature of ignition, i. e. the fire-hazard of a material, as is the constant-air-temperature method.

VI. Summary

A new method and apparatus were developed from consideration of the principles of ignition, as explained in section II. The ignition characteristics and thermal behavior of materials were determined in this apparatus under well-controlled conditions.

Operation of this apparatus by the constant-air-temperature method is simple at temperatures up to 800° C. The air temperature around the specimen, in spite of the readily sustained constant temperature of the wall, is very sensitive to the velocity of air flow and to the heat radiated from the specimen during the exothermic reaction. The first factor can be controlled with an approximately optimum air flow, adjusted for a favorable rate of ignition as indicated by the rate of temperature rise. The second factor has no appreciable effect on the results if other temperatures in the apparatus remain constant. The effect of the second factor can be minimized, if necessary, either by shielding the thermocouple (Th_2) that indicates the temperature of air approaching the specimen, or by shifting it farther away from the specimen.

The lowest values of the temperatures defined as "flash" and "self-ignition" were selected to indicate the fire hazards of the plastics. The flash temperatures for most of the plastics listed in tables 1 and 2, are in the range from 280° to 525° C, with the exception of cellulose nitrate, which flashes at 141° C. The self-ignition temperatures for 17 of the 27 specimens tested lie in the range from 430° to 500° C. Cellulose nitrate, however, self-ignites at 141° C, whereas specimens of glass-cloth melamine laminate ignited at 623° and 645° C. The values of these temperatures were found to be reproducible to within 1 or 2 deg C.

The effect of heat on the physical state of various plastics is illustrated in figures 8, 9, and 10. Of particular interest is the ability of a material to retain its transparency and resist discoloration and carbonization. The transparency of most of the plastics in the thermoplastic group, as shown in figures 9 and 10, disappears in the range of 130° to 250° C, although cellulose nitrate loses its

transparency at 105° C. For the reinforced thermosetting plastics, discoloration and carbonization depend not only upon the temperature, but also upon the duration of heating.

The specimens shown in figures 8, 9, and 10 were chosen at random and do not necessarily represent uniform steps in the process of degradation. The temperature and time data have only relative and incidental significance. The examples in figure 10 show that the most heat-resistant plastics were those consisting of glass-cloth with silicone, melamine, or polyester resins. These withstood heating to 300° C for approximately 1 hr without appreciable discoloration. The thermoplastic group, with the exception of methyl methacrylate (6), did not withstand even 200° C without considerable bubbling or melting.

The new method for the determination of ignition characteristics of materials is the first major step in evaluating the ignition properties of a material in terms of the temperature and controllable condition that may be as important as for other physical properties such as density, conductivity, etc.

VII. References

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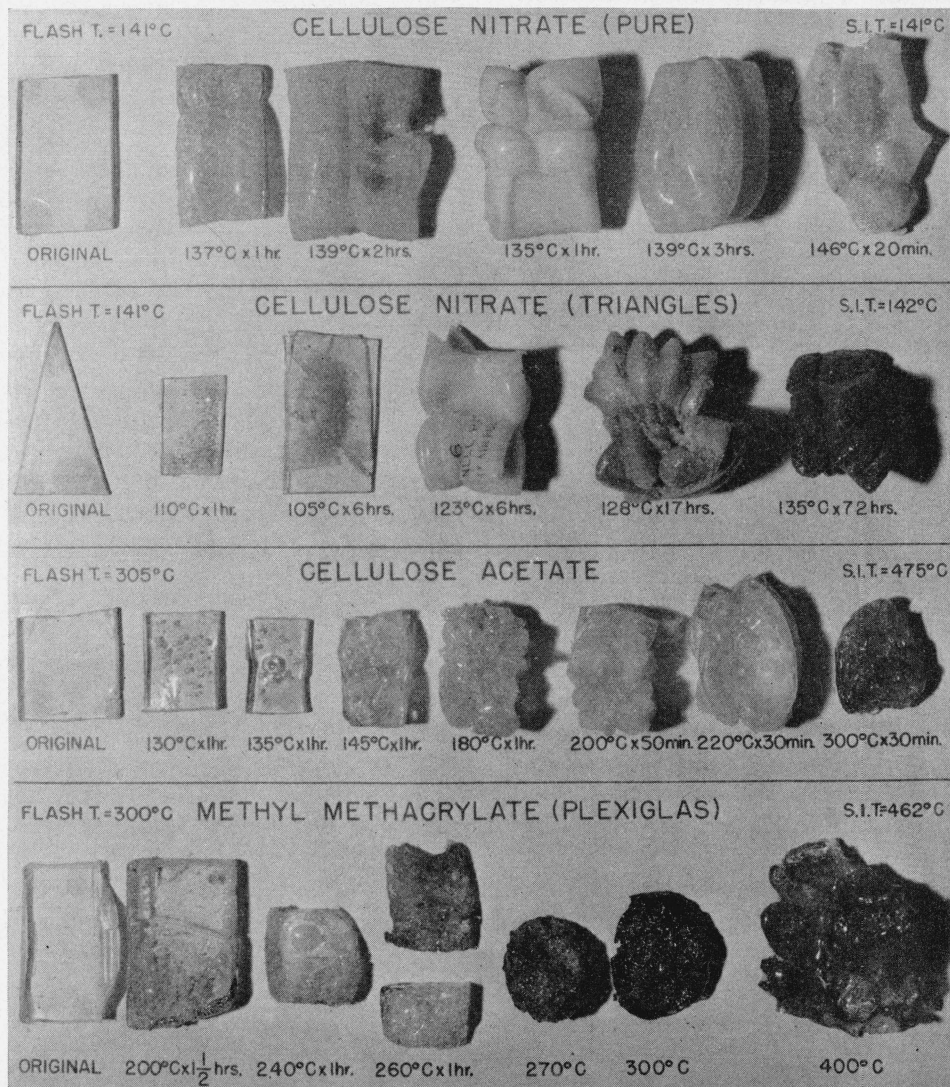


FIGURE 8. Appearance of plastics after being heated at indicated temperatures for designated period.

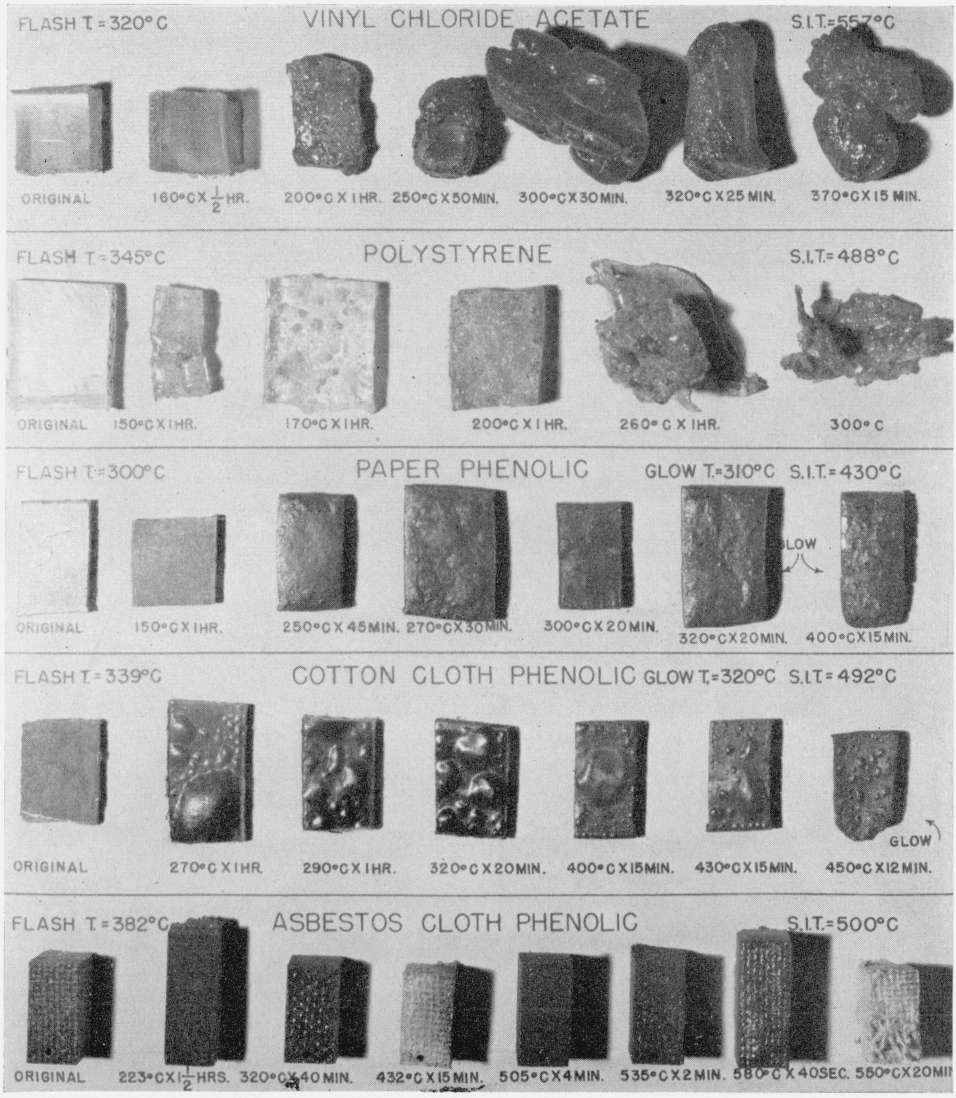


FIGURE 9. Appearance of plastics after being heated at indicated temperatures for designated period.

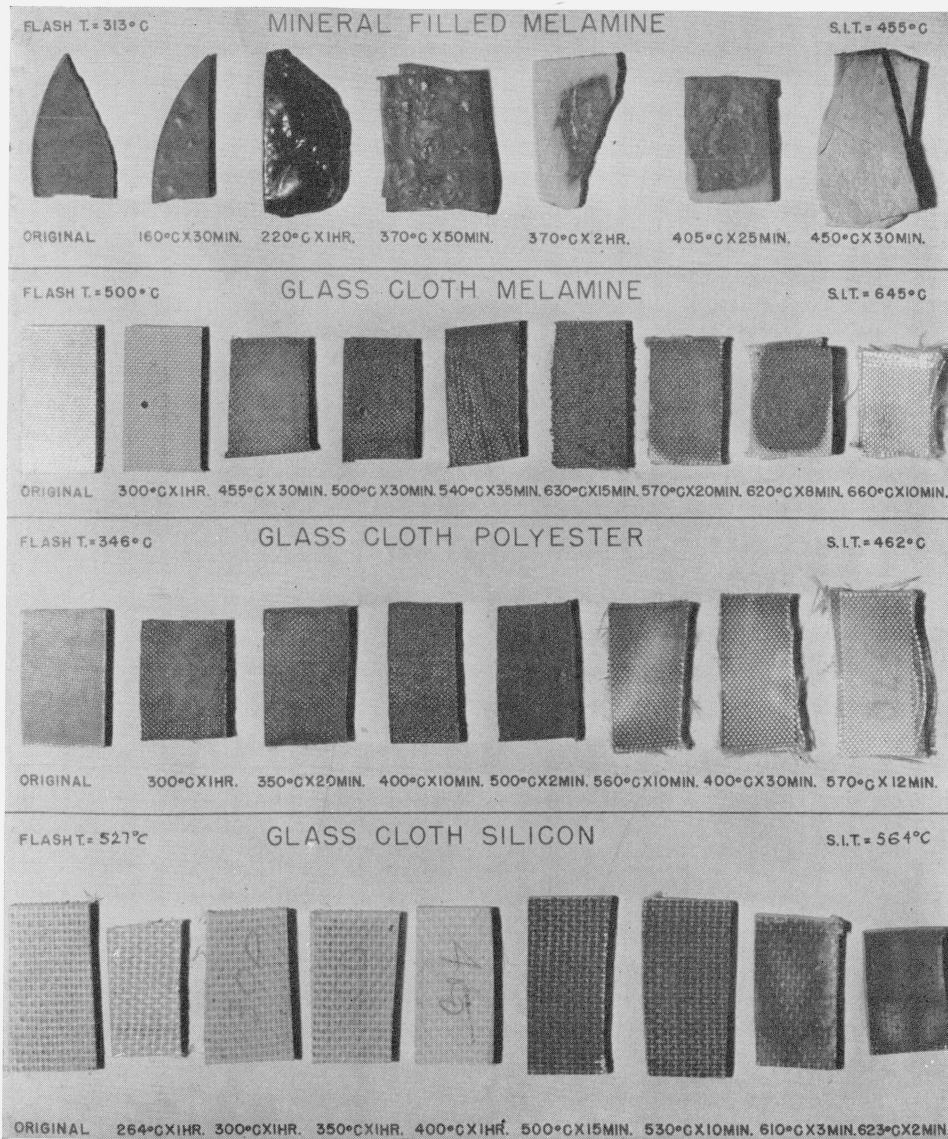


FIGURE 10. *Appearance of plastics after being heated at indicated temperatures for designated period.*

WASHINGTON, March 16, 1949.