U. S. Department of Commerce — National Bureau of Standards

RESEARCH PAPER RP788

Part of Journal of Research of the National Bureau of Standards, Volume 14, May 1935

FIRE-RESISTANT DOPED FABRIC FOR AIRCRAFT

By Gordon M. Kline

ABSTRACT

Cellulose nitrate dope now commonly used to cover the fabric on the wings and fuselage of airplanes is very flammable and its replacement by a less-hazardous product is desirable. The development of a satisfactory nonflammable dope by the use of natural and synthetic resins or mixtures of synthetic resins with cellulose nitrate and cellulose acetate has not proved to be feasible. An airplane covering with very good resistance to ignition may be obtained by the application of a 3:7 boric-acid-borax mixture to airplane cloth and subsequently doping it with cellulose acetate. Cellulose acetate dope is now only moderately more expensive than cellulose nitrate dope. The cost difference becomes insignificant when the lower fire hazard resulting from the use of the much less flammable cellulose acetate dope is considered.

CONTENTS

I. INTRODUCTION

The rapid growth of the aviation industry in this country has brought to the fore the problem of eliminating the fire hazard inherent in fabric doped with cellulose nitrate, now commonly used to cover the wings and fuselage of airplanes. The destruction of costly aircraft because of the accidental ignition of the flammable covering by the backfiring of the motor, the careless toss of a lighted match or cigarette, or the chance settling of a spark from a nearby flue, has become too general an occurrence. The rapid spread of flames following a minor crash presents a formidable obstacle to the rescue of trapped survivors. It has been stated that the use of metal will eliminate this hazard, but it is probable that, particularly for service airplanes, fabric will continue in use for some time to come because of its lower cost, availability, and ease of application, factors which facilitate rapid replacement of losses in time of war. An investigation was, therefore, undertaken by the National Bureau of Standards, with the financial assistance of the National Advisory Committee for Aeronautics, to develop a nonflammable doped fabric for aircraft.

The use of cellulose nitrate and cellulose acetate in airplane dopes during the war has been described by Esselen (3),[1] Smith (5) Deschiens (10, 11, 12, 17, 23, 25), Drinker (18), and Britton (28, 29). Very little work on the use of other materials for airplane dopes has been reported. Two Japanese investigators, Araki and Nagamote, have described experiments with ethylcellulose (37) and benzylcellulose (43). Deschiens (23) foresaw the day when "the formates, butyrates, oxalates, and benzoates of cellulose, the phenylcelluloses, the esters of the higher fatty acids, and many other cellulose derivatives that are now being explored will be of industrial importance." Gardner (39) recommended a study of phthalic anhydride-glycerin resins for coating wing surfaces. Other resins and cellulose esters and ethers have been proposed for airplane dopes in various patents, but no detailed study of the properties of these compounds relating to their satisfactory use for such purpose has been published. This paper presents the results of a comparative study of cellulose nitrate, cellulose acetate, and various natural and synthetic resins as constituents of airplane dopes, with particular emphasis upon the development of a nonflammable doped fabric. The effect of fireproofing airplane cloth on the fire resistance of the product covered with cellulosic dopes has also been determined.

A satisfactory airplane dope should tauten the fabric to which it is applied, dry relatively rapidly without "blushing", i. e., precipitating the cellulose derivative in white patches because of moisture condensation, give a smooth, durable surface, and permit a low film weight. To these we believe should be added the requirement that the doped fabric should be fire resistant. The properties of the doped fabric which were measured in this study were weight, tautness, and flammability. Resistance to weathering, which necessarily requires long periods for its determination, was not investigated in this exploratory work, but was reserved for later study with those materials which satisfy the other requirements.

II. TEST METHODS

1. TAUTNESS OF DOPED FABRIC

Square panels 12 inches (30.5 cm) inside dimension were prepared from 1.5 by 0.75 inch (3.8 by 1.9 cm) dressed white pine.[2] Grade A mercerized cotton airplane cloth, corresponding to U. S. Navy Department specification 27c12, was applied to one face only of the panel and fastened by tacks along the sides at intervals of about 1.5 inches (3.8 cm). The various materials, dissolved in suitable solvents, were brushed on the cloth, usually by a four-coat application. After drying overnight at room temperature, the panels were placed in a

[1] The numbers in parentheses refer to the bibliography at the end of this paper.

[2] In later work not reported in this paper square panels 12.25 inches (31.1 cm) inside dimension prepared from 1.5 by 1 inch (3.8 by 2.5 cm) spruce strips according to U. S. Naval Aircraft Factory proposed aeronautical process specification for covering of panels for exposure tests, SP-16, dated October 6, 1932, were used and are considered to be preferable.

room kept at about 21° C and 65 percent relative humidity. After approximately 48 hours the tautness was determined with a McGowan tautness meter (47) (see fig. 1). The values given in the tables for the tautness determinations are the deflections of the plunger, resting on the doped surface, when a load of 15 ounces (425 grams) is added. It is considered that for satisfactory tautness the deflection caused by the 15-ounce weight should not be greater than 0.130 inch (0.33 cm) for the size of panel used.

2. WEIGHT OF DOPED FABRIC

The doped fabric was removed from the panels and three 2 by 4 inch (5.1 by 10.2 cm) pieces were cut by a die from a strip at the center. These cut samples were weighed on a chemical balance in the conditioning room.

3. FLAMMABILITY OF DOPED FABRIC

Methods of determining the flammability of fireproofed fabrics have been discussed by Ramsbottom and Snoad (66), and of plasticizers by Van Heuckeroth.[3] A vertical burning test was employed in each case; however, the cloth was ignited at the bottom by the former investigators, whereas in the work with the plasticizers, the lacquered paper was ignited at the top. In our work a horizontal burning test, which results in rates of burning intermediate between the two vertical tests mentioned above, was preferred because it accentuated any differences in the flammability of the various materials tested. The apparatus used is shown in figure 2 and was developed by C. R. Brown, of the Fire Resistance Section of the National Bureau of Standards. It consists of two parallel steel clamps supported by a steel frame, the distances between the clamps being adjustable. The specimen to be tested is fastened between the clamps and ignited at one end. The time required for the flame front to travel over a given distance as measured along the clamps is recorded with a stop watch and the rate of burning in inches per minute is calculated. Any length of specimen up to 24 inches (61 cm) and any width up to 7 inches (17.8 cm) can be burned in this apparatus. Brown found that no appreciable effect could be noted due to differences in length provided the specimens were well ignited before starting the time record. He also studied the effect of variation in the free width of the specimen held between the clamps and found that, in general, an increase in width causes an increase in the rate of burning. Inasmuch as the specimens 6 inches (15.2 cm) in width burned irregularly and consequently gave greater variations in the results, he recommended that strips 2 inches (5.1 cm) in width be used for this test. It will be noted that this apparatus can also be used for a vertical burning test. This vertical test was used for the experiments on cloth containing fireproofing compounds, which make the fabric practically nonflammable in the horizontal position. To obtain the results presented in this paper, specimens with surfaces 2 inches (5.1 cm) in width for the horizontal test and 1 inch (2.5 cm) in width for the vertical test were exposed between the clamps, the cloth was ignited with a safety match, and the time recorded for the flame front

[3] A. W. Van Heuckeroth, Some properties of lacquer plasticizers in nitrocellulose films and solutions, Am. Paint Varnish Mfrs. Assn. Cir. 383, p. 187 (1931).

to travel 12 inches (30.5 cm) after starts of 2 and 3 inches (5.1 and 7.6 cm), respectively, for the horizontal and vertical positions. The experiments were made in the still air of the laboratory. The fabrics were left in the conditioning room approximately one week after doping before determining their flammability.

III. EXPERIMENTAL WORK

1. RESINS, CASEIN, AND CELLULOSE DERIVATIVES AS DOPE CONSTITUENTS

The flammability and tautness of airplane cloth doped with various natural and synthetic resins, casein, and cellulose derivatives are shown in table 1. These data are summarized from a considerably larger number of experiments on various commercial resins of the types indicated, and the relative flammability of the various chemical types was definitely maintained in the whole series. In applying these materials to the airplane cloth low-boiling solvents were used instead of the usual blend of low-, medium-, and high-boiling solvents, in order to lessen the possibility of the solvent remaining in the film and influencing the rate of burning. Because of the diverse solubilities of the materials studied four different solvents, namely, acetone, ethyl alcohol, benzene, and aqueous ammonia, had to be employed. The five experiments listed at the bottom of table 1 indicate that the use of different solvents did not affect the comparative nature of the results.

TABLE 1.—*Flammability and tautness of airplane cloth doped with natural and synthetic resins, casein, and cellulose derivatives*

Doping material	Solvent	Total weight	Rate of burning	Deflection of tautness meter plunger under 15-oz load
		Oz/sq yd	In./min	In.
Chlorodiphenyl resin	Acetone	6.2	2.2	Slack
Vinyl chloride resin	do	6.3	3.5	0.140
Casein	Aqueous NH_3	6.1	3.7	.148
Vinyl acetate resin	Acetone	6.0	4.8	Slack
Cellulose acetate	do	5.8	4.8	.097
None		3.9	5.9	
Phthalic acid ester resin	Acetone	6.2	7.2	.229
Rosin-glycerin resin	do	6.2	7.2	.220
Shellac	Ethanol	5.7	7.7	.179
Phenol-formaldehyde resin	Acetone	6.2	7.9	.209
Cumaron resin	do	5.7	8.0	.163
Macassar gum	Ethanol	6.1	9.4	Slack
Modified phenol-formaldehyde resin	Benzene	6.2	9.8	.158
Urea-formaldehyde resin	Acetone	6.0	9.9	Slack
Spar varnish		6.1	10.0	.249
Petroleum hydrocarbon resin	Benzene	5.7	10.2	.193
Manila gum	Ethanol	5.9	10.9	Slack
Cyclohexanone-vinyl resin	Acetone 1 pt, Benzene 1 pt	6.0	14.0	.237
Cellulose nitrate	Acetone	5.9	23.2	.113
Vinyl acetate resin	Acetone	6.1	5.1	.152
Do	Benzene	6.3	5.5	.178
Do	Toluene	6.2	5.1	.182
Do	Ethanol	6.0	4.6	Slack
Do	Ethyl acetate	6.2	5.0	.175

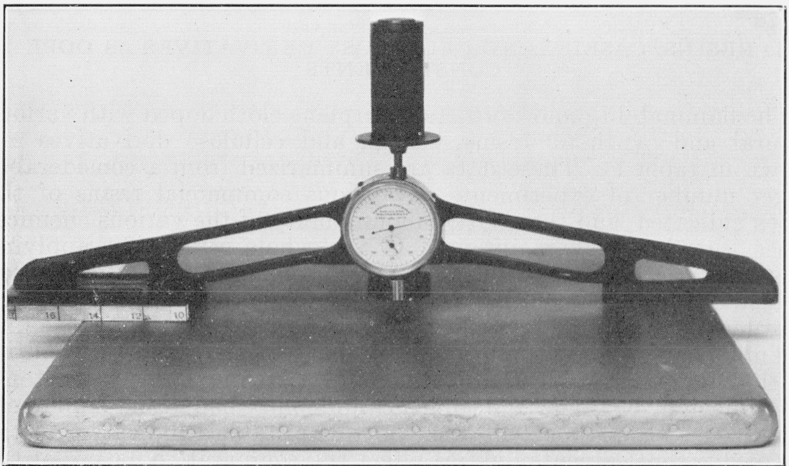

FIGURE 1.—*McGowan tautness meter.*

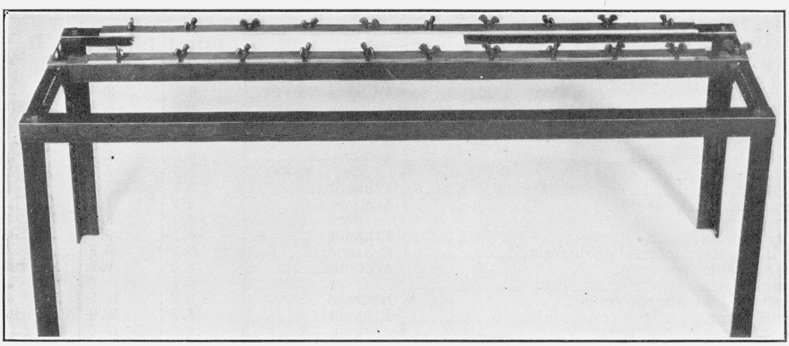

FIGURE 2.—*Brown's apparatus for determining rate of burning.*

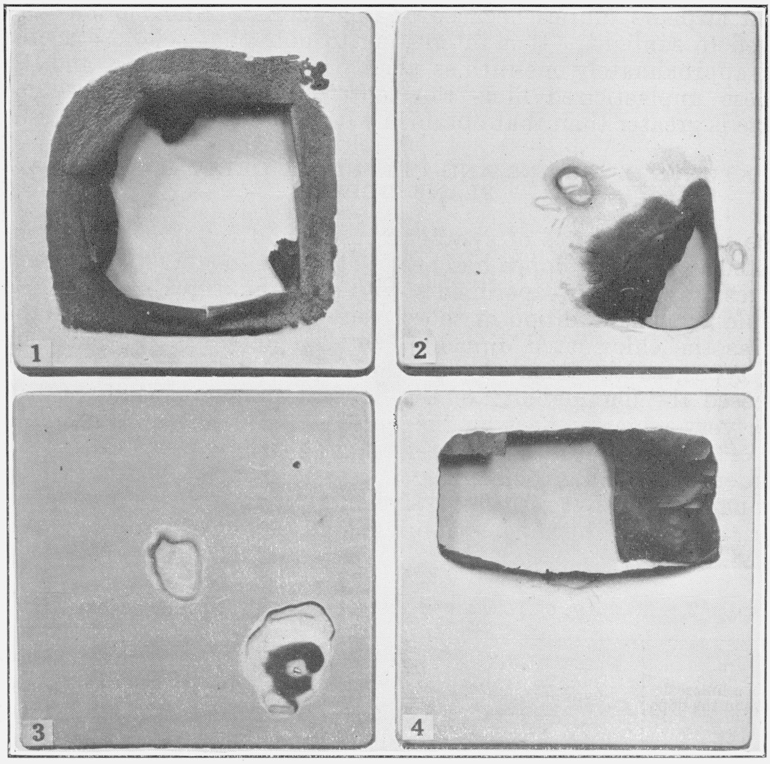

FIGURE 3.—*Flammability tests on doped fabrics.*

Four coats of clear dope and two coats of aluminum pigmented dope were applied to airplane cloth tacked on wooden frames. The square gray areas surrounding the charred doped fabric are the aluminum pigmented surfaces.

1, Untreated airplane cloth doped with cellulose nitrate. The flames spread rapidly when burning gasoline ignited the nitrate doped fabric at the center of the panel.

2, Untreated airplane cloth doped with cellulose acetate. Note the slightly charred area at the center of the panel where burning gasoline did not ignite the acetate doped fabric. When one corner of the panel was cut to expose the cloth, the doped fabric was ignited and burned slowly.

3, Fireproofed airplane cloth doped with cellulose acetate. Burning gasoline did not set fire to the acetate doped fabric with or without exposure of the cloth surface.

4, Fireproofed airplane cloth doped with cellulose nitrate on the upper half of the panel and with cellulose acetate on the lower half. Burning gasoline ignited the nitrate doped fabric, but note that the resultant fire did not ignite the acetate doped fabric.

It will be noted that only three materials yielded a doped fabric which had a greater resistance to burning than cellulose acetate, namely, chlorinated diphenyl resins, vinyl chloride resins, and casein. These resins as well as those which were more flammable than cellulose acetate did not give satisfactory tautness. An occasional panel was secured with vinyl chloride resin which showed good tautness, but this material was not investigated further as chlorinated products, particularly of the aliphatic type, are not believed to be desirable for use on airplane fabrics because of their deteriorating action when exposed to sunlight. It is interesting to note that cellulose acetate burns approximately one-fifth as rapidly as cellulose nitrate, and that in these unplasticized films the tautness obtained with cellulose acetate is greater than that obtained with cellulose nitrate.

2. MIXTURES OF RESINS AND CELLULOSE DERIVATIVES AS AIRPLANE DOPES

The use of mixtures of synthetic resins and cellulose nitrate and acetate for airplane dopes has been suggested in numerous patents. The results of some experiments with such mixtures are presented in table 2. The addition of those resins which are least flammable, such as the chlorinated diphenyl, vinyl acetate, and phthalic acid ester types, to the usual dopes prepared from cellulose derivatives decreased the flammability of the doped fabric somewhat, but also had a very adverse effect on the tautness. In general, a minimum ratio of 3:1 of cellulose nitrate or acetate with these resins is necessary in order to attain satisfactory tautness. The application of the chlorinated diphenyl resin as a surface coating did not appreciably lower the rate of burning of fabrics doped with cellulose nitrate or acetate.

TABLE 2.—*Mixtures of resins and cellulose derivatives as airplane dopes*

Type of cellulose derivative in the dope	Type of resin in the dope	Weight ratio of cellulose derivative to resin	Total weight	Rate of burning	Deflection of tautness-meter plunger under 15-oz load
			Oz/sq yd	In./min	In.
Acetate	None		6.6	5.0	0.096
Do	Chlorinated diphenyl	1:1	6.4	2.9	.186
Do	do	2:1	6.3	3.8	.157
Do	do	3:1	6.1	4.6	.152
Do	Vinyl acetate	3:1	5.9	5.0	.117
Do	Phthalic acid ester	3:1	5.9	5.8	.109
Nitrate	None		6.6	21.3	.101
Do	Chlorinated diphenyl	1:1	6.9	14.8	.161
Do	do	2:1	6.4	16.6	.169
Do	do	3:1	7.6	22.9	.112
Do	Vinyl acetate	2:1	7.9	14.0	.123
Do	do	3:1	7.7	17.8	.093
Do	Phthalic acid ester	3:1	6.4	20.6	.120

3. FIREPROOFING OF CLOTH

When it became apparent that the problem of developing a fire-resistant doped fabric could not be solved by the addition of nonflammable resins to the cellulosic dopes, or by the complete substitution of resins for the cellulose derivatives in the dope, the course of this investigation was directed toward the production of an airplane fabric doped with cellulose acetate and fireproofed by the addition of fire-retarding salts. Some experiments were performed on the direct addition to the dope of some inorganic materials of known fireproofing qualities, but this method was largely unsuccessful because of the insolubility of inorganic substances in the organic solvents commonly used in airplane dopes. Furthermore, the cloth underlying the fireproofed film served as a wick to prevent the flame from extinguishing. The problem of fireproofing the fabric before application of the dope was, therefore, considered.

A survey of the literature indicated that the inorganic salts most generally recommended for fireproofing fabrics are ammonium sulphate, ammonium phosphate, and a mixture of boric acid and borax. A bibliography of the recent literature on fireproofing is given at the end of this paper. Ramsbottom and Snoad's (66) investigation included the above-mentioned materials as well as many others, and they concluded that a mixture of 30 percent boric acid and 70 percent borax is one of the most suitable soluble fireproofing agents for cotton fabric. They found that when it is present to the extent of about 6 percent of the weight of the fabric it prevents the propagation of the flame. They also noted the lack of any marked deteriorating effect of this mixture on the cloth. The boric-acid-borax mixture also has the advantages of being nonpoisonous and slightly germicidal.

TABLE 3.—*Fireproofing of cloth.*

Material added to cloth	Increase in weight	Rate of burning	
		Horizontal	Vertical
	Percent	In./min	In./sec
Borax	4.6	No flame spread	0.65
Do	8.8	No flame spread	.65
Boric acid	5.3	3.8	.92
Do	7.4	4.2	1.04
3:7 Boric acid-borax	2.8	3.8	.71
Do	3.7	No flame spread	.57
Do	4.6	No flame spread	No flame spread
Commercial product no. 1	3.2	3.7	1.15
Do	6.0	No flame spread	No flame spread
Commercial product no. 2	4.2	4.1	1.04
Do	4.8	No flame spread	No flame spread
Commercial product no. 3	3.4	No flame spread	.90
Do	5.7	No flame spread	No flame spread
Ammonium borate	4.6	No flame spread	.76
Barium borate	5.4	6.0	.88
Magnesium perborate	7.2	3.3	.74
Sodium acetate	5.5	3.5	No flame spread
Sodium formate	8.8	No flame spread	No flame spread
Triphenyl phosphate	8.6	5.7	1.15
None	----------	5.9	1.15

The results of measurements of the rates of burning of airplane cloth impregnated with boric acid, borax, and a mixture of 30 percent boric acid and 70 percent borax are shown in table 3. They confirm the tests of Ramsbottom and Snoad and indicate that the mixture is efficient in very small amounts, a feature which is particularly desirable for aeronautical use where weight is a predominant factor. The results of tests with other borates, some commercial products, and a few miscellaneous materials are also shown in table 3; none of them was found to be more efficient in fireproofing than the boric-acid-borax mixture.

4. EFFECT OF FIREPROOFING AIRPLANE CLOTH ON THE FIRE RESISTANCE OF THE PRODUCT COVERED WITH CELLULOSIC DOPES

Test results on ordinary and fireproofed airplanes fabrics coated with commercial cellulose nitrate and cellulose acetate dopes are shown in table 4 and figure 3. Ordinary airplane fabric coated with cellulose acetate dope does not ignite readily when lighted matches or cigarettes are dropped on it, even in a fan breeze. Once ignited, however, it burns at a comparatively slow rate without extinguishing itself. Ordinary airplane fabric coated with cellulose nitrate dope is instantly ignited by a lighted safety match dropped on the panel placed in a horizontal position, and is soon completely consumed. The data in table 4 show that satisfactory protection against ignition may be obtained by the application of the boric-acid-borax mixture to the cloth before doping it with cellulose acetate. This doped and fireproofed cloth will not burn 12 inches (30.4 cm) in either a horizontal or vertical position. Furthermore, gasoline (approximately 3 ml) splashed on the horizontal surface and ignited is burned off without setting fire to the doped fabric. The amount of fireproofing mixture required on the cloth is approximately 5 percent of the total weight. It will be noted that one specimen covered with four coats of clear cellulose acetate dope and two coats of aluminum-pigmented cellulose acetate dope, but which contained only about 3.5 percent of the boric-acid-borax mixture, would burn when ignited, whereas a similar panel on which the fireproofing mixture represented 4 percent of the total weight was protected against ignition by lighted match or burning gasoline.

TABLE 4.—*Flammability and tautness of airplane fabric with and without boric-acid-borax mixture when it is doped with cellulose nitrate and cellulose acetate*

Amount of boric acid-borax on the cloth	Doping scheme	Total weight	Rate of burning	Action of burning match on the fabric	Action of burning gasoline on the fabric	Deflection of tautness-meter plunger under 15-oz load
Oz/sq yd		Oz/sq yd	In./min			In.
None	None	3.88	5.9	Ignited	Ignited	
0.31	do	4.19	No flame spread	Charred	Charred	
None	6 coats clear acetate	7.5	4.3	do	Ignited	0.079
0.31	do	7.7	No flame spread	do	Charred	.082
None	4 coats clear acetate 2 coats Al-pigmented acetate	8.5	6.9	do	Ignited	.075
0.31	4 coats clear acetate 2 coats Al-pigmented acetate	8.8	3.1	do	do	.079
0.31	4 coats clear acetate 2 coats Al-pigmented acetate	7.9	No flame spread	do	Charred	.086
None	6 coats clear nitrate	7.3	19.2	Ignited	Ignited	.091
0.31	do	7.4	14.4	do	do	.094
None	4 coats clear nitrate 2 coats Al-pigmented nitrate	8.4	18.2	do	do	.083
0.31	4 coats clear nitrate 2 coats Al-pigmented nitrate	8.7	13.6	do	do	.081
1.3	4 coats clear nitrate 2 coats Al-pigmented nitrate	12.2	3.8	do	do	.072
None	6 coats orange-yellow semi-pigmented nitrate.	7.4	18.9	do	do	.099
0.31	6 coats orange-yellow semi-pigmented nitrate.	8.0	12.9	do	do	.096
None	4 coats clear acetate 2 coats clear nitrate	6.8	9.4	do	do	.098
None	4 coats clear acetate 2 coats Al-pigmented nitrate	7.5	13.0	do	do	.099
None	4 coats clear nitrate 2 coats clear acetate	7.0	15.9	do	do	.105
None	4 coats clear nitrate 2 coats Al-pigmented acetate	8.0	19.5	do	do	.097

The greater ease of ignition of the cellulose nitrate coatings can be ascribed to the lower temperatures causing decomposition and ignition. The basic difference in decomposition and burning of cellulose nitrate and cellulose acetate is that the former burns independently of an exterior source of oxygen supply to an extent permitting partial combustion of the gases formed. Although it is preferable to have a combination which is self-extinguishing, such as can be obtained by fireproofing the airplane cloth before doping with cellulose acetate, if one is choosing between two materials which will support combustion, it is important to have the ignition temperature as high as possible. Various definitions and methods of measurement of ignition temperature have been proposed by investigators in this field. The National Bureau of Standards has not adopted or endorsed as standard any definition or method of measurement of ignition temperature. There is general agreement in the literature that the ignition temperature of cellulose nitrate is approximately 200° C below that of cellulose acetate. Thus, the values found for the ignition temperature of cellulose nitrate products by Barr,[4] Brown,[5] and Nuckolls[6] are respectively 200, 135, and 149° C, whereas their values for cellulose acetate products are 380, 314, and 371 to 427° C, respectively. When it is considered that the temperature of ordinary incandescent lights, steam pipes, and lighted cigarettes and matches exceeds 149° C,[6] the constant risk of fire on an airplane doped with cellulose nitrate is readily apparent.

The dopes used in the experiments described in table 4 were commercial products containing only small amounts of high-boiling solvents. Some experiments were also performed with a cellulose acetate dope prepared in the laboratory according to the British Standard Reference Dope formula,[7] except that ethyl acetate was substituted for benzene, and ethyl lactate for benzyl alcohol, to yield the following percentage composition:

Cellulose acetate	7. 1
Triphenyl phosphate	1. 1
Acetone	46. 8
Ethyl acetate	20. 0
Ethyl alcohol	20. 0
Ethyl lactate	5. 0

The results were similar to those obtained with the commercial cellulose acetate dope. It is recognized that a higher percentage of high-boiling solvents is required to permit satisfactory doping operations at relative humidities of 65 percent or higher. The retention of high-boiling solvent in the cellulose acetate film or the substitution of a flammable plasticizer for the nonflammable triphenyl phosphate would make the doped fabric considerably less fire-resistant than were the fabrics described in table 4. It is planned to determine the effect of larger percentages of high-boiling solvents and of various plasticizers on the fire resistance of the doped fabric.

[4] G. Barr, The Inflammability of Doped Fabrics, Advisory Comm. for Aeronautics, Repts. and Mem. 573 (1919).

[5] C. R. Brown, Tests of Stability at Elevated Temperatures of Nitrocellulose X-ray Film, Proc. of a Board of the Chem. Warfare Service (re Cleveland Clinic Disaster May 15, 1929), p. 46 (1929); compare also p. 37. The Determination of the Ignition Temperatures of Solid Materials, Doctoral Dissertation, Catholic University of America, Washington, D. C. (1934). The ignition temperatures of solid materials, Quart. Nat. Fire Protect. Assn. **28**, 135 (1934). Compare H. N. Stokes and H. C. P. Weber, Tech. Pap. BS T98 (1917).

[6] A. H. Nuckolls, Cellulose nitrate and acetate film, Quart. Nat. Fire Protect. Assn. **23**, 236 (1930). H. E. Hofmann, and E. W. Reid, Cellulose acetate lacquers, Ind. Eng. Chem. **21**, 955 (1929).

5. EFFECT OF MIXED CELLULOSE NITRATE AND CELLULOSE ACETATE DOPING SCHEMES ON THE FIRE RESISTANCE OF THE DOPED FABRIC

The use of mixtures of cellulose acetate and cellulose nitrate for airplane dopes has been proposed in various patents. Recent army and navy specifications for the application of dopes to fabric surfaces of aircraft have permitted the application of base coats of clear cellulose acetate dope, when followed by pigmented cellulose nitrate dope. The last four experiments shown in table 4 indicate that the fire protection offered by cellulose acetate dope is largely lost if cellulose nitrate dope is used for the outer coats. To secure the greater protection afforded by cellulose acetate, its use should be specified for the entire doping scheme.

IV. DISCUSSION OF RESULTS

A thorough study of the use of cellulose nitrate and cellulose acetate as airplane dopes was undertaken by the United States Government during the period of the war. Published reports indicate that cellulose nitrate was considered undesirable for use at the "front" because of its flammability, and that cellulose acetate dope was preferred and, in general, prescribed for airplanes to be used in the zone of fire. Considering the comparative meagerness of the technological information concerning cellulose acetate in that period, its preferential use for doping airplanes is surprising and is indicative of the attitude of the wartime aeronautical engineers toward the fire hazard of cellulose nitrate dope. After the war the development of cellulose nitrate lacquers received a remarkable impetus in the need of a low-cost, quick-drying coating material for many industrial purposes, notably automobile bodies, and rapid technical advances were made. New solvents were developed for cellulose nitrate, the common solvents were reduced in price by improvements in manufacturing methods and volume production, and the spraying process was perfected. As a result the improved cellulose nitrate lacquers, with a few changes to make them suitable for doping airplane cloth, gradually replaced the less hazardous cellulose acetate dope which was technically dead in that post-war period. Today, however, the technical position of cellulose acetate has been altered. The rapid increase in the use of motion-picture and X-ray films made from cellulose nitrate was accompanied by a number of serious conflagrations, which centered attention on the desirability of a relatively nonflammable film prepared from cellulose acetate. This acted as a stimulus to research on the production of cellulose acetate and its solvents, and resulted in a rapid growth of the manufacture of safety film and cellulose acetate plastics. Cellulose acetate dopes are, therefore, now only moderately more expensive than cellulose nitrate dopes. When it is considered that the cost of the dope is much less than 1 percent of the total cost of an airplane, this difference in price of the two dopes becomes insignificant as compared with the potential loss resulting from the destruction of the airplane by the accidental ignition of the fabric doped with the very flammable cellulose nitrate.

It has been stated that fabric doped with cellulose acetate temporarily loses its tautness on long-continued exposure to a humid atmosphere. Preliminary experiments in this laboratory have indicated that this is not necessarily true of all cellulose acetate dopes. Sheppard and Newsome[8] have observed that esterification of the hydroxyl groups of cellulose with acetic acid decreases the hygroscopicity of the material. It is probable that any slackening off of the doped fabric is closely associated with the hygroscopic nature of the plasticizer used. The loss of tautness observed with the cellulose acetate dopes of the wartime period may also be ascribable to the hydrolysis of the cellulose acetate by the acid liberated by the decomposition of chlorinated solvents (6) generally employed at that time. These solvents are no longer permitted in airplane dopes for service use in this country. The fact that cellulose acetate dope is required and the very flammable cellulose nitrate excluded from use on service airplanes by the French is evidence that satisfactory performance can be attained with cellulose acetate dope. Furthermore cellulose acetate is specified and found to be satisfactory for doping the outer cover of airships in this country. The further precaution of fireproofing the cloth, with the small increment of weight found to be necessary in this investigation might well be considered for the large dirigibles, the destruction of which by fire represents a large economic loss.

Further work on the permanence of the fire protection which would be afforded by the use of boric-acid-borax mixture on airplane wings and fuselage is necessary. There is every reason to believe that the aluminum-pigmented cellulose acetate coating would prevent for long periods the removal of the soluble salts on exposure to atmospheric weathering. The much greater durability of cellulose acetate over that of cellulose nitrate on weathering was well established during the period of the war (3), and by subsequent experimental work with the two materials on exposure to ultraviolet light. The lack of any marked deteriorating action of the boric-acid-borax mixture on cotton cloth, noted by Ramsbottom and Snoad, has already been mentioned. In view of the necessity of concentrating many airplanes in a limited space on airplane carriers, on which there exists increased danger of the ignition of cellulose nitrate by flying sparks or by spontaneous decomposition due to storage close to hot pipes or other sources of heat, it is believed that serious consideration should be given to the use of fireproofed doped fabric on aircraft, and that the investigation of such materials both in the laboratory and on test airplanes should be actively pursued.

V. SUMMARY AND CONCLUSIONS

1. The comparative flammability and tautness of fabric doped with natural and synthetic resins have been determined. The resins studied do not tighten the fabric sufficiently to be satisfactory as airplane dopes.

2. The use of mixtures of synthetic resins and cellulose derivatives as airplane dopes has been investigated. In general, a 3:1 ratio of cellulose derivative to resin is necessary to attain satisfactory tautness. In this proportion even the least flammable synthetic resins do not markedly improve the fire-resistance of the doped fabric.

[8] S. E. Sheppard and P. T. Newsome. The sorption of water vapor by cellulose and its derivatives. J. Phys. Chem. **33**, 1817 (1929).

3. No method has been found to fireproof airplane fabric doped with cellulose nitrate and maintain satisfactory tautness and weight requirements.

4. An airplane covering with very good resistance to ignition may be obtained by the application of a 3:7 boric-acid-borax mixture to airplane cloth and subsequently doping it with cellulose acetate. This doped and fireproofed cloth, containing approximately 5 percent of the boric-acid-borax mixture by weight, will not burn in a horizontal or vertical position and is not ignited by lighted matches or burning gasoline.

VI. BIBLIOGRAPHY

1. AIRPLANE FINISHING

(1) Anonymous, Report of the Advisory Committee on Aeronautics. India Rubber J. **45,** 1344 (1913).

(2) G. Hubener, Balloon and airplane materials. Kunststoffe **3,** 141, 164, 189, 207, 344, 364, 385, 407 (1913).

(3) G. J. Esselen, Jr., Airplane dopes. Ind. Eng. Chem. **10,** 135 (1918).

(4) Alice Hamilton, Dope poisoning in the making of airplanes. Monthly Rev. U. S. Bureau Labor Statistics **6,** 289 (1918).

(5) W. H. Smith, Airplane dopes and doping. Nat. Advisory Comm. Aeronaut. Rept. 38, (1918).

(5a) W. S. Smith, Nonpoisonous dope. Chem. Trade J. **63,** 44 (1918).

(6) G. Barr and L. L. Bircumshaw, Cellulose acetate. Advisory Comm. Aeronaut. Repts. and Mem. 303; compare Repts. and Mem. 318 and 573.

(7) W. D. Milne, Fire hazard in airplane manufacture. Nat. Fire Protect. Assn. Quart. p. 345 (April 1919).

(8) A. Rusch, Jr., Aviation textiles and chemistry. Textile World J. **56,** 363 (1919).

(9) A. W. Chapman, Chemistry of aeronautics. Chem. Age (London) **2,** 438 (1920).

(10) M. Deschiens, Cellulose acetate and its industrial uses. Chimie & Industrie **3,** 591 (1920).

(11) M. Deschiens, Airplane dopes. Rev. Prod. Chim. **23,** 177 (1920).

(12) M. Deschiens, Dope manufacture. Chem. Trade J. **67,** 603 (1920).

(13) H. J. H. Fenton and A. J. Berry, Cellulose acetate. Proc. Cambridge Phil. Soc. **20,** 16 (1920).

(14) A. Fuchs, Materials and dopes for airplanes. Chimie & Industrie **3,** 167 (1920).

(15) H. A. Gardner, An emollient for skin protection in the dope and varnish using industries. Paint Mfrs. Assn. U. S. Cir. 91 (May 1920).

(16) G. W. C. Kaye, British Standard of Reference for Aircraft Dope and Protective Covering. (Crosby Lockwood and Son, London, 1918).

(17) M. Deschiens, Airplane dopes. Rev. Prod. Chim. **24,** 3 (1921).

(18) P. Drinker, European practice in cellulose acetate and dopes during the war. Ind. Eng. Chem. **13,** 831 (1921).

(19) A. W. Judge, Aircraft and Automobile Materials of Construction. **II.** Nonferrous and Organic Materials. (Sir Isaac Pitman and Sons, Ltd., London, 1921).

(20) J. R. S. Cochrane, Airplane dopes. Materials, Plant, and Process for Production of Cellulose Acetate. Commonwealth Australia Munitions Supply Board Tech. Repts. (1921–22).

(21) H. W. van Urk, Poisoning symptoms from the solvents of airplane lacquers. Pharm. Weekblad **60,** 293 (1923).

(22) A. Feil, Occupational poisoning with tetrachloroethane. Chimie & Industrie, Special no., page 763 (May 1924).

(23) M. Deschiens, Aviation dopes or varnishes. J. Soc. Chem. Ind., Chem. and Ind. Rev. **44,** 902 (1925).

(24) H. Hepworth, Industrial nitrocellulose products. Ind. Chemist **1,** 323 (1925).

(25) M. Deschiens, Airplane dopes. Chimie & Industrie **15,** 18 (1926).

124792—35——5

(26) H. A. Gardner, Durability of airplane doping and varnishing systems. A study of cellulose acetate and cellulose nitrate tautening and proofing schemes for fabric surfaces. Paint Mfrs. Assn. U. S. Cir. 274, 61 (1926).
(27) A. Hutin, Mixed dopes from cellulose acetate and rubber. Rev. gén. mat. plastiques, **2**, 308 (1926).
(28) H. T. S. Britton, Cellulose acetates for aero dopes. Ind. Chemist **3**, 59 (1927).
(29) H. T. S. Britton, Aero dopes and varnishes. Ind. Chemist **3**, 116 (1927).
(30) K. Atsuki and R. Shinoda, Composition of cellulose acetate lacquer for airplane dope. Rept. Aeronaut. Research Inst., Tokyo Imp. Univ. **3**, 49 (1928).
(31) R. C. Martin, Finishing modern aircraft. Chem. Met. Eng. **35**, 404 (1928).
(32) M. C. Roberts, Modern airplane finishing, Ind. Finishing **4**, 29 (Sept. 1928).
(33) D. M. Liddell, Chemicals in aviation. Chem. Markets **25**, 249 (1929).
(34) C. J. Staud, Technology of cellulose acetate. Its relation to plasticizers and solvents. Paint, Oil, Chem. Rev. **88**, no. 19, 9 (1929).
(35) G. E. Walker, How chemical engineering has improved aircraft. Chem. Met. Eng. **36**, 348 (1929).
(36) Anonymous, Report of Fact-Finding Committee on Control of Airplane Hangar Fires by Automatic Application of Water. Aeronautics Branch, U. S. Department of Commerce (September 1930).
(37) T. Araki and T. Nagamote, Ethylcellulose dope. J. Soc. Chem. Ind. Japan, **33** (supplemental binding) 382 (1930).
(38) H. A. Backus, Specifications and materials control for aircraft construction. Proc. Am. Soc. Testing Materials **30**, part 2, 109 (1930).
(39) H. A. Gardner, Notes on aircraft finishes. Proc. Am. Soc. Testing Materials **30**, part 2, 68 (1930).
(40) T. Lyons, Metals used in airplane construction. Monthly Rev. Am. Electroplaters' Soc. **18**, no. 9, 26 (1931).
(41) J. L. McCloud, Requirements of airplane coatings. Ind. Eng. Chem. **23**, 1334 (1931).
(42) O. Merz, Paints for aircraft and their testing. Farben-Ztg. **36**, 2156, 2197 (1931).
(43) T. Araki and T. Nagamote, Benzylcellulose dope. J. Soc. Chem. Ind. Japan, **35** (supplemental binding) 68 (1932).
(44) R. A. Denne, The problem of fire in aircraft. Aircraft Eng. **4**, 98 (1932).
(45) E. K. O. Schmidt, Preservation of airplane fabrics. Farben-Chem. **3**, 165, 209 (1932).
(46) H. T. Tizard, Chemical engineering and the aircraft industry. Trans. Inst. Chem. Engrs. **10**, 87 (1932).
(47) G. M. Kline, Estimation of tautness of doped fabrics. Am. Paint Varnish Mfrs. Assn. Cir. 443, 266 (1933).
(48) P. Meunier and A. Lucain, Properties and application of benzylcellulose. Rev. gén. mat. plastiques **9**, 127 (1933).
(49) O. Merz, Paint materials for airplane construction and their testing. Malyarnoe Delo **1932**, no. 516, 31. Compare Chem. Zentr. **1933**, I, 2182.
(50) C. F. Nagel, Jr., and G. O. Hoglund, Developments in aluminum alloys in relation to economies in aircraft construction. Trans. Am. Soc. Mech. Engrs. (Aeronaut. Eng.) **5**, 75 (1933).
(51) M. R. Whitmore, Aircraft finishing, Ind. Eng. Chem. **25**, 19 (1933).
(52) C. A. Young, Dope poisoning as a potential hazard in spray-coating airplane wings. U. S. Naval Med. Bul. **31**, 63 (1933).
(53) J. J. A. Gilmore, Airplane doping schemes. Aircraft Eng. **6**, 161 (1934).
(54) R. Lecoeuvre, Repair and upkeep of metal hulls and floats for hydroplanes. Chimie & Industrie, Special no., page 547 (1934).
(55) M. W. Mason, Aircraft finishing. Ind. Finishing **10**, no. 5, 18; no. 6, 16; no. 7, 16; no. 8, 32 (1934).
(56) W. Mutchler, Weathering of aluminum alloy sheet materials used in aircraft. Nat. Advisory Comm. Aeronaut. Rept. 490 (1934).
(57) E. K. O. Schmidt, Determining the tautness of airplane dopes. Farben-Ztg. **39**, 1049 (1934).
(58) R. Stratta, Adhesion of a film of cellulose acetate to airplane fabric. Industria chimica **9**, 319 (1934)
(59) G. M. Kline, Moisture relations of aircraft fabrics. J. Research NBS **14**, 67 (1935) RP758.

(60) G. M. Kline, Absorption of moisture by aeronautical textiles. Am. Dyestuff Rept. **24**, 4 (1935).

2. FIREPROOFING

(61) Anonymous, The manufacture of fireproof coating materials. Farbe u. Lack **1926**, 456.
(62) A. Eichengrun, Chemical protection against fire. Z. angew. Chem. **42**, 214 (1929).
(63) C. O. Clark, Fabric proofing. Textile Weekly **4**, 696 (1930).
(64) F. Grove-Palmer, Fire-resisting rayon goods. Am. Dyestuff Reptr. **19**, 715 (1930).
(65) G. M. Hunt, T. R. Truax, and C. A. Harrison, Experiments in fireproofing wood. Proc. Am. Wood-Preservers' Assn. **1930**, 130, 159; **1931**, 104; **1932**, 71; **1933**, 107.
(66) J. E. Ramsbottom and A. W. Snoad, Fireproofing of Fabrics. Dept. Sci. Ind. Research, Second Report of Fabrics Coordinating Research Comm. page 16 (1930).
(67) R. Chesneau, Fireproofing of cloth. Bul. soc. ind. Rouen **60**, 265 (1932).
(68) K. Micksch, Flame protectives for rayon. Kunstseide **14**, 64 (1932).
(69) F. I. Sadov and P. V. Sterlov, Fireproofing of fabrics. Za. Rek. Textiln. Prom. **11**, 39 (1932). Compare Chimie & Industrie **28**, 668 (1932).
(70) C. G. Schwalbe and K. Berling, New cheap fire-protecting material for wood. Chem-Ztg. **56**, 909 (1932).
(71) H. Stadlinger, Chemical fireproofing agents. Synthetic and Applied Finishes **3**, 91 (1932).
(72) R. Chesneau, The flame-proofing of textiles. Textile Colorist **55**, 375 (1933).
(73) W. F. Brosnan, Fireproofed textiles. Textile World **84**, 2399 (1934).
(74) E. Kunze, Air defense and fire-protective paints. Farbe u. Lack **1934**, 134.
(75) L. P. Michel, Permanent fireproofing of fabrics. Tiba **12**, 3 (1934).

WASHINGTON, March 9, 1935.