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PIGMENT COLOR RESEARCH REPORT

Progress Report

EFFECT OF AA-33-D ON FLAMMABILITY OF CELLULOSE ACETATE

NOVEMBER, 1953 - JUNE, 1954

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NEWARK PLANT

CHEMICAL DIVISION - COLORS

Progress Report

EFFECT OF AA-33-D ON FLAMMABILITY OF CELLULOSE ACETATE

NOVEMBER, 1953 - JUNE, 1954

CHARGE: 1101-11-277
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SUBMITTED BY: J. JACKSON DATE SUBMITTED: 6/10/54

APPROVED BY: B. H. PERKINS DATE ISSUED: 6/22/54

INTRODUCTION:

This report summarizes the current status of a problem having as its objective the development of a flame retardent for cellulose acetate rug fiber. The U. S. consumption of acetate rug fiber has been estimated (letter M. Couper - J.J. 4/2/54) as 10-15 million lbs. of fiber in 1952, and a potential of 40 million lbs. in the near future seems possible. DuPont's share of this potential market could be as high as 5 million lbs. The attainment of this objective will necessitate the development of a suitable flame retardent resistant to water washing. The trade is apparently willing to pay approximately $.02 - $.05 per pound of yarn to achieve this goal.

This study was undertaken as part of a broad program on the subject of inorganic pigment modifiers for organic polymers. The related subjects have been reported on in KN Reports 53-6, 54-13, 14, 15, 17, 18, and 19.

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SUMMARY AND CONCLUSIONS:

1. AA-33-D, a coprecipitated $(Fe_4(P_2O_7)_x)\ (Na_4P_2O_7)_y(H_2O)_z$, when suitably dispersed within the structure of the polymer, has been found to markedly decrease the flammability of cellulose acetate either in the form of cast films or co-spun rug type fiber.

2. The pigment in its original form loses its beneficial effects upon the flammability characteristics of cellulose acetate when the cast films or rug fiber is extracted in a boiling detergent or soap solution. This gain in flammability of pigmented polymer is not shown in "dry cleaning" washes.

3. Modifications of the original pigment involving antimony (1470-28C) or titanium treatments (1470-28E) have been found to markedly improve the flammability characteristics after washing tests in which the original pigment has failed. (Memoranda - D. A. Rausch - J.J. 6/7/54).

4. Co-pigmentation of cellulose acetate with AA-33-D and urea has resulted in cast films or rug fibers which are flame retardent only after water washing, i.e., the polymer develops its retardency during a water contact and is not retardent unless subjected to this treatment.

5. The effects of these pigments upon such properties of the cellulose acetate fiber as -

a) physical properties
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will have to be determined before a decision as to their commercial merit can be determined.

6. Studies upon the effects of iron and antimony pyrophosphates on Orlon films are of doubtful significance. The magnitude of the potential market for a flame retardent in this fiber is undetermined at this time.

PATENT STATUS

A survey of the literature will be made to determine the possibility of patenting these compositions of matter for the purposes outlined in this report.

A literature survey on the chemistry of iron pyrophosphate has been previously written (J.J. 1/29/54).

The idea of attempting to develop flame retardency in a cellulose acetate film or fiber by means of co-spinning a pigmented yarn was discussed by A. Siegel and J. Jackson on or about 11/17/53. The broad concept that inorganic film fortifiers might be used to alter the physical properties of organic polymers had been discussed previously (Memo BHP & JFH, Oct. 23, 1952). Various possibilities including that of flame retardency were discussed. The first experiment was run on 11/18, 1953, and recorded in N.B.1470-8.

The results of these experiments were disclosed to B.H.Perkins on 11/19/53. Contact was made with the Textile Fibers group, and first experimental samples submitted on 12/9/53 (J.J.→W.G. Mikell).

No samples have been submitted outside the company as of this date.

RECOMMENDATIONS FOR FUTURE WORK:

Suitable samples of 1470-28C, 1470-28E, and AA-33-D are being prepared for submission to Textile Fibers for large scale testing. The results of these studies should be followed to determine the course of the future program. The use of the AA-33-D/urea technique is of particular interest to us, since this pigment may be of value for other applications such as a transparent film fortifier for alkyd and lacquer systems.

The modifications involving antimony and titanium are more highly colored and less transparent. In the writer's opinion, they would be less durable in an alkyd system. This point has not been examined, however.

The possibilities of flame retardents and general film fortification effects in other polymeric systems should be determined. "Vinyon" (vinyl chloride-vinyl acetate co-polymer) and "Dynel" (vinyl chloride acrylonitrile co-polymer) are both solvent spun and should readily lend themselves to this type study. The flammability of "Dynel" is reported to be very low.

The effects of transparent pigments upon the protein type polymers "Vicara" is unknown.

The effects of iron and antimony or iron-titanium combinations on cellulose might be worthy of study if they have not been considered in the work on "Erifon".

REFERENCES:

1. Correspondence on this subject is filed in DSN-54-8.

2. Chemistry of AA-33-D is discussed in DSN-53-4.

3. Effects of transparent film fortifiers on unsupported polymers -(KN-54-15).

4. N.B. references - 1470

5. Monthly Summary of Inorganic Laboratory - December 1953 - July, 1954.

Publications of interest in this field include -

1. U.S. Department of Commerce 1B-150
   Biography of Reports on Flame Proofing of Textiles.

2. Literature and Patent Survey - "The Flame Proofing of Textiles"
   QM Research and Development Laboratories.
   Bibliographic Series #18.

3. Malowan Canadian Patent 499,723
   Use of Water Soluble N-P. Compounds as flame retardents.

4. U.S. Patent 2,662,834.
   Use of brominated alkyl phosphate to flame retard cellulose acetate.

5. Rayon Department - Acetate Research Section - WP-123 1-14-43
   Flame Proofing of Cellulose Acetate.

6. R. W. Little. Flame Proofing Textile Fabrics.
   ACS Monograph #104. Reinhold Pub. Co. 1947.

7. Davis, et al. Journal of The Textile Institute
40 T-839-854 1949.
The Urea-Phosphoric Acid Method of Flame Proofing Textiles.

8. Flame Retardents - Symposium - Church, et al.
Ind. Eng. Chem. 42 418 1950.

DISCUSSION:

A - Scope of Study

These activities are part of a broad program on the subject of inorganic modifiers for organic polymers. (Project 701). See KN-53-6, 54-15.

Most of the emphasis in this report has been placed on the evaluation of pigment possibilities for flame retardents in cellulose acetate, since early suggestions made to those working in the Orlon field did not prove to be of interest. (J.J. - W.G.Mikell 12/9/53) (Record of conversations: J.J. - W.G.Mikell 1/11/54 - 1/19/54).

At the time the original samples were submitted (Dec. 1953) both the Orlon group and the cellulose acetate group were working with an Orchem product (polyphosphonate from ethanephosphonyl-dichloride and diphenylpropane ± $2./lb.) which appeared to offer promise as a flame retardent for the materials. This product has since been abandoned by the Orlon group because of detrimental effects upon the polymer (dyeability, lightfastness, etc.). (J.J. Report of visit 5/20/54 - Textile Fibers, Waynesboro, Va.). Work on the flammability of Orlon was reported to have been dropped (Dr. W. G. Mikell) and it would appear that no emphasis be placed on this subject until the market possibilities for the application be clarified.

B - Flame Retardency Mechanisms

No fully satisfactory explanation of flame retardency has been advanced to date.

Several hypotheses are currently in use -

1. Chemical theory - catalyzed combustion, lower exothermicity.
2. Coating theory - low melting point. Substances cover combustion site.
3. Gas theory - inert gas to smother flame.
4. Thermal theory - endothermic reaction to reduce energy source.

Chemical theory involves concepts that the flame retardent is chemically bound to the molecule of cellulose or cellulose acetate in such a fashion as to promote the formation of reactions which are of lower exothermicity than those prevalent in their absence. Such products as strong alkalies or mineral acids such as sulfuric or phosphoric have a definite effect upon cellulose to catalyze its decomposition in the presence of heat. The ideal reaction from this point of view is

$$(C_6H_{10}O_5)_x \xrightarrow[\Delta]{H_3PO_4} 6_xC + 5_x\ H_2O.$$

instead of combustible tars and gases.

C - Urea - Phosphate Flame Retardency

A standard method of flame retarding cellulose involves a treatment of cellulose with a urea/phosphoric bath treatment followed by a fusion step.

Cellulose esterification is believed to take place as a result of the high temperature reactions between the Hydroxyl groups of the cellulose and the phosphoric acid or $(NH_4)_2\ H_2PO_4$ treatment in the urea/phosphoric acid flame retardency procedures.

$$\left[\text{cell} - CH_2 - O - P(=O)(O)O\right]^{=}_{2} \left[NH_4\right]^{+}$$

The retardency is thought to result from this esterification of the free hydroxyl groups of the cellulose molecule. The formation of cellulose esters makes cellulose more resistant to combustion. Cellulose acetate is more resistant to combustion than cellulose but does contain free hydroxyl groups which can conceivably perform in a similar fashion to those of free cellulose. It is not inconceivable, therefore, that the mechanism of flame retardency involved in these studies is the formation of a more highly esterified cellulose acetate in which the pyrophosphate ion attaches itself to the free hydroxyl groups of cellulose acetate via esterification or hydrogen bonding. The acidic nature of AA-33-D lends weight to the hypothesis that there are groups in the structure of the pigment capable of esterification. Substitution of cellulosic hydroxyl groups for water molecules in the AA-33-D is also possible. The bonds formed in the original non-aqueous dispersions of pigment and cellulose acetate may conceivably be disrupted during aqueous washing (hydrolysis of the ester).

EXPERIMENTAL:

A - Technique

The effects of various pigments on the flammability of cellulose acetate and Orlon have been determined. The technique used in these studies has been -

1. Grind pigment 24-72 hrs. in the solvent in which the polymer is soluble.
   Cellulose Acetate: 15% Pigment - 81% Acetone - 4% cellulose acetate.
   Orlon: 15% Pigment - 85% dimethyl formamide.
2. Add 2-5% of dispersed pigment (dry basis) to a solution of the polymer in a suitable solvent.
3. Insure good mixing of dispersed pigment and polymer by stirring one hour with air driven propeller agitators fitted with water cooled condenser covers to prevent evaporation of solvent.
4. Make .015" or .006" (wet film thickness) draw-downs on plate glass and dry 30-45 min. at 160°F to evaporate solvent.
5. Cut films into 1" x 5" strips and determine flammability with the longer dimension held vertically. Characteristics such as -
   a) ease of ignition
   b) ease of propogation or lack of propogation of flame
   c) relative amount of volatile combustible gases evolved
   d) degree of softening of polymer during burning
   e) tendency to after-glow in residue

   were determined.

In the early work an attempt was made to determine the time required to burn each strip. Both the accuracy and the precision of this procedure is low and, in the absence of standard A.S.T.C.C. burning equipment, qualitative observations of the type previously indicated are probably satisfactory. Observations made in repeated tests, using a micro burner (flame from a drawn out glass tube), have been shown to correlate qualitatively with actual A.S.T.C.C. type tests on pile fabrics.

The slow evaporation of acetone or DMF from within a dry film has to be considered. Occasionally improper results were experienced when tests were made on films which were apparently free of solvent, but which showed much improved flammability characteristics after standing 24-48 hrs. (Evaporation of solvent?).

Cellulose Acetate burns quite vigorously giving off copious volumes of highly flammable gases. The substance melts during combustion and the tarry mass continues to burn. The addition of 2%-5% of AA-33-D apparently increases the ignition temperature and reduces the amount of combustible volatile gases. The melted tars do not appear to be self sustaining in flammability characteristics. The softening point of the pigmented cellulose acetate appears to be lower than that of the unpigmented material. Orlon possesses characteristics similar to cellulose acetate, but burns much more violently.

6. After preliminary determination of flammability in cellulose acetate, the pigmented films have been subject to a standard washing cycle consisting of a 30 minute boil in a .2% Dupanol WA solution. In this test films or fibers pigmented with products such as SW-1567, lose their retardency characteristics, i.e. they burn in a manner similar to the unpigmented polymer.

This point (6) has received considerable study since a satisfactory flame retardent for this application must be resistant to washing. Analysis of fibers before and after washing show that the explanation of the loss in retardency cannot be an extraction of the pigment from the fiber (N.B.1470-20). No change in the X-ray pattern of the pigment was detected as a result of incorporation into the cellulose acetate, and subsequent washing of the cast films.

This loss in flame retardency during washing was found to proceed more rapidly if thin films (.006" wet) were used in place of .015" films. Washing of the films in acidified Dupanol WA solution appears to markedly reduce the loss in flame retardency ordinarily experienced in the Dupanol or soap and water wash. (N.B.1470-23)

The suggestion made by G. Seidel that washing in NH_4OH containing solutions might benefit the system was tested and found to be ineffective. (N.B. 1470-30).

It is interesting to note that AA-33-D dispersions made with acetone-water mixtures are inferior in flame retardency to a similar composition dispersed in acetone. (N.B. 1470-26).

B - <u>Modifications of AA-33-D</u>

1. Since the major deficiency of the original pigment tested (AA-33-D - SW-1567, 1570) appears to be its loss in flame retardency effects after washing, emphasis has been placed on attempts to modify this pigment rather than seek entirely new pigment possibilities. This product also has possible utility as a colorless, transparent film fortifier for alkyd and lacquer samples. See KN-53-6, KN-54-18.

2. Variables studied.

	Reference	Variables
1.	1470-12	Vary Fe/Na ratio in precipitate.
2.	1470-22	Treat precipitate with metal salts to reduce sodium content Fe^{+3}, Pb^{+2}, Ca^{+2}, Mn^{+2}
3.	1470-23	Make pigment surface hydrophobic instead of hydrophilic. Used "Hyponate" petroleum sulfonate Naphthenic acid "Arquad S" cationic agent Silicone SC-50 (sodium methyl siliconate G.E.)
4.	1470-25	Dehydration of the AA-33-D prior to acetone grind.
5.	1470-28,36	Coprecipitation of Fe/Sb, Fe/Al pyrophosphate. Filming with Al, Sb, Ti compounds.
6.	1470-29	Filming with Fe, and Pb salts of carboxy methyl cellulose. Precipitation with $K_3HP_2O_7$ in place of $Na_4P_2O_7$
7.	1470-37	Copigmentation with AA-33-D and urea
8.	1470-38	Copigmentation with AA-33-D and Carbopul 934 AA-33-D and Urea-formaldehyde
9.	1470-39	Filming with urea-formaldehyde.
10.	1470-42	Copigmentation with water insoluble, solvent soluble urea formaldehyde resin Aerotex P-200.

The results of these studies in cellulose acetate are tabulated in Table I, and in Orlon in Table II.

As can be seen from Table I, the products of particular interest at this time are 1470-28C - .8 mol Fe/.2 mol Sb pyrophosphate (?) and 1470-28E - $Fe_4(P_2O_7)_3$ filmed with TiO_2 (?). The exact chemical composition of these products is unknown. These products were designed on the assumption that (1) metallic combinations might give better results than those from a single metal (similar to Erifon studies). (2) filming of the AA-33-D particle might affect its water sensitivity. These combinations have not been exhaustively studied and it is entirely possible that some other Fe/Sb or Fe/Ti, or possibly Fe/Sb/Ti combination, might give even superior results.

The urea/AA-33-D copigmentation work is also extremely interesting and should be pursued further. This makes use of the AA-33-D in its original form, which would probably be more useful in other pigment applications than the Sb and Ti treated variations.

The published work on the urea-phosphoric treatment of cellulose was of value in this phase of the study (Davis, et al J. Textile Inst. 40 T-839 1949) (Little - Flame Proofing of Textile Fabrics. ACS Monograph 104 Reinhold Pub. 1947), and offers a possible explanation of the mechanism of phosphate type flame retardents.

C. Other Studies on Flammability

1. Alkyd Resin

A dispersion of AA-33-D - SW-1567 at P/B = .15 in a Syntex 26/Resimene 881 system was compared in flammability characteristics with a clear of the same vehicle. Films of .015 wet film thickness were made on glass plates and subsequently baked and stripped. The inclusion of AA-33-D had a beneficial retarding effect on the rate of combustion of these strips. (N.B.1470-11).

2. Paper

The use of AA-33-D in a casein brushout formulation applied to the surface of paper stock had some beneficial effect on the rate of combustion of the paper. Attempts to incorporate the pigment within paper stock by a beater dyeing procedure gave no improvement in flammability characteristics. (N.B.1470-35).

3. Viscose

AA-33-D as such is decomposed by the highly alkaline solutions encountered in this field. The pigment in its present form would be unsatisfactory since it could not be incorporated into the fibers by co-spinning.

4. Vinyl

A sample of AA-33-D (1567) has been submitted to Newburgh (F&F) for evaluation of possible flame retardency in vinyl films. (R.H.Z. - Luzena 4/6/54, 4/8/54).

TABLE I — EXPERIMENTAL RESULTS OBTAINED

CELLULOSE ACETATE STUDIES - CAST FILMS

Pigment	Lot	Amount	Reference	Effect on Flammability
AA-22-D	1499	2%	1470-8	slight retardency
AA-33-D SW-1567/	1470	2%	1470-8	Retardent - effect lost on washing.
AA-33-D Variation in	Na/Fe	2%	1470-12	Retardent - effect lost on washing
AA-33-D Treated with	Fe^{+3}	4%	1470-22	Retardent - effect lost on washing
" "	Ca^{+2}	4%	"	" - " " " "
" "	Pb^{+2}	4%	"	" - " " " "
" "	Mn^{+2}	4%	"	" - v.sl.better than AA-33-D
" "	Hyponate	4%	1470-23	" - lost on washing
" "	Naphthenic Acid	4%	"	" - " " " "
" "	"Arquad S"	4%	"	" - " " " "
" "	Silicone SC-50	4%	"	" - " " " "
"	dehydration	4%	1470-25	" - " " " "
"	pH variations	4%	1470-24	" - " " " "
"	co pptd Fe/Sb	4%	1470-28*	" - much better than AA-33-D
"	Fe/Al	4%	"	" - Sl. " " "
"	Film with Al	4%	"	" - v.sl. " " "
"	" " Sb	4%	"	" - sl. " " "
"	" " Ti	4%	"	" - sl. " " "
"	" " FeCMC	4%	1470-29	" - lost on washing
"	" " PbCMC	4%	"	" - " " " "
Use K to eliminate Na		4%	"	" - " " " "
AA-33-D Co-spin with	Urea	4%	AA-33-D 1470-37	Not retardent - Retardent after washing
		2%	Urea	
" Co-spun	Carbopul 934	4%	1470-38	slight retardent - lost on washing
" Co-spin	Urea-Formaldehyde	4%	"	not retardent - not retardent after washing
" Film with	Urea-Formaldehyde	4%	1470-39	Retardent - slight retardent after washing
" Co-spin	AA-33-D Aerotex P-200	4% 2%	1470-42	Not " - Not retardent after washing

*See also 1470-36

TABLE I (Cont'd.)

Pigment	Lot	Amount	Reference	Effect on Flammability
GI-734-D	SW-1709	2%	1470-8	Ineffective
AA-34-D	1690	2%	1470-8	"
Tetrachlor phthalic anhydride		2%	1470-11	"
Tetrachlor phthalimide		2%	1470-11	"
$Mn_5(P_3O_{10})_3$	1376-28B	4%	1470-23	"
$Fe_3(PO_4)_2$	1376-18A	4%	1470-23	"
$Fe_2P_2O_7$	1376-18B	4%	1470-23	Not as good as AA-33-D. Effect lost on washing.
5/6 $Fe_4(P_2O_7)_3$ 1/6 $Fe(OH)_3$	1415-77A	4%	1470-23	± = AA-33-D Effect lost on washing.
2/3 $Fe_4(P_2O_7)_3$ 1/3 $Fe(OH)_3$	1415-77B	4%	1470-23	± = AA-33-D Effect lost on washing.
$FePO_4$	1470-24	4%	1470-24	± = AA-33-D Effect lost on washing.
$Fe_5(P_3O_{10})_3$	1470-24	4%	1470-24	± = AA-33-D Effect lost on washing.
$Mg_2P_2O_7$	1415-6	4%	1470-31	slightly retardent. Effect lost on washing.
$Sb_2P_2O_7$	1470-13C	4%	1470-44	Not retardent - Not retardent after washing.
$Ti_2P_2O_7$	1376-54A & 54B	4%	1470-44	Retardent - Effect lost on washing.
$Ti(OH)_4$	1376-14	4%	1470-44	Not retardent - Not retardent after washing.
Urea		4%	1470-44	Not retardent - Not retardent after washing.

TABLE II

ORLON STUDIES - CAST FILMS

Pigment	Lot	Amount	Reference	Effect on Flammability
AA-22-D	1499	3%	1470-9	Ineffective *
AA-33-D	1567	3%	1470-9	Slightly less flammable*
		6%		Not as good as 3% *
GI-734-D	1576	3%	1470-9	Ineffective *
AA-34-D	1690	3%	1470-9	Ineffective *
Basic Alum. Sulfate	1446-29	3%	1470-9	Ineffective *
A-I-D		3%	1470-9	Ineffective *
$Sb_4(P_2O_7)_3$	1376-86D	3%	1470-9	Beneficial - less flammable*
Tetrachlor phthalic anhydride		3%	1470-9	v.sl. less flammable
50/50 #2 & #8		3%	1470-9	Not different from AA-33-D.
50/50 #7 & #8		3%	1470-9	Not different from $Sb_4(P_2O_7)_3$
50/50 #2 & #7		3%	1470-9	Inferior to #7
$Sb_4(P_2O_7)_3$ various compositions		3%	1470-13	Less flammable than control
DV 1858**		3-6%	1470-12	sl.less flammable than control

* No change in results when films washed 30 min. .2% Dupanol WA. at 212°F

** Product supplied by Orchem-Polyphosphonate from ethane-phosphonyl dichloride and diphenylol propane.

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SUBMITTED BY: Julius Jackson J. JACKSON DATE SUBMITTED: 6/10/54

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The possibilities of flame retardents and general film fortification effects in other polymeric systems should be determined. "Vinyon" (vinyl chloride-vinyl acetate co-polymer) and "Dynel" (vinyl chloride acrylonitrile co-polymer) are both solvent spun and should readily lend themselves to this type study. The flammability of "Dynel" is reported to be very low.

The effects of transparent pigments upon the protein type polymers "Vicara" is unknown.

The effects of iron and antimony or iron-titanium combinations on cellulose might be worthy of study if they have not been considered in the work on "Erifon".

REFERENCES:

1. Correspondence on this subject is filed in DSN-54-8.

2. Chemistry of AA-33-D is discussed in DSN-53-4.

3. Effects of transparent film fortifiers on unsupported polymers -(KN-54-15).

4. N.B. references - 1470

5. Monthly Summary of Inorganic Laboratory - December 1953 - July, 1954.

Publications of interest in this field include -

1. U.S. Department of Commerce 1B-150
Biography of Reports on Flame Proofing of Textiles.

2. Literature and Patent Survey - "The Flame Proofing of Textiles"
QM Research and Development Laboratories.
Bibliographic Series #18.

3. Malowan Canadian Patent 499,723
Use of Water Soluble N-P. Compounds as flame retardents.

4. U.S. Patent 2,662,834.
Use of brominated alkyl phosphate to flame retard cellulose acetate.

5. Rayon Department - Acetate Research Section - WP-123 1-14-43
Flame Proofing of Cellulose Acetate.

6. R. W. Little. Flame Proofing Textile Fabrics.
ACS Monograph #104. Reinhold Pub. Co. 1947.

7. Davis, et al. Journal of The Textile Institute
40 T-839-854 1949.
The Urea-Phosphoric Acid Method of Flame Proofing Textiles.

8. Flame Retardents - Symposium - Church, et al.
Ind. Eng. Chem. 42 418 1950.

DISCUSSION:

A - Scope of Study

These activities are part of a broad program on the subject of inorganic modifiers for organic polymers. (Project 701). See KN-53-6, 54-15.

Most of the emphasis in this report has been placed on the evaluation of pigment possibilities for flame retardents in cellulose acetate, since early suggestions made to those working in the Orlon field did not prove to be of interest. (J.J. - W.G.Mikell 12/9/53) (Record of conversations: J.J. - W.G.Mikell 1/11/54 - 1/19/54).

At the time the original samples were submitted (Dec. 1953) both the Orlon group and the cellulose acetate group were working with an Orchem product (polyphosphonate from ethanephosphonyl-dichloride and diphenylpropane ± $2./lb.) which appeared to offer promise as a flame retardent for the materials. This product has since been abandoned by the Orlon group because of detrimental effects upon the polymer (dyeability, lightfastness, etc.). (J.J. Report of visit 5/20/54 - Textile Fibers, Waynesboro, Va.). Work on the flammability of Orlon was reported to have been dropped (Dr. W. G. Mikell) and it would appear that no emphasis be placed on this subject until the market possibilities for the application be clarified.

B - Flame Retardency Mechanisms

No fully satisfactory explanation of flame retardency has been advanced to date.

Several hypotheses are currently in use -

1. Chemical theory - catalyzed combustion, lower exothermicity.
2. Coating theory - low melting point. Substances cover combustion site.
3. Gas theory - inert gas to smother flame.
4. Thermal theory - endothermic reaction to reduce energy source.

Chemical theory involves concepts that the flame retardent is chemically bound to the molecule of cellulose or cellulose acetate in such a fashion as to promote the formation of reactions which are of lower exothermicity than those prevalent in their absence. Such products as strong alkalies or mineral acids such as sulfuric or phosphoric have a definite effect upon cellulose to catalyze its decomposition in the presence of heat. The ideal reaction from this point of view is

$$(C_6H_{10}O_5)_x \xrightarrow[\Delta]{H_3PO_4} 6_xC + 5_x H_2O,$$

instead of combustible tars and gases.

C - Urea - Phosphate Flame Retardency

A standard method of flame retarding cellulose involves a treatment of cellulose with a urea/phosphoric bath treatment followed by a fusion step.

Cellulose esterification is believed to take place as a result of the high temperature reactions between the Hydroxyl groups of the cellulose and the phosphoric acid or $(NH_4)_2 H_2PO_4$ treatment in the urea/phosphoric acid flame retardency procedures.

$$\left[\text{cell} - CH_2 - O - P(=O)(O)O\right]^{=}_{2} \left[NH_4\right]^{+}$$

The retardency is thought to result from this esterification of the free hydroxyl groups of the cellulose molecule. The formation of cellulose esters makes cellulose more resistant to combustion. Cellulose acetate is more resistant to combustion than cellulose but does contain free hydroxyl groups which can conceivably perform in a similar fashion to those of free cellulose. It is not inconceivable, therefore, that the mechanism of flame retardency involved in these studies is the formation of a more highly esterified cellulose acetate in which the pyrophosphate ion attaches itself to the free hydroxyl groups of cellulose acetate via esterification or hydrogen bonding. The acidic nature of AA-33-D lends weight to the hypothesis that there are groups in the structure of the pigment capable of esterification. Substitution of cellulosic hydroxyl groups for water molecules in the AA-33-D is also possible. The bonds formed in the original non-aqueous dispersions of pigment and cellulose acetate may conceivably be disrupted during aqueous washing (hydrolysis of the ester).

EXPERIMENTAL:

A - Technique

The effects of various pigments on the flammability of cellulose acetate and Orlon have been determined. The technique used in these studies has been -

1. Grind pigment 24-72 hrs. in the solvent in which the polymer is soluble,
   Cellulose Acetate: 15% Pigment - 81% Acetone - 4% cellulose acetate.
   Orlon: 15% Pigment - 85% dimethyl formamide.
2. Add 2-5% of dispersed pigment (dry basis) to a solution of the polymer in a suitable solvent.
3. Insure good mixing of dispersed pigment and polymer by stirring one hour with air driven propeller agitators fitted with water cooled condenser covers to prevent evaporation of solvent.
4. Make .015" or .006" (wet film thickness) draw-downs on plate glass and dry 30-45 min. at 160°F to evaporate solvent.
5. Cut films into 1" x 5" strips and determine flammability with the longer dimension held vertically. Characteristics such as -
   a) ease of ignition
   b) ease of propogation or lack of propogation of flame
   c) relative amount of volatile combustible gases evolved
   d) degree of softening of polymer during burning
   e) tendency to after-glow in residue

   were determined.

In the early work an attempt was made to determine the time required to burn each strip. Both the accuracy and the precision of this procedure is low and, in the absence of standard A.S.T.C.C. burning equipment, qualitative observations of the type previously indicated are probably satisfactory. Observations made in repeated tests, using a micro burner (flame from a drawn out glass tube), have been shown to correlate qualitatively with actual A.S.T.C.C. type tests on pile fabrics.

The slow evaporation of acetone or DMF from within a dry film has to be considered. Occasionally improper results were experienced when tests were made on films which were apparently free of solvent, but which showed much improved flammability characteristics after standing 24-48 hrs. (Evaporation of solvent?).

Cellulose Acetate burns quite vigorously giving off copious volumes of highly flammable gases. The substance melts during combustion and the tarry mass continues to burn. The addition of 2%-5% of AA-33-D apparently increases the ignition temperature and reduces the amount of combustible volatile gases. The melted tars do not appear to be self sustaining in flammability characteristics. The softening point of the pigmented cellulose acetate appears to be lower than that of the unpigmented material. Orlon possesses characteristics similar to cellulose acetate, but burns much more violently.

6. After preliminary determination of flammability in cellulose acetate, the pigmented films have been subject to a standard washing cycle consisting of a 30 minute boil in a .2% Dupanol WA solution. In this test films or fibers pigmented with products such as SW-1567, lose their retardency characteristics, i.e. they burn in a manner similar to the unpigmented polymer.

This point (6) has received considerable study since a satisfactory flame retardent for this application must be resistant to washing. Analysis of fibers before and after washing show that the explanation of the loss in retardency cannot be an extraction of the pigment from the fiber (N.B.1470-20). No change in the X-ray pattern of the pigment was detected as a result of incorporation into the cellulose acetate, and subsequent washing of the cast films.

This loss in flame retardency during washing was found to proceed more rapidly if thin films (.006" wet) were used in place of .015" films. Washing of the films in acidified Dupanol WA solution appears to markedly reduce the loss in flame retardency ordinarily experienced in the Dupanol or soap and water wash. (N.B.1470-23)

The suggestion made by G. Seidel that washing in NH_4OH containing solutions might benefit the system was tested and found to be ineffective. (N.B. 1470-30).

It is interesting to note that AA-33-D dispersions made with acetone-water mixtures are inferior in flame retardency to a similar composition dispersed in acetone. (N.B. 1470-26).

B - <u>Modifications of AA-33-D</u>

1. Since the major deficiency of the original pigment tested (AA-33-D - SW-1567, 1570) appears to be its loss in flame retardency effects after washing, emphasis has been placed on attempts to modify this pigment rather than seek entirely new pigment possibilities. This product also has possible utility as a colorless, transparent film fortifier for alkyd and lacquer samples. See KN-53-6, KN-54-18.

2. Variables studied.

	Reference	Variables
1.	1470-12	Vary Fe/Na ratio in precipitate.
2.	1470-22	Treat precipitate with metal salts to reduce sodium content Fe^{+3}, Pb^{+2}, Ca^{+2}, Mn^{+2}
3.	1470-23	Make pigment surface hydrophobic instead of hydrophilic. Used "Hyponate" petroleum sulfonate Naphthenic acid "Arquad S" cationic agent Silicone SC-50 (sodium methyl siliconate G.E.)
4.	1470-25	Dehydration of the AA-33-D prior to acetone grind.
5.	1470-28,36	Coprecipitation of Fe/Sb, Fe/Al pyrophosphate. Filming with Al, Sb, Ti compounds.
6.	1470-29	Filming with Fe, and Pb salts of carboxy methyl cellulose. Precipitation with $K_3HP_2O_7$ in place of $Na_4P_2O_7$
7.	1470-37	Copigmentation with AA-33-D and urea
8.	1470-38	Copigmentation with AA-33-D and Carbopul 934 AA-33-D and Urea-formaldehyde
9.	1470-39	Filming with urea-formaldehyde.
10.	1470-42	Copigmentation with water insoluble, solvent soluble urea formaldehyde resin Aerotex P-200.

The results of these studies in cellulose acetate are tabulated in Table I, and in Orlon in Table II.

As can be seen from Table I, the products of particular interest at this time are 1470-28C - .8 mol Fe/.2 mol Sb pyrophosphate (?) and 1470-28E - $Fe_4(P_2O_7)_3$ filmed with TiO_2 (?). The exact chemical composition of these products is unknown. These products were designed on the assumption that (1) metallic combinations might give better results than those from a single metal (similar to Erifon studies). (2) filming of the AA-33-D particle might affect its water sensitivity. These combinations have not been exhaustively studied and it is entirely possible that some other Fe/Sb or Fe/Ti, or possibly Fe/Sb/Ti combination, might give even superior results.

The urea/AA-33-D copigmentation work is also extremely interesting and should be pursued further. This makes use of the AA-33-D in its original form, which would probably be more useful in other pigment applications than the Sb and Ti treated variations.

The published work on the urea-phosphoric treatment of cellulose was of value in this phase of the study (Davis, et al J. Textile Inst. 40 T-839 1949) (Little - Flame Proofing of Textile Fabrics. ACS Monograph 104 Reinhold Pub. 1947), and offers a possible explanation of the mechanism of phosphate type flame retardents.

C. Other Studies on Flammability

1. Alkyd Resin

A dispersion of AA-33-D - SW-1567 at P/B = .15 in a Syntex 26/Resimene 881 system was compared in flammability characteristics with a clear of the same vehicle. Films of .015 wet film thickness were made on glass plates and subsequently baked and stripped. The inclusion of AA-33-D had a beneficial retarding effect on the rate of combustion of these strips. (N.B.1470-11).

2. Paper

The use of AA-33-D in a casein brushout formulation applied to the surface of paper stock had some beneficial effect on the rate of combustion of the paper. Attempts to incorporate the pigment within paper stock by a beater dyeing procedure gave no improvement in flammability characteristics. (N.B.1470-35).

3. Viscose

AA-33-D as such is decomposed by the highly alkaline solutions encountered in this field. The pigment in its present form would be unsatisfactory since it could not be incorporated into the fibers by co-spinning.

4. Vinyl

A sample of AA-33-D (1567) has been submitted to Newburgh (F&R) for evaluation of possible flame retardency in vinyl films. (R.H.Z. - Luzena 4/6/54, 4/8/54).

TABLE I — EXPERIMENTAL RESULTS OBTAINED

CELLULOSE ACETATE STUDIES - CAST FILMS

Pigment	Lot	Amount	Reference	Effect on Flammability
AA-22-D	1499	2%	1470-8	slight retardency
AA-33-D	SW-1567/ 1470	2%	1470-8	Retardent - effect lost on washing.
AA-33-D	Variation in Na/Fe	2%	1470-12	Retardent - effect lost on washing
AA-33-D	Treated with Fe^{+3}	4%	1470-22	Retardent - effect lost on washing
"	" Ca^{+2}	4%	"	" - " " " "
"	" Pb^{+2}	4%	"	" - " " " "
"	" Mn^{+2}	4%	"	" - v.sl.better than AA-33-D
"	" Hyponate	4%	1470-23	" - lost on washing
"	" Naphthenic Acid	4%	"	" - " " " "
"	" "Arquad S"	4%	"	" - " " " "
"	" Silicone SC-50	4%	"	" - " " " "
"	dehydration	4%	1470-25	" - " " " "
"	pH variations	4%	1470-24	" - " " " "
"	co pptd Fe/Sb	4%	1470-28*	" - much better than AA-33-D
"	Fe/Al	4%	"	" - sl. " " "
"	Film with Al	4%	"	" - v.sl. " " "
"	" " Sb	4%	"	" - sl. " " "
"	" " Ti	4%	"	" - sl. " " "
"	" " FeCMC	4%	1470-29	" - lost on washing "
"	" " PbCMC	4%	"	" - " " " "
Use K to eliminate Na		4%	"	" - " " " "
AA-33-D	Co-spin with Urea	4%	AA-33-D 1470-37	Not retardent - Retardent after washing
		2%	Urea	
"	Co-spun Carbopul 934	4%	1470-38	slight retardent - lost on washing
"	Co-spin Urea-Formaldehyde	4%	"	not retardent - not retardent after washing
"	Film with Urea-Formaldehyde	4%	1470-39	slight retardent - Retardent after washing
"	Co-spin AA-33-D Aerotex P-200	4% 2%	1470-42	Not " - Not retardent after washing

*See also 1470-36

TABLE I (Cont'd.)

Pigment	Lot	Amount	Reference	Effect on Flammability
GI-734-D	SW-1709	2%	1470-8	Ineffective
AA-34-D	1690	2%	1470-8	"
Tetrachlor phthalic anhydride		2%	1470-11	"
Tetrachlor phthalimide		2%	1470-11	"
$Mn_5(P_3O_{10})_3$	1376-28B	4%	1470-23	"
$Fe_3(PO_4)_2$	1376-18A	4%	1470-23	"
$Fe_2P_2O_7$	1376-18B	4%	1470-23	Not as good as AA-33-D. Effect lost on washing.
5/6 $Fe_4(P_2O_7)_3$ 1/6 $Fe(OH)_3$	1415-77A	4%	1470-23	± = AA-33-D Effect lost on washing.
2/3 $Fe_4(P_2O_7)_3$ 1/3 $Fe(OH)_3$	1415-77B	4%	1470-23	± = AA-33-D Effect lost on washing.
$FePO_4$	1470-24	4%	1470-24	± = AA-33-D Effect lost on washing.
$Fe_5(P_3O_{10})_3$	1470-24	4%	1470-24	± = AA-33-D Effect lost on washing.
$Mg_2P_2O_7$	1415-6	4%	1470-31	slightly retardent. Effect lost on washing.
$Sb_2P_2O_7$	1470-13C	4%	1470-44	Not retardent - Not retardent after washing.
$Ti_2P_2O_7$	1376-54A & 54B	4%	1470-44	Retardent - Effect lost on washing.
$Ti(OH)_4$	1376-14	4%	1470-44	Not retardent - Not retardent after washing.
Urea		4%	1470-44	Not retardent - Not retardent after washing.

TABLE II

ORLON STUDIES - CAST FILMS

Pigment	Lot	Amount	Reference	Effect on Flammability
AA-22-D	1499	3%	1470-9	Ineffective *
AA-33-D	1567	3%	1470-9	Slightly less flammable*
		6%		Not as good as 3% *
GI-734-D	1576	3%	1470-9	Ineffective *
AA-34-D	1690	3%	1470-9	Ineffective *
Basic Alum. Sulfate	1446-29	3%	1470-9	Ineffective *
A-I-D		3%	1470-9	Ineffective *
$Sb_4(P_2O_7)_3$	1376-86D	3%	1470-9	Beneficial - less flammable*
Tetrachlor phthalic anhydride		3%	1470-9	v.sl. less flammable
50/50 #2 & #8		3%	1470-9	Not different from AA-33-D.
50/50 #7 & #8		3%	1470-9	Not different from $Sb_4(P_2O_7)_3$
50/50 #2 & #7		3%	1470-9	Inferior to #7
$Sb_4(P_2O_7)_3$ various compositions		3%	1470-13	Less flammable than control
DV 1858**		3-6%	1470-12	sl.less flammable than control

* No change in results when films washed 30 min. at 212°F .2% Dupanol WA.

** Product supplied by Orchem-Polyphosphonate from ethane-phosphonyl dichloride and diphenylol propane.