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PHOSPHORUS-CONTAINING TRIAZINES

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Int. Cl. C07d 55/20
U.S. Cl. 260—249.8 2 Claims

ABSTRACT OF THE DISCLOSURE

New processes for preparing aminoalkoxyphosphinyl-1,3,5-triazines and processes for producing flame resistant cellulosic materials by treating the cellulosic materials with the formaldehyde derivatives of the aminoalkoxyphosphinyl triazines.

A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This invention relates to new methods of preparing phosphorus-containing triazines, and to processes for imparting flame resistance to cellulosic textiles by treating said textiles with certain of the phosphorus-containing triazines. More specifically, this invention relates to the preparation of aminoalkyloxyphosphinyl triazines and their formaldehyde derivatives, and to the use of these derivatives as flame retardant finishes for cellulosic textiles.

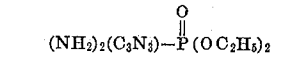
The main object of the instant invention is to disclose new methods of preparing aminoalkoxyphosphinyl triazines.

A second object of the instant invention is to provide a process for preparing the formaldehyde derivatives of the compounds prepared by methods of the instant invention.

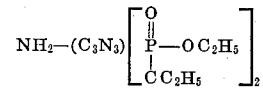
A third object of the instant invention is to provide a process for imparting to cotton and other cellulosic material, improved flame resistance, using the formaldehyde derivatives of the compounds prepared by methods of the instant invention.

Searching the prior art we find that Gaetano F. D'Alelio claims to have prepared aminoalkoxyphosphinyl triazines by the reaction of chloroamino-triazines with trialkyl phosphites by way of the well known Arbusov reaction. [Gaetano F. D'Alelio, U.S. Pat. 3,011,998, Dec. 5, 1961, and U.S. Pat. 3,210,350, Oct. 5, 1965.] We were unable to duplicate D'Alelio's method. When we tried to duplicate D'Alelio's Example 1 which states:

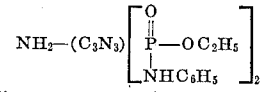
"In a suitable reactor equipped with stirrer and reflux condenser a mixture of 145.5 parts of 2,4-diamino-6-monochloro-1,3,5-triazine and 200 parts of triethyl phosphite and 200 parts of benzene are heated at reflux for eight hours, at which time no more ethyl chloride is released from the reaction. The reaction is then cooled and the solid



separated by filtration, washed with alcohol and dried, which on analysis gives the following values: 34% carbon, 28.1% nitrogen, 5.35% hydrogen, and 12.2% phosphorous, and a molecular weight of 246.1, which values are in close agreement with the theoretical values. When 165 parts of the corresponding monoamino-dichlorotriazine are reacted instead of the monochlorotriazine with 380 parts of triethyl phosphite, and the reaction product isolated, there is obtained an almost quantitative yield of

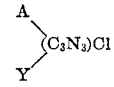


which on analysis gives values of 35.16% carbon, 5.89% hydrogen, 15.35% nitrogen, and 17.21% phosphorus, and a molecular weight of 367.1, which values are in close agreement with the theoretical values. When this diester is allowed to stand at room temperature with aniline, the corresponding



is obtained. These compounds are very effective as fire retardants when impregnated into wood, etc. according to standard methods, and are also effective as tanning agents for leather."

"When halotriazines of the formula $(A)_2(C_3N_3)Cl$, or

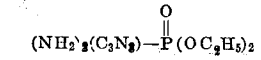


or $A(C_3N_3)Cl_2$ are used instead of the halotriazines of the preceding example, the corresponding triazine derivatives are obtained. These products show very good fire retardant properties"

We obtained none of the expected product when either triethyl phosphite or trimethyl phosphite was allowed to react with 2,4-diamino-6-chloro-1,3,5-triazine. The latter compound was recovered unchanged in yields up to 92%. We have found new methods of preparing aminoalkoxyphosphinyl triazines which are an improvement over the methods of the prior art. We have also found that it is advantageous to carry out the reaction of formaldehyde with aminoalkoxyphosphinyl triazines under acidic conditions at temperatures of 85–95° C. for periods of time less than 30 minutes. When the reaction is carried out at 85–95° C. for less than 30 minutes condensation of the formaldehyde derivative is minimized, producing a water soluble further polymerizable product which is suitable for application to cellulosic textiles.

We have found that when the aminoalkoxyphosphinyl triazines are heated with alkaline aqueous formaldehyde the solutions become acidic due to hydrolysis. Thus, we were not able to prepare formaldehyde derivatives suitable for cellulose textile application by boiling the aminoalkoxyphosphinyl triazines with aqueous formaldehyde under alkaline conditions as described by D'Alelio in Example 2 of U.S. Pat. 3,011,998, said example states:

"Twenty-one parts of

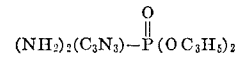


and 32 parts of aqueous formaldehyde (approximately 37% HCHO) are heated together with 0.02 part of sodium hydroxide under reflux at the boiling point of the mixture, for 30 minutes, yielding a resinous reaction product that cures to an insoluble, infusible mass when a sample is heated on a hot plate at 150° C. A satisfactory molding compound that shows adequate flow characteristics during molding is produced by mixing a portion of the resinous syrup with a weight of alpha cellulose equal to the solids content of the syrup followed by drying at low temperature to remove the excess water. A well-cured molded piece is obtained by molding a sample of the dried and ground molding compound for 3 minutes at 145° C. under a pressure of 5000 pounds per square inch. Instead of heating the reactants under reflux, as described above, the mixture is stirred for a longer period, 72 hours, at room temperautre to effect reaction between the components and to obtain a soluble, fusible reaction product which is heat hardenable."

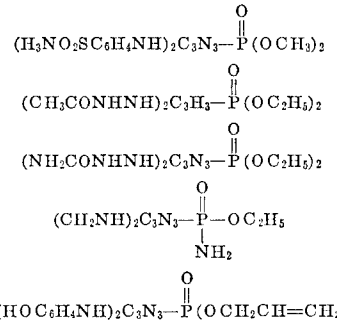
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"Other alkaline condensation catalysts that can be used include sodium carbonate, ammonia, triethanol amine, hexamethylene tetramine, etc., and acidic curing catalysts include acetic acid, phthalic acid, ammonium chloride, ammonium phosphate, glycine, chloroacetamide, chloroacetyl urea, etc., or substances which under the influence of the reaction or heat produce such acidic substances."

"When instead of



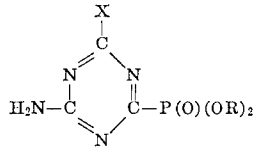
there is used an equivalent amount of



etc., heat convertible condensation products are obtained."

Formaldehyde derivatives prepared by D'Alelio's method form condensation products which make cellulosic materials too stiff and boardy for textile uses.

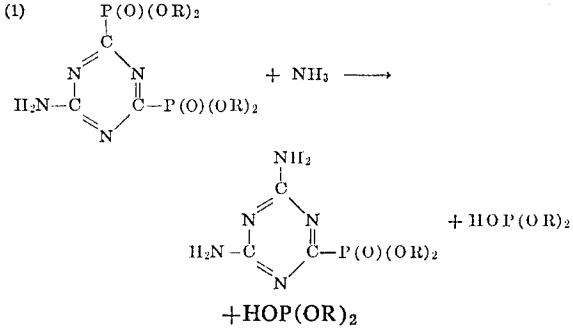
Compounds of this invention comprise triazine derivatives of the general formula:



where R represents an alkyl radical or a haloalkyl radical, X represents NH_2 or $—P(O)(OR)_2$, where R is an alkyl radical or a haloalkyl radical.

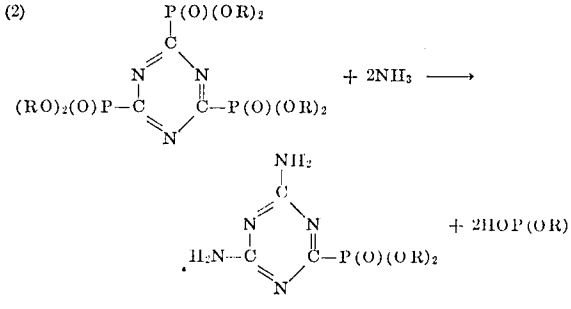
We have found that the compounds of this invention can be prepared by new improved methods according to the following equations:

(1)



where R represents an alkyl radical or a haloalkyl radical.

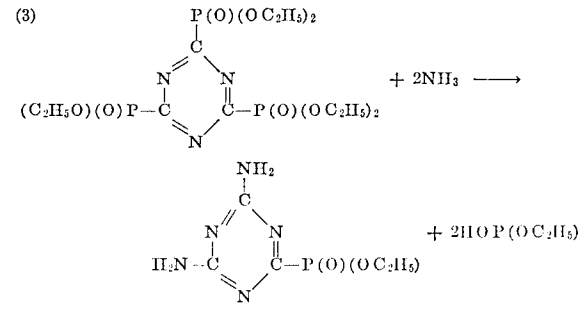
(2)



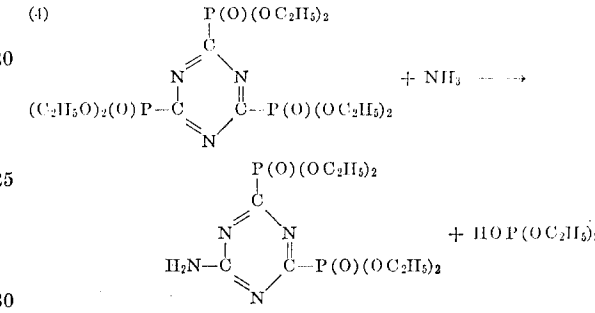
where R represents an alkyl or a haloalkyl radical.

Specific examples of the reactions of this invention are represented by the following equations:

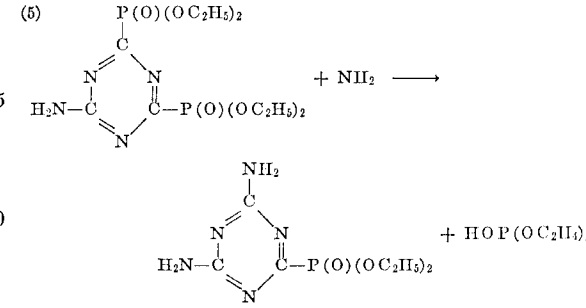
(3)



(4)



(5)

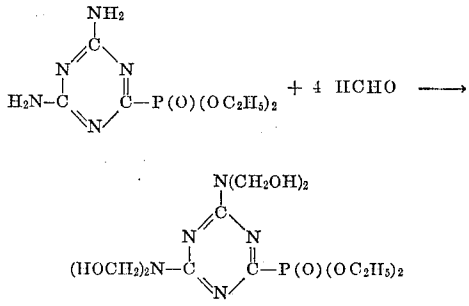


In accordance with the present invention a 2,4,6-tris (dialkoxyphosphinyl) 1,3,5-triazine (represented by Equation 2) or a 2-amino-4,6-bis(dialkoxyphosphinyl)-1,3,5-triazine (represented by Equation 1) is allowed to react with ammonia. Triazines particularly suitable for the invention are 2,4,6-tris(diethoxyphosphinyl)-1,3,5-triazine, 2,4,6-tris(dimethoxphosphinyl) 1,3,5-triazine, 2,4,6-tris(β-chloroethoxyphenosphinyl)-1,3,5-triazine, and 2-amino-4, 6-bis(diethoxyphosphinyl)-1,3,5-triazine. The preferred compounds are 2,4,6-tris(diethoxyphosphinyl) 1,3,5-triazine and 2-amino-4,6-bis(diethoxyphosphinyl)-1,3,5-triazine, Solvents suitable for the reaction are polar solvents such as water or ethanol and non-polar solvents such as benzene. While other organic solvents may be used, the preferred solvent is ethanol.

The reaction of the phosphinyl triazines with ammonia may be carried out at temperature about from 0° C. to 40° C. The reaction is preferably carried out by dissolving the triazines in the solvent and then adding the ammonia. The preferred temperature for adding the ammonia is about from 0° C. to 15° C. After the addition of the ammonia is complete the reaction is allowed to take place at room temperature for about from 24 hours to 72 hours. The preferred time is about 72 hours.

Theoretically, 4 moles of formaldehyde can react with one mole of a diaminoalkoxyphosphinyl triazine and 2 moles of formaldehyde can react with aminobis(alkoxyphosphinyl) triazines. In practice, however, it is advantageous to use formaldehyde in excess of the theoretical amount in order to insure as complete a reaction as possi-

ble. A typical reaction of formaldehyde with a triazine is represented by the following equation:



It is not likely, however, that a tetramethylol derivative is actually produced in the acidic media employed in the reaction. Apparently, low molecular weight water soluble condensation products of the formaldehyde derivatives are formed which are capable of polymerizing further to cross-linked polymers which are insoluble in water and most organic solvents. The formaldehyde derivaties are preferably formed by mixing the aminoalkoxyphosphinyl triazine with aqueous formaldehyde in a mole ratio of 1:4 to 1:6.5. The preferable ratio of triazine to formaldehyde is 1:5. The initial pH of the mixture is 3.3, but at the end of the heating period drops to about from 2.6 to 3.0. The mixture is then placed in a suitable preheated bath and the reaction mixture brought as quickly as possible to 85–95° C. A water bath was used but any suitable heating device may be used. The heating time may be varied about from 15 minutes to 27 minutes. The preferable time is about from 15 to 17 minutes.

After the heating period is completed, the solution is cooled to room temperature quickly and adjusted to the desired pH with aqueous sodium hydroxide for application to cellulosic materials. Other suitable bases may be used.

The polymerization on cellulosic materials may be carried out by impregnating the cellulosic material with a solution of the further polymerizable formaldehyde derivatives, drying, and curing at temperatures ranging about from 150° to 170° C. for periods of time about from 5 to 7 minutes. Latent acid catalysts such as magnesium chloride or zinc nitrate may be used in the application to cellulosic materials, but it is preferable to use no catalyst. Textile lubricants or softening agents may be added to the treating baths to improve the strength and abrasion resistance of the treated textiles. A pad bath pH of 6.5–6.6 is preferred for best fabric strength and abrasion resistance and flame resistance.

Cotton fabrics treated by the processes of this invention possess good flame resistance which is durable to repeated laundering. Fabric strength and abrasion resistance properties are also good.

Cotton fabrics which have been treated by the processes of this invention were tested by the standard methods of the American Society for Testing Materials, Philadelphia, Pa., Committee D–13. Wrinkle recovery was determined by the Monsanto Method. ASTM designation, D1295–53T; breaking strength by the one-inch strip method, D39–59; tearing strength by the Elmendorf Method, D1295–60T; flex abrasion resistance by the Stoll Method, D1175–65T. Flame resistance was determined by the standard vertical method, U.S. Federal Supply Service "Textile Test Methods," Federal Specification CCC–T–191b, Method 5902. Durability of the flame resistant finish to laundering was determined by washing in an agitator-type washing machine under normal washing conditions for cotton, using a commercial detergent. Each laundering cycle was followed by tumble dryin gfor 20 minutes.

The following examples illustrate the methods of carrying out the invention, but the invention is not restricted

to these examples. In the examples the following abbreviations will be used: 2,4,6-tris(diethoxyphosphinyl)triazine will be referred to as TEPT; 2,4-diamino-6-diethoxyphosphinyl triazine, as DAPT; 2-amino-4,6-bis(diethoxyphosphinyl)triazine, as ADPT; the formaledhyde derivative DAPT, as N-methylol DAPT or M DAPT.

EXAMPLE 1

2,4-diamino - 6 - diethoxyphosphinyl triazine (DAPT): DAPT was prepared by the reaction of TEPT with ammonia in (a) ethanol, (b) benzene, and (c) water.

Ethanol procedure: 2,4,6-tris(diethoxyphosphinyl)-1,3,5-triazine (TEPT) (97.9 grams, M.P. 93–95° C.) was dissolved in 400 ml. of absolute ethanol. The solution was cooled in an ice-salt bath to approximately 0° C., and then saturated with ammonia gas. The addition was regulated so that the reaction temperature did not rise above 15° C. The solution was allowed to stand for three days. After cooling, the precipitated white solid was removed by filtration, washed thoroughly with water then acetone and dried to give 41.2 grams (83% yield) of DAPT.

When the above reaction was carried out without cooling during the ammonia addition the temperature rose from 22° to 40° C. in 5–10 minutes. After standing at room temperature for 24 hours, the DAPT was isolated as above in yields of only 30%. Diethyl hydrogen phosphite was recovered by vacuum distillation as the major byproduct in 75% yield.

A sample of DAPT, recrystallized from boiling water, had a M.P. of 273° C. with decomposition. The IR spectrum showed absorption bands at 2.99, 3.12 microns (s.) (NH stretching); 6.00, 6.14 microns (s.) (NH deformation); 6.46, 6.56 microns (s.) (ring stretching); 8.18 microns (s.) (P=O); 9.77, 13.47 microns (s.) (w.) (P—O—C); and 12.24, 12.59 microns (w.) (ring bending). The PMR spectrum (DMSO) gave a triplet at 4.17 p.p.m. ($J_{HH}=J_{PH}=7$ cps.) and a singlet at 7.00 p.p.m. The spectrum integrated 3:2:2, respectively.

Analysis.—Calcd. for $C_7H_{14}N_5O_3P$ (percent): C, 34.01; H, 5.71; N, 28.33; P, 12.53. Found (percent): C, 34.00; H, 5.66; N, 28.38; P, 12.60.

Benzene procedure: TEPT (0.023 mole, 11.4 grams) was dissolved in 35 ml. of benzene, the solution cooled and then saturated with ammonia. After cooling overnight, the white precipitate was removed by filtration to give 0.93 gram (0.004 mole, 17.4% yield) of DAPT. The filtrate was concentrated and diethyl hydrogen phosphite (0.022 moles, 3.1 grams) removed by vacuum distillation. The residue, which solidified overnight, was triturated in petroleum ether, filtered and dried to give 6.21 grams of a white crystalline compound. A sample of this compound, after recrystallization from diethyl ether, had elemental analyses and melting point consistent with an authentic sample of 2-amino-4,6-bisdiethoxyphosphinyl-1,3,5-triazine (ADPT) as prepared by D'Alelio [U. S. Pat. 3,210,350 (1965)]. This constitutes a new method for preparing ADPT.

Water procedure: TEPT (0.05 mole, 24.5 grams) was added in increments to 75.5 grams of NH_4 (28% NH_3). The reaction temperature rose spontaneously to 34° C. After standing at room temperature for five days, the white precipitate was removed by filtration, washed thoroughly with water then acetone and dried to give 2.11 grams (0.009 mole, 18% yield) of DAPT.

EXAMPLE 2

DAPT was also prepared by the ethanol procedure described in Example 1 except that ADPT was used instead of TEPT. (see Equation 5 of specification.)

EXAMPLE 3

Preparation of N-methylol DAPT (MDAPT)

MDAPT was prepared by the following typical procedure, DAPT (49.4 g., 0.2 mole), formaldehyde (83.0 g. of 36.6% HCHO, 1.0 mole), and water (43.0 g.) were

placed in a 300 ml. flask equipped with a reflux condenser, stirrer, and thermometer (immersed in the liquid). This was a mole ratio of DAPT:HCHO of 1:5. The flask was immersed in a water bath which had been preheated to boiling. After approximately 10 minutes of heating and stirring, the DAPT dissolved completely forming a clear solution. At this point the solution temperature was about 94–95° C. Heating and stirring at this temperature were continued for an additional 6 minutes, for a total heating time of about 16 minutes. If possible, the total heating time should not exceed 16 minutes. If the solution is heated too long, excessive condensation of MDAPT apparently occurs. Even under the conditions described, it is believed that some condensation occurs, but the product is of low molecular weight and hence very water soluble.

After the heating was completed, the flask was immediately cooled by immersing the flask in cold water. The pH of the resulting solution was 2.7. The solution was adjusted to the desired pH with sodium hydroxide solution and served as a stock solution.

In one experiment crude MDAPT was isolated as a clear colorless, very viscous material by evaporation of the water under high vacuum at about 50° C. This material was not as stable upon storage as the water solution, and set to a gel in two or three weeks.

Analysis.—Calculated for $C_{11}H_{22}N_5O_7P$ (percent) (tetramethylol derivative of DAPT): C, 35.97; H, 6.04; N, 19.07; P, 8.43. Found (percent): C, 37.68; H, 6.44; N, 18.29; P, 8.29.

Solutions of the formaldehyde derivatives of DAPT were also prepared in a similar manner as above in which the heating time was varied from 15 minutes to 27 minutes. Heating periods of 16–17 minutes were considered optimum. Temperatures as low as 85° C. were used for heating periods above 20 minutes.

Solutions were also prepared in a similar manner in which the DAPT to formaldehyde ratio was 1:4 and 1:6. When the ratio was 1:4 a longer heating period (25 minutes) was needed to solubilize the DAPT.

EXAMPLE 4

Fabric treatment with MDAPT

The fabric used in the experiments was an 8.5 oz. white cotton sateen.

The stock solutions prepared as described above are stable for several days without any loss of efficiency when applied to cotton fabric. (A solution stored for 2 months at room temperature [27° C.] did not get, and when applied to cotton fabric had an efficiency 17–18% less than a freshly prepared solution.) The pH of the solutions shifts downward during storage. Therefore, it is necessary to adjust to the desired pH just prior to treating cotton fabrics. All of the pad baths used in this report contained 0.1% wetting agent and 1.5% softener (dry solids basis). The solution as prepared above, after addition of the wetting agent and softener, contained approximately 27% DAPT (or 40% MDAPT calculated as the tetramethylol derivatives). These values were based on the total weight of the solution. Just prior to fabric treatment, the solution was diluted to the desired concentration, and finally adjusted to the desired pH with aqueous sodium hydroxide solution.

In some of the experiments, magnesium chloride hexahydrate was used as a catalyst. The percent catalyst (as the hexahydrate) was based on the total weight of the solution as it was applied to the fabrics.

The solutions were applied to the fabrics by padding procedures to give a wet pickup of about 80% on sateen. The fabrics were dried for 5 minutes at 85° C. and cured for 3–7 minutes at temperatures ranging from 150° C.–170° C. The fabrics were finally rinsed in hot water and dried.

Table I shows the properties of white 8 oz. cotton sateen containing polymer add-ons of 14.7%, 17.6%, and 19.5%. These add-ons were obtained by using pad bath concentrations approximately 20%, 24%, and 27%, respectively, based on actual DAPT content. The ratio of DAPT to formaldehyde in the pad baths was 1:5. The fabrics were dried for 5 minutes at 85° C. and cured for 7 minutes at 160° C.

TABLE I.—PHYSICAL PROPERTIES OF COTTON SATEEN

Fabric properties	Untreated control	Resin add-on, percent		
		14.7	17.6	19.5
Phosphorus, percent		1.70	1.76	1.86
Nitrogen, percent		3.46	3.61	4.00
Char length, inches		3.1	3.4	3.1
Flex abrasion (F), cycles	1,134	1,595	2,215	2,264
Tear strength (F), gms	5,300	3,400	3,400	3,167
Breaking strength (F), lbs	105	84.4	89.2	82.5

The fabric samples shown in Table I were subjected to repeated laundering cycles followed by tumble drying. The flame resistance as measured by char length in the standard vertical flame test were as follows: at 14.7% add-on the char length was 5.3 inches after 15 launderings; at the 17.6% add-on the char length was 5.0 inches after 30 launderings; and at the 19.5% add-on the char length was 5.5 inches after 35 launderings.

EXAMPLE 5

Table II shows the influence of the mole ratio of DAPT: formaldehyde. The most efficient process according to percent add-on was that based on a mole ratio of DAPT: HCHO of 1:5.

The percent efficiency used in this example and subsequent examples was calculated according to the following equation:

$$\text{Percent efficiency} = \frac{\text{add-on (grams)}}{\text{wet pickup (grams) DAPT conc. (\%)}} \times 100$$

Add-on=weight gain of cotton after curing and rinsing
Wet pickup=weight of cotton+solution before drying
DAPT conc.=concentration of DAPT in pad bath

TABLE II.—INFLUENCE OF MOLE RATIO OF DAPT:HCHO

Mole ratio, DAPT:HCHO	Pad bath conc., percent DAPT	Resin add-on, percent	Efficiency, percent
1:4	20	10.8	73
1:5	20	14.0	93
1:6.5	15.4	10.3	91

NOTE.—Sateen fabric; dried 5 min. at 85° C., cured 7 min. at 160° C.

EXAMPLE 6

Table III shows the influence of curing time on the resin add-on and efficiency. They increase with increasing temperature.

TABLE III.—INFLUENCE OF CURING TEMPERATURE

Curing temp., ° C.	Resin add-on percent	Efficiency percent
150	7.8	52
160	12.4	81
170	12.9	86

EXAMPLE 7

Table IV shows the influence of curing time on some fabric properties. Highest add-on and flame resistance are obtained at the 7 minute cure time.

TABLE IV.—INFLUENCE OF CURING TIME

Curing time, min.	Resin add-on, percent	Efficiency, percent	Char length, warp	Flex abrasion (W), cycles	Flex abrasion (F), gms
3	7.7	51	[2] BEL	2,899	(1)
5	12.2	81	5.1	2,020	4,800
7	14.0	92	4.0	1,136	3,900
Control				833	5,300

[1] Over capacity of machine.
[2] BEL=burned entire length.

NOTE.—Sateen fabric; pad bath conc., 20% DAPT cure temp., 160° C.

EXAMPLE 8

Table V shows the influence of pad bath pH on some fabric properties. Although higher add-ons were obtained at pH values of 3.0 and 4.5 the strength losses were excessive. A pH of 6.6 was considered optimum for flame resistance versus strength and abrasion resistance.

TABLE V.—INFLUENCE ON PAD BATH pH

Pad bath pH	Resin add-on, percent	Abrasion resistance (W), cycles	Tearing strength (F), gms.
	Control	833	5,300
3.0	11.8	708	3,933
4.5	10.9	1,150	5,167
6.6	10.3	1,732	5,500
8.0	9.2	1,667	5,607

EXAMPLE 9

Table VI shows a comparison of fabric properties resulting from treatments in which no catalyst was used with those in which magnesium chloride was used. It is clear that the best strength and abrasion properties are obtained with no catalyst. The only advantage in using the catalyst is that slightly higher wrinkle recovery is obtained.

TABLE VI.—INFLUENCE OF CATALYST, $MgCl_2.6H_2O$

$MgCl_2.6H_2O$, percent	Resin add-on, percent	Efficiency, percent	Tear strength (F), gms.	Breaking strength (W), lbs.	Abrasion resistance (W), cycles	Wrinkle recovery (cond.-(W+F), degrees
0	[1] 14.5	94	3,400	84.4	1,136	238
2	10.8	70	2,833	68.1	601	254
3	10.9	72	2,500	65.0	478	249
4	11.7	76	2,317	60.9	347	257
4	[1] 14.1	94	1,617	48.2	138	258
	Control		5,300	105.0	833	173

[1] Cured 7 min. at 160° C.

NOTE.—Sateen fabric; pad bath conc., 20% DAPT; cured 5 min. at 150° C.

EXAMPLE 10

A typical procedure for preparing a formulation for application to cotton fabric using 2-amino-bis(diethoxyphosphinyl)triazine (ADPT) consisted of (1) refluxing ADPT in aqueous formaldehyde (mole ratio 1:2) for 30 minutes, (2) adding a softening agent and a wetting agent, and (3) adding trimethylolmelamine (TMM) (mole ratio of TMM:ADPT of 2:1) previously dissolved in water, and (4) diluting to 40% reactive solids (total weight ADPT, HCHO, and TMM). White 8 oz. cotton sateen was padded to approximately 80% wet pickup, dried for 5 minutes at 85° C., and cured for 7 minutes at 160° C. After rinsing and drying, the weight gain of the fabric was 20%. The fabric had good flame resistance as determined by a char length of 2.7 inches.

We claim:

1. A process for preparing 2,4-diamino-6-diethoxyphosphinyl-1,3,5-triazine which process comprises:
   (a) dissolving 2,4,6 - tris(diethoxyphosphinyl) - 1, 3,5-triazine in a solvent selected from the group consisting of ethyl alcohol and benzene,
   (b) cooling the solution from (a) and saturating with ammonia gas,
   (c) allowing the reaction mixture from (b) to stand for a period of about 24 to 72 hours at a temperature of not more than 75° C.,
   (d) mechanically removing the 2,4 - diaminoethoxyphosphinyl-1,3,5-triazine.

2. A process for preparing 2,4-diamino-6-diethoxyphosphinyl-1,3,5-triazine which process comprises:
   (a) dissolving 2 - amino - 4,6 - bis(diethoxyphosphinyl)1,3,5-triazine in ethanol,
   (b) cooling the solution from (a) and saturating with ammonium gas,
   (c) allowing the reaction mixture from (b) to stand for a period of about 24 to 72 hours at a temperature of not more than 15° C.,
   (d) mechanically removing the 2,4 - diaminoethoxyphosphinyl-1,3,5-triazine.

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