This invention relates to the imparting of flame-resistance to cellulose and protein fibrous materials, especially textiles, such, for example, as dress goods, duck, tarpaulins, draperies, and the like, in which the original hand and feel of the fabric is substantially retained and in the production of which no objectionable sacrifice of strength of the fabric results. The finish for optimum results should have long life and should be resistant to water, repeated washing, soapings, and dry-cleaning and while it will burn on the application of a flame, the fire should go out on withdrawal of the flame, and there should be no undesirable afterglow.

This application is a continuation in part of our copending application Serial No. 514,622, filed December 18, 1943; now abandoned, and of our copending application Serial No. 539,798, filed June 10, 1944.

As set forth in said applications, we have discovered that a finish having the above characteristics can be obtained by treating the material with a strong acid, such as ortho-phosphoric acid, and with a soluble organic nitrogen containing base, for example, urea, as will be further described. We are aware that ortho-phosphoric acid and various phosphates have heretofore been suggested as flameproofing substances for fabrics. It has also been suggested to react phosphoric acid and urea, dissolve the reaction product, impregnate, and dry. To the best of our information and belief, none of these has resulted in a commercially successful finish, the finish either being not permanent to water, soaping, or dry-cleaning, detrimentally destructive of hand and strength, or otherwise objectionable.

In the following description, reference will be specifically made to cellulose materials. However, we have found that when protein materials, such as wool or silk, are subjected to the same chemical and physical conditions, satisfactory durable flameproof properties are obtained without unduly affecting the hand and strength of the fabric.

By the treatments hereinafter described, a combination (i.e., a compound) with the cellulose is obtained by reason of which the finish is made resistant to water and repeated washings. We believe that during the curing an extensive esterification of the cellulose takes place, the acid combining with the cellulose and with the nitrogen base (or the products formed therefrom) to give a complex which is quite durable to subsequent leaching, soapings, washing and drycleaning treatments. Apparently the acid in combining with the cellulose carries with it into the complex, nitrogen containing groups from the base or compounds derived from the base during the processing.

That there is a combination of the cellulose, phosphoric acid and the base is proven by the fact that the fabric gives a definite quantitative test for both nitrogen and phosphorus after the finishing, which includes washing and drying, following the curing. Subsequent washings remove only negligible amounts of these elements so that after repeated washings satisfactory quantitative tests may be obtained for both nitrogen and phosphorus, proving that the durable flame-resistance properties are produced by the presence of the phosphorus and the nitrogen in the complex. Taking urea as an example of certain of the usable bases, it, among other functions, seems to act as a buffer which prevents a tendering effect by the phosphoric acid on the fabric, in consequence of which the original strength of the fabric is retained in large part. This is true also of other similar weak bases, if present in sufficient quantity.

When woolen fabrics or fabrics containing wool are given the treatment, a combination with the wool is obtained.

According to one mode of procedure, we may mix the acid and the base in the cold and add water. The resulting solution or mixture is applied to the fabric by padding or other conventional method, and the padded fabric is then dried, preferably on a tenter frame, and cured, the curing bringing about the combination with the cellulose hereinafter described and being controlled as to temperature and time, as will hereinafter be pointed out, to effect the combination and to assist in substantially maintaining the strength of the fabric. The fabric is finally washed in warm water and dried.

According to another method, the mixture of the acid and base is heated to say about 190° F., cooled, the water added, and the solution or mixture applied as before. In this manner ammonia and complex nitrogen compounds are usually formed from the base and the solution or mixture is more nearly neutral at the time of application to the fabric which tends to obviate an attack on the equipment. Higher temperatures and longer time of heating may be used, thus obtaining solutions of a substantially neutral character.

In some cases the external heating is not necessary, the ingredients reacting spontaneously in the solution, so at times the cooling is necessary to control the reaction. At other times the mixture
may be heated for a short time, when exothermic reactions set in, necessitating cooling of the mixture in order to control the reaction. In these cases the heating has usually resulted, as will be further described, in the alteration to some extent of the original nitrogen compound or compounds into new and generally more complex compounds. Ammonia is often liberated in these reactions. Another method is to melt together the acid and the base, cool, add water, and proceed as above indicated.

Although the solution is generally applied to the fabrics at room temperatures, it may be applied at somewhat higher temperatures if so desired. At higher temperatures greater solubility of the ingredients is generally obtained. This is very beneficial, and in some cases the solution may be applied at nearly the boil, providing that no detrimental action takes place, as will be further shown.

During the drying, which is of conventional character, the water is to be very largely removed from the material, and for this purpose we have found, merely by way of illustration, that passing the fabric through a drying atmosphere of 300°F. is sufficient. The cloth remains in the dryer about 30 seconds, but only comes to 300°F. for about several seconds.

The curing temperature should be carefully controlled. It must be high enough to cure, i.e., to bring about the chemical combination, within a practical time limit, but should be so high that undesirable alterations of the cellulose and a corresponding loss of fabric strength occur. The time of curing is closely related to the temperature as can easily be understood, the higher the temperature the shorter the time and the lower the temperature the longer the time.

As will further appear, there must be sufficient acid and urea (or other usable base) on the material to ensure the presence in the complex of the finished material (i.e., the cured material after it has been washed for, say, 10 minutes in water at 180°F. and dried) of sufficient of the base element of the acid and of nitrogen to give the desired results. The amounts on the material and the time and temperature have an important relationship. By way of illustration, we have observed the following when a piece of cotton fabric is padded with a solution containing 130 grams orthophosphoric acid (75%), 180 grams urea and 340 grams water (a molecular ratio of 1 phosphoric acid to 3 urea, and 15% phosphoric acid in the solution), given an ordinary squeegee (giving approximately 100% solution pick up by weight) and dried: (a) when cured at 250°F. for 120 minutes, the fabric has good flame-resistance after a 10 to 20 minute washing in water at 180°F. but only fair resistance. If given a soaking for 15 minutes in 4% Igepon T (a substituted amide of olefinic acid—CH3CONMeCH2CONH2SO3Na) at 180°F., 100 parts Igepon T solution to 1 part cloth by weight; (b) when cured at 260°F. for 120 minutes, the flame-resistance is excellent after such a water wash, and is still good after such soaking; (c) when cured at 270°F. for 120 minutes, the flame-resistance is excellent after such a washing or such a soaking; (d) when cured at 270°F. for 60 minutes, the flame-resistance is excellent after such a washing or such a soaking; (e) when cured at 280°F. for 30 minutes, the flame-resistance is excellent after such a washing or soaking; (f) when cured at 340°F. for 10 minutes, the flame-resistance is excellent after the washing or after the soaping; (g) when cured at 340°F. for 1 minute, the flame-resistance is excellent after such a washing, but is not as good after such a soaping.

If, now, the acid in the solution is reduced, say to 6.9%, with the same solution pick up on the fabric, no results are obtained, whereas if the fabric is cured at 340°F. for 5 minutes, good results are obtained even after washing or soaping.

Within the range of curing temperatures mentioned, we have found that best results for most commercial purposes are secured in the range between 320°F. and 360°F. Curing times will vary, at these temperatures, from 15 minutes to 3 minutes.

The reaction on the cellulose takes place effectively on the acid side (lower pH), rather than on the basic side (higher pH), the pH being determined in this case by means of indicator solutions on the cured fabric. We have found that between the pH values of 2 to 7 on the cured cloth (before washing) satisfactory results may be obtained. The preferred range of pH on the cloth fabric is from about 3 to 6. The durability of the finish will vary somewhat but, as indicated, a pH from 3 to 6 gives satisfactory all-around results.

The pH of the solution prior to the application is otherwise not very important as it can usually be adjusted, if necessary, by the addition of bases which will volatilize during the curing, leaving the pH on the cellulose of such an acid value that the reactions of the process will take place during the curing as described above. Among the volatile bases suitable for the adjustment of the solution pH we may mention ammonium hydroxide, diethyle amine, and isopropyl amine. For all practical purposes, ammonium hydroxide is satisfactory. In any case, the quantity of base added to adjust the pH of the solution is very small, the solution itself being usually of a satisfactory pH value. Of course, if pH is too high, flame resistance imparting acid may be added to adjust the pH of the solution. Generally, all that is required is that the pH of the solution, and that it should be such that, during the curing, the pH in the cloth will be brought down to the values previously mentioned. Usually, a pH for the solution approximately ½ pH higher than that of the cured cloth is satisfactory. One may go higher, provided that the pH comes down during the curing so as to produce the pH of the cured cloth above set forth.

The pH value of the cloth during curing determines to some extent the rate and degree of reaction between the acid and the cellulose. The lower the pH, the faster and more complete is the reaction, and the higher the pH, the slower and less complete is the reaction for a given time and temperature of curing. Also, at a given pH the completeness or extent of reaction may be increased by increasing the time of curing, the temperature of curing, or both. For example, at a pH of 3.5, a curing time of 4 minutes and a temperature of 330°F. may be necessary to obtain a given degree of durability, while at a pH of 5.5 a curing time of 5 minutes and a temperature of 330°F. may be needed to obtain the same degree of durability.

On fabrics, in addition to the padding described, the solution may be applied by any of the methods well known in the textile art, such as spraying, jiggling, printing, coating, and the like. Irrespective of the method of application employed, the...
cloth is dried as described to largely remove the water.

The concentration of the solution itself is not critical and depends upon the number of applications, but the ultimate take-on on the finished fabric is important. For example, where the solution is to be applied by one run of the fabric therethrough, a solution of from about 30% to 70% active solids will suffice, depending upon the weight, absorptivity and purity of the fabric, the squeeze after impregnation, and the like. This, with a substantially 100% solution pick up, will give an ultimate “take-on” (chemical take-on by combination) in the finished fabric of from about 8% to about 30% solids, which is a take-on which we have found to give satisfactory general all around results. A lower take-on may be had, providing only fair flame-resistance is desired. A take-on higher than 30% offers no substantial advantage. The ultimate take-on drops to these figures owing to the fact that there is some loss during the curing, and a further loss in the washing (which removes soluble excess chemicals). If it be desired to make a number of separate impregnations and dryings, a dilute solution may be employed, the number of runs being dependent upon such dilution. For example, with 20% to 30% solids solution, the desired results may be obtained in two runs, and at most three, usually. The ultimate take-on of basic element of the acid and of nitrogen in the finished (i.e. cured and washed and dried) material is important, as will further appear.

As to the acids, orthophosphoric acid (H₃PO₄) is most satisfactory. However, any strong acid which will not impart flammability to the fabric may be employed, such as, for example, as pyrophosphoric, orthophosphorous, pyrophosphorous, sulphuric, and phytic acids, may be employed as hereinafter indicated.

Acids which are excessively volatile under the conditions of the process, or acids which create conditions or produce chemicals having an excessive degrading action on the cellulose, such as active oxygen or active halogens, are not recommended. Thus hydrochloric acid is not useful and nitric acid is not recommended, although the latter may be used in conjunction with other acids such as orthophosphoric acid as will be further shown.

Monobasic acids give the least satisfactory results, and the dibasic acids, while better, are not as desirable as the polybasic acids, as will further appear. The so-called polyacids containing excess atoms of the acid element are satisfactory, especially if they have a polybasic character. Many of these acids are known, especially of the phosphorous type.

Salts of the acids may be used, providing the base making up the salt is either volatile during the conditions of the processing, or takes an active part in the process. Among the former we mention ammonium phosphate, dimethyl amine phosphate, and isopropyl amine phosphate; among the latter, guanidine phosphate, guanly urea phosphate, and urea phosphate.

Substitution products of the acids may be used, providing the substitute groups do not destroy the flameproofing properties. Examples are sulphuric, phosphoric and di-nitro phosphoric acid. Other acids of complex nature containing nitrogen and phosphorus may be used, providing they are strong enough to combine with the fibers in question. Most of these acids, however, are not commercially avail-

able. The so-called organic esters may be used, provided they do not contain excessive carbon and do not prevent the acid group from forming the required combination with the cellulose. For example, mono-methyl phosphoric acid may be used. Halogen substituted acids are not recommended, except fluorophosphoric acid, because of the instability of the halogen groups in solution and on the fabric.

As to the organic bases, which are desirable always present in excess, these may be weak or strong. However, when comparing the acid used in the process with the nitrogen bases the weak all have a decided basic character, the distinguishing between weak and strong being based upon their behavior in the solution and on curing. For example, if a substantial change in concentration of the base causes no appreciable change in the solution pH or the cured cloth pH, then the base is classified as weak. If, however, the same change is made and a decided change in pH is obtained then the base is classified as a strong base. For example excess urea may be added to a fixed solution without appreciably altering the pH; on the other hand, if guanidine is added to a finished solution the pH will be substantially increased, and if sufficient quantity is added the solution may become so decidedly basic that unsatisfactory results will be obtained. In other words, with the strong bases, any excess must be such as will not put the cured cloth (before washing) definitely on the basic side.

For weak bases we may, for example, use urea, biuret, cyanuric acid, semicarbazide, dicyandiamide, acetamide, formamide and leucine. In some cases, where the solubility of the weak base is not high even in hot solutions, it becomes undesirable to use said base alone, but it can be effectively used in conjunction with another base or bases. For example, melamine is not sufficiently soluble with phosphoric acid to produce a good working solution. It may, however, for example, in conjunction with urea, serve to produce a good working solution.

Salts of these bases with a flame-resistant acid may be used in part, such as, for example, the sulfates, phosphates, and nitrates, in which cases the acid introduced by the base replaces a corresponding quantity of acid in the solution formula.

Substitution products of the weak bases may be used such as those containing the amino, hydroxy, halogen or organic groups, provided the essential characteristics of the compounds which render them useful in the process are not destroyed. Thus amino and hydroxy groups may increase the basic character of the base to such an extent that the weak base becomes a strong base and must be used accordingly. For example urea is a weak base but imino-urea (guanidine) is a strong base. The halogens tend to create a complex having halogen in its constitution and this is not particularly desirable due to the instability of halogen compounds. Organic groupings containing carbon may be used but these tend to reduce the flame-resistance of the fabric. A compound like methyl urea may be used instead of urea, but little is gained.

Strong bases may be employed, but since the strong bases are likely to throw the solution over on the alkaline side if used in sufficient excess, they should be used in conjunction with weak base or bases. Moreover, the weak bases provide a buffering action with respect to the acid and
the cellulose which is not so noticeably the case with the strong bases; and since a decided buffering action is desired in order to obtain reaction control and prevent undue tending, for this reason also, the strong base should preferably be used only in conjunction with a weak base. Apparently what happens is that the combination of the weak base with the acid is replaced during the curing, thus giving a buffering or reaction control. The amount of strong base should be insufficient to satisfy all of the acidity of the acid during curing. The use of strong bases in conjunction with weak bases results in greater strength in the ultimate fabric. The mixture of the weak bases with a strong base containing considerable nitrogen, besides affording a control over the pH and giving a buffering action, also supplies plenty of nitrogen as will be further explained to enter into the phosphorus-nitrogen-cellulose complex, thus enhancing durability. Among the strong bases which may be utilized, we here mention guanidine, carbodrazine, dihydroxyguanidine, guany lurea, oxalamidine, and biguanide.

Substitution of the strong bases may be used, providing these compounds have satisfactory solubility in the solution and are reasonably stable after being applied to the fabric. Such substitution compounds are the amino, hydroxy, halogen, and organic-radical substitution products. The latter type of compound should not contain groupings with excess carbon chains as this is detrimental to the flame-resistance.

Salts of the strong bases with volatile, decomposable, or weak acids may be employed, such, for example, as guanidine carbonate, amino guanidine acetate, the maleate, and biguanide borate. The guanidine carbonate is especially useful and has been extensively used in large scale production.

Salts of the strong base and the flameproofing acid may also be employed such as, for example, guanidine carbonate, guanyl-urea sulfate, and carbodrazine pyrophosphate. In these cases the acid part of the salt replaces part of the acid in the solution formula.

The general requirement of the base, whether volatile or strong, or mixtures thereof, are that it should be soluble in water, react with the acid so as to thereby introduce nitrogen into the phosphorus cellulose complex, should preferably be higher in nitrogen than in carbon, and, in the case where a strong base or bases is or are employed, there should be also present a weak base generally in excess for ease of reaction control by providing the desired buffering action between the acid and the cellulose. The weak bases afford a buffering action by reason of the fact that they apparently compete with the cellulose for the acid. The reason for having a base high in nitrogen and low in carbon is that the more carbon there is present, the less is the resultant flameproofness. For this reason, substituted ureas and other nitrogen compounds having relatively large amounts of carbon are not beneficial, where optimum results are desired.

In general our purpose is to introduce as much nitrogen and as little carbon as possible into the acid-cellulose complex. This nitrogen should be as firmly bound as possible and should not be appreciably removed when the fabric is subjected to leaching and soaping treatments. It does not matter whether this excess nitrogen is introduced by a weak base or by a strong base, however it has been found that to obtain a complex

weak base nitrogen compound having a high solubility, the reaction mixture is almost impossible. To obtain sufficient solubility it is beneficial to work with the lower molecular weight nitrogen compounds such as urea, acetamide or formamide.

In case of the strong bases which are never used separately as above described, the extent of solubility does not become so material a factor as they are not used in relatively large quantities, and quite a few compounds having a high nitrogen content and low carbon content are available.

Analysis has shown that with a nitrogen rich strong base more nitrogen becomes a part of the complex. For example, if urea and phosphoric acid are used the atomic ratio of nitrogen to phosphorus on the finished cloth may be 1 nitrogen to 1 phosphorus while if a mixture of urea, guanidine and phosphoric acid is used, the ratio is 3 nitrogen to 1 phosphorus, showing a substantial increase in nitrogen due to the guanidine. During the heating of the solution or during the curing of the fabric many changes take place in the nitrogen bases and, in general, the resulting complex contains a nitrogen compounds. It is therefore not possible to give the exact composition of the complex formed. For example, dicyandiamide with mono or di-ammonium phosphate forms a substantial quantity of guanidine phosphate when heated; dicyandiamide with phosphoric acid forms a substantial quantity of guanyl urea phosphate, also when dicyandiamide and guanidine are heated together cyanoan, biguanide and melamine may be formed.

This formation of the more complex nitrogen compounds aids in obtaining good flame-resistance and also increases the durability to water since the compounds so formed tend to increase the stability of the complex.

Insofar as the solution is concerned, it should be preferably, to secure flameproofing and more even action on the material to be flameproofed. In the case of phosphoric acid, the amount of acid should be such that the phosphorus remaining in the flame-resistant fabric after the final washing and drying should preferably range from 1.2% to 2.75%. Below this percentage, mediocre flameproof properties are usually obtained and above this percentage little is gained.

Again referring to ultimate take-on and using or phosphoric acid for illustration, the percentage of phosphorus necessary to impart flame-resistance to a given fabric is also dependent upon the quantity of nitrogen present. For example, if the nitrogen content in the finished fabric is 2%, the phosphorus necessary to secure effective flame-resistance is approximately 2.85%: while if the nitrogen present is 3%, the phosphorus may drop to as low as 2.20% while still obtaining satisfactory flame-resistance. If the nitrogen content drops to a very low figure, say a small fraction of 1%, flame-resistance will be poor, even if a high percentage of phosphorus is present. The preferred range of nitrogen content is from about .25% to about 6%, and the preferred phosphorus limits are about 1% to 5%. Enough of the acid and the base must be present on the cloth at the curing to ensure this ultimate chemical take-up. Below the .25% nitrogen, the influence of the element becomes negligible and above 6% nitrogen, although excellent flame-resistance is obtained,
nothing seems to be especially gained. Below 0.5% phosphorus an excessively large amount of nitrogen and phosphorus required to produce a satisfactory end product. For example, if a halogen such as chlorine is introduced as a part of the flame-resistant complex, the other ingredients may be reduced. As before pointed out, however, the introduction of a halogen is not particularly desirable because of instability in sunlight, heat, and moisture, which liberates halogen acids. After-glow resistance, however, may be obtained with the phosphorus as low as 0.1%.

Since wool and silk contain nitrogen, sulphur and phosphorus in their natural chemical make-up, the above figures are to be understood as being in addition to these naturally occurring elements.

The cellulosic materials processed by this method, in addition to the flame-resistant characteristics, are also decidedly resistant to mildew, which adds a valuable property to the end product. This is not the case with protein fabrics.

Cellulosic materials treated by the process may be subject to swelling when immersed for a length of time in water. In certain cases this property is a valuable asset, but if not desired it may be compensated for by employing an aldehyde as fully described in our copending application Serial No. 539,798, and this swelling characteristic may also be reduced by altering the hydrophobic character of the finished product by aftertreatment with formaldehyde or waterproofing agents. It is not desirable to process protein fibers with the aldehyde.

This process may be applied to fibrous materials having previously been given other treatments such, for example, as bleaching, mercerization, pamphletization, dyeing, printing and sizing, prime dyeing or any other treatment is such as does not interfere with the flame-resistance. Further processing such, as for example, sizing, waterproofing, coating, and mechanical finishing may also be done after applying the flame-resistant finish provided such treatments do not destroy the flame-resistance. Such additional processing forms no part of the present invention.

Since no resin, plastic, plasticizer, or solvent soluble material need be used in producing this finish, excellent durability to drycleaning solutions is obtained.

In all the examples herein given, the finished fabrics were considered as having very satisfactory durable flame-resistance if samples of the treated fabric, after being subjected to the following series of tests, upon being held vertically in a flame for 10 seconds, did not thereafter continue to burn:

(a) After 24 hours leaching in distilled water.
(b) After ½ hour boil in distilled water.
(c) After 15 minutes soaking in a ¼% solution of Igepon T (a substituted amide of oleic acid—C₁₇H₃₃CONMeCH₂CH₂SO₃Na) at 180° F., 100-1, followed by two rinses in hot water.

Example 1

A water mixture containing 49.6% urea and 18.4% orthophosphoric acid (100%) by weight or in the ratio of 2.7 parts of urea to 1 part of phosphoric acid, was padded on the fabric, the fabric (herringbone twill) was flame dried at 300° F. for about 30 seconds as described, and the dried fabric was oven cured at a temperature of 345° F. for 2 minutes. The finish produced had the characteristics above set forth. Any appreciably longer curing, while increasing durability, would result in reduced tensile strength.

Example 2

The same mixture was padded on the fabric, the fabric dried as described, and then cured at 300° F. for 15 minutes. The curing temperature being lower, a longer time was required for the cure and to duplicate the results. The same finish was obtained. By duplication of results is meant the obtaining of a finish withstandng the same tests. With all usable bases, weak or strong, this holds true.

Example 3

The same mixture was padded on, the fabric dried as described, and the dried fabric cured at 280° F. for 23 minutes, the time required for curing and duplication of results being thus again longer with the lower temperature. The desired finish was obtained.

The curing temperature of 280° F. of the above example is quite close to the lower temperature limit possible for successful commercial operation within reasonable times. At the sacrifice of time, up to about 45 minutes or a little longer, the temperature may be dropped a little below 280° F. As before indicated, however, lower temperatures may be used with longer curing times. Thus with a temperature of 250° F. and a time of 120 minutes, good results may be obtained providing adequate concentration is employed. A temperature of substantially 250° F. seems to be about the low practical limit with conventional apparatus. This is true with all the bases usable in the process.

Save as before indicated, the ratio of the weak bases such as urea to phosphoric acid is not critical as will be seen from the following examples.

Example 4

A water mixture containing 66.4% urea and 16.6% orthophosphoric acid (100%) by weight or in the ratio of 4 parts of urea to 1 part of phosphoric acid was padded on the fabric, the fabric dried at 300° F. for about 30 seconds as described, and the dried fabric cured at 300° F. for 20 minutes. Comparing this with Example 2, it will be seen that the increased amount of urea, at a curing temperature of 300° F., requires a longer time to effect a cure and duplication of results.

The resultant finish had the characteristics above described.

Example 5

A water mixture containing 20% urea and 20% orthophosphoric acid (100%) by weight or in the
ratio of 1 part of urea to 1 part of phosphoric acid was padded, dried as described, and cured at 300° F, the time required for curing being 12 minutes. Comparing this with Example 2, it will be seen that with the smaller amount of urea, and keeping the concentration of the phosphoric acid substantially the same, the curing time is diminished in duplicating the results.

The resultant finish had the characteristics above described. It will be seen from the foregoing that as the temperature of curing goes down, the length of time required for the cure increases. It will also be seen that the higher the ratio and, therefore, the greater the protective influence of the urea, the longer will be the time of curing without producing detrimental results on strength. The lower the ratio of urea to phosphoric acid and the less the protective influence of the urea, the shorter should be the time for the cure. From a practical standpoint a ratio of 4 to 1 by weight of the urea to the phosphoric acid is about the highest possible without involving objectionable wastage of urea. One may go higher, say as high as 10 to 1 when the loss becomes prohibitive. It is, of course, to be understood that in all of the examples given the cloth is washed after the cure and any unneeded urea is washed out, only that portion of the urea entering into the combination remaining in the fabric. We prefer to employ 2.7 parts of urea to 1 part phosphoric acid (a ratio of 4.4 mols to 1) but one may go somewhat lower or higher as above indicated.

This applies to all usable weak bases. With the strong bases, as pointed out, care must be exercised to ensure that the solution does not go definitely basic. The degree of permanency of the flame-proof finish depends among other factors upon the concentration of the phosphoric acid in the solution. As the following examples show, this concentration may be varied between wide limits, depending upon the permanency desired, provided sufficient urea or other weak base or bases are present to give the necessary protection and providing a sufficient amount of acid groupings and nitrogen are present in the complex as before pointed out. This is also true of other acids usable in the process.

**Example 6**

A water mixture containing 30% urea and 30% orthophosphoric acid (100%) by weight, or a ratio of 1 urea to 1 of phosphoric acid was padded, dried as described, and cured at 300° F, for 12 minutes.

**Example 7**

A water mixture containing 25% urea and 9.3% orthophosphoric acid (100%) by weight or a ratio of 2.7 parts of urea to 1 part of phosphoric acid was padded, dried as described, and cured at 345° F, for 2 minutes.

In both the above examples, 6 and 7, a satisfactory durable flameproof finish was obtained, but the permanent flameproof properties of the fabric obtained in Example 6 were slightly superior to those obtained in Example 7.

**Example 8**

A mixture containing 49.6% urea and 18.4% orthophosphoric acid (100%) by weight was applied to a cotton fabric followed by drying in a tenter frame. The dried cloth was cured 1 minute at 400° F, and finally washed in water and dried. The resultant finish had the characteristics above described.

**Example 9**

100 parts of urea and 50 parts orthophosphoric acid (75%) by weight were mixed and heated rapidly to 375° F. The resulting mixture was cooled, 75 parts of water was added, followed by the addition of 7 parts of ammonium hydroxide (82%) and 10 parts of formaldehyde (37%). In this end the following examples, all parts given are by weight.

The resulting solution was water clear and a cotton fabric (herringbone twill) was impregnated with the same by passing it through a regular textile impregnating mangle, the operation consisting in dipping the cloth into the solution followed by a squeeze to remove excess solution. Then followed drying on the regular tenter frame, the temperature being approximately 300° F. The cloth was allowed to remain in the frame long enough to remove substantially all the water by evaporation.

One section of the cotton fabric was cured at a temperature of 345° F. for a period of 2 minutes and 10 seconds. This was followed by washing in hot water and drying.

Another part of the same cloth was cured at 300° F. for a period of 13 minutes, this again being followed by the wash in hot water and drying.

The two samples were found to be substantially equal in flameproof qualities and the respective finishes were of substantially equal durability.

This example also illustrates one way in which the pH of the solution may be externally adjusted, e.g., through the use of the ammonium hydroxide. It also illustrates how resistance to swelling or standing in water may be imparted through the use of an aldehyde.

**Example 10**

A mixture containing 100 parts dicyandiamide, 200 parts phosphoric acid (75%), 100 parts of water, 15 parts of ammonium hydroxide (28%), and 25 parts formaldehyde (37%), was applied with the usual procedure described above. The curing was done at 330° F. for 5 minutes. The desired results were obtained.

This example illustrates the use of a different weak base, the external adjustment of the pH, and the use of an aldehyde for increasing resistance to swelling.

Still another illustration of the same character is the following:

**Example 11**

A mixture consisting of 200 parts bluet, 100 parts phosphoric acid (75%), 150 parts water, 25 parts ammonium hydroxide (28%) and 25 parts formaldehyde (37%) was used with the procedure above described. The curing was done at 345° F. for 5 minutes. The desired results were obtained.

As an example showing the use of an acid forming oxide, attention is directed to the following example:

**Example 12**

A mixture consisting of 300 parts of urea, 100 parts phosphorus pentoxide (P2O5), 200 parts of water, 100 parts of ammonium hydroxide (28%) and 50 parts formaldehyde (37%) was used in
accordance with the procedure described. The curing was done at 310° F. for 12 minutes. The desired results were obtained.

As examples showing the use of acids other than ortho-phosphoric acid, attention is directed to the following:

**Example 13**

A mixture comprising 180 parts urea, 60 parts sulphuric acid (conc.), 50 parts water, 15 parts ammonium hydroxide (38%) and 50 parts formaldehyde (37%) was used under the regular procedure. The curing was done at a temperature of 340° F. for 6 minutes. The desired results were obtained.

**Example 14**

A mixture comprising 100 parts of ortho-phosphorous acid, 100 parts of urea, 100 parts acetamide and 100 parts of water was applied to a cotton fabric, dried, cured 20 minutes at 290° F., washed and dried. (Here is also illustrated the use of a mixture of weak bases.) The desired results were obtained.

**Example 15**

A mixture was prepared consisting of 100 parts metaphosphoric acid, 200 parts urea and 100 parts of water, the method of application being the same as the preceding example. The curing was done at 340° F. for a period of 4 minutes. The desired results were obtained.

**Example 16**

A mixture of 300 parts of concentrated sulfuric acid and 900 parts of urea was heated 3 hours at 180° F. and then left standing 24 hours. Sufficient warm water was added to form a clear solution, and this applied to a cotton fabric with the regular procedure. A fabric was obtained having good flame-resistance.

**Example 17**

A solution was prepared by warming 180 parts calcium phytate, 120 parts oxalic acid, 250 parts urea and 250 parts formamide followed by addition of 500 parts of water. The precipitate containing primarily calcium oxalate was filtered off and the filtrate containing primarily phytic acid, urea and formamide was applied to a cotton fabric by impregnation followed by drying. The curing was done at 310° F. for 8 minutes, followed by washing in water and drying. The fabric had fair flame-resistance.

The following illustrate the use of mixed acids.

**Example 18**

A solution comprised of 200 parts urea, 50 parts of orthophosphoric acid (75%), 50 parts sulphuric acid (conc.), 100 parts of water, 15 parts of ammonium hydroxide (28%) and 50 parts formaldehyde (37%) was used under the regular procedure. Curing was done at 340° F. for a period of 5 minutes, and the desired results were obtained.

**Example 19**

A mixture was prepared consisting of 100 parts orthophosphoric acid (75%), 55 parts nitric acid (conc.), 200 parts urea and 100 parts of water, the method of application to a cotton fabric was as above described, the curing being done 20 minutes at 290° F. The desired results were obtained.

A mixture was prepared comprising 50 parts pyrophosphoric acid, 50 parts metaphosphoric acid, 200 parts acetamide and 180 parts of water, the method of application being as previously described with curing time of 5 minutes at 330° F. The desired results were obtained.

As further examples of mixed weak bases we cite the following:

**Example 21**

A solution comprising 75.0 parts dicyandiamide, 75.0 parts acetamide, 100 parts pyrophosphoric acid and 200 parts of water was used under the regular procedure. The curing was done at 320° F. for 5 minutes. The desired results were obtained.

**Example 22**

A mixture was prepared comprising 132 parts urea, 8 parts melamine, 66 parts diammonium phosphate and 150 parts water, and this applied to a cotton fabric in the usual manner, the curing being done at 335° F. for 3 minutes. The desired results were obtained.

**Example 23**

A mixture was prepared comprising 35 parts urea, 100 parts cyanoacetamide, 50 parts orthophosphoric acid (75%) and 165 parts water. This was applied to a cotton fabric and the desired results obtained, the curing being done at 315° F. for 5 minutes. Repeating this without the cyanoacetamide caused excessive tendering.

As illustrative of the use of salts of the base, attention is directed to the following:

**Example 24**

A mixture was prepared consisting of 160 parts of amino guanidine bicarbonate, 300 parts urea, 150 parts orthophosphoric acid (75%) and 500 parts water. The process was applied by the regular procedure, the curing being done at 350° F. for 4 minutes. The desired results were obtained.

**Example 25**

A mixture was prepared consisting of 61 parts semicarbazide hydrochloride, 48 parts guanidine carbonate, 45 parts cyanoacetamide, 55 parts urea, 50 parts orthophosphoric acid (75%) and 60 parts water, the regular method was used in the application, the curing time 4 minutes at 335° F. The desired results were obtained.

The following are additional examples of the use of the mixed bases wherein a strong base is employed for maximum retention of strength and a weak base or bases is or are employed to afford buffering action and control of the reaction.

**Example 26**

A solution comprising 100 parts urea, 100 parts amino guanidine carbonate, 100 parts orthophosphoric acid (75%), 100 parts water, 15 parts ammonium hydroxide (28%), 50 parts formaldehyde (37%) was used under the regular procedure. The curing was done at 340° F. for a period of 5 minutes, and the desired results were obtained.

**Example 27**

A mixture was prepared comprising 50 parts dicyandiamide, 113 parts urea, 10.5 parts guani-
dine carbonate, 75 parts orthophosphoric acid (75%), and 158 parts water. This was applied to a cotton fabric by the regular procedure, curing being done at 340° F. for 10 minutes. A very durable flame-resistant result was obtained.

**Example 28**

A mixture was prepared comprising 57 parts polypropylenephosphoric acid, 66 parts guanidine carbonate, 132 parts urea, and 255 parts water, and the mixture applied by the usual procedure, the curing being done at 330° F. for 5 minutes. Excellent flame-resistance and durability were obtained on a cotton fabric.

**Example 29**

A mixture was prepared comprising 40 parts guanyl urea sulfate, 81 parts urea, 53 parts orthophosphoric acid (75%), and 90 parts water, and the mixture applied to cotton in the usual manner, with curing at 320° F. for 5 minutes.

Very good flame-resistance was obtained.

**Example 30**

A mixture was prepared comprising 300 parts urea, 160 parts aminoquandine bicarbonate, 150 parts orthophosphoric acid (75%) and 500 parts water. This was applied to a cotton fabric by the usual procedure, and a very good flame-resistant fabric obtained. The curing was done at 340° F. for five minutes.

The following are examples of the use of a weak base to partly produce a strong base.

**Example 31**

65.0 parts of dicyandiamide, 100 parts orthophosphoric acid (75%) and 160 parts water were heated to 165° F. when a violent reaction took place and the temperature increased. Under these conditions a substantial quantity of guanylurea is formed. To this was added 150 parts urea and 110 parts water and the resultant solution applied to a cotton fabric followed by drying, curing at 340° F. for 5 minutes, washing, and drying.

Excellent durable flame-resistance was obtained.

**Example 32**

53.4 parts dicyandiamide, 168 parts diammonium hydrogen orthophosphate were heated in a covered container to 515° F. under which condition a substantial quantity of guanidine was formed, as guanidine phosphate. 34 parts of the above material was mixed with 150 parts of warm water and the resulting solution applied to a cotton fabric using the regular procedure. Good results were obtained.

The following examples illustrate the use of substitution products of the base.

**Example 33**

A mixture was prepared comprising 65 parts dicyandiamide, 100 parts orthophosphoric acid (75%), 100 parts urea, 20 parts phenyl biguanide, and 210 parts of water. This was applied by the regular procedure.

Good flame-resistant results were obtained.

**Example 34**

A mixture was prepared comprising 50 parts dicyandiamide, 120 parts methyl urea, 10 parts guanidine carbonate, 75 parts orthophosphoric acid (75%) and 200 parts water. The mixture was applied to a cotton fabric by the usual procedure, and a good flame-resistant finish obtained.

As an illustration of the use of substituted acids, attention is directed to the following:

**Example 35**

A mixture consisting of 200 parts urea, 100 parts sulphamic acid, 100 parts water, 15 parts ammonium hydroxide (38%) and 50 parts formaldehyde (37%) was used in accordance with the procedure described.

The desired results were obtained.

**Example 36**

A mixture comprising 150 parts urea, 100 parts ammonium hexaphosphatidinitride and 350 parts of water was applied to a cotton fabric, dried, cured at 320° F. for 7 minutes, washed, and dried.

Good durable flame-resistant results were obtained.

**Example 37**

A mixture was prepared by first heating together 1 hour at 180° F. 300 parts of sulphamic acid, 300 parts of urea and 100 parts of water. A thick syrup was formed and this was further diluted with 200 parts of water. A cotton fabric was impregnated, dried, cured, washed and dried as in previous examples.

The fabric had good resistance to flaming.

**Example 38**

140 parts phosphorous pentoxide and 130 parts ammonium carbonate were reacted to form dianidophosphoric acid, to this were added 300 parts urea, 125 parts guanidine carbonate and 650 parts water. This mixture was applied to a cotton fabric using the regular procedure.

Good results were obtained.

The above formulas have all been applied to cotton cellulose material. The following example illustrates the use of this process to wood pulp.

**Example 39**

Sheet wood pulp as used in the manufacture of viscose was steeped in a warm solution of 57 parts polypropylenephosphoric acid, 66 parts urea and 350 parts of water. It was then thoroughly squeezed, dried and cured at 340° F. for 5 minutes. The resulting pulp which had the appearance of ordinary pulp was extremely flame-resistant.

As an example of the application to rayon fabrics we refer to the following using highly combustible napped knitted rayon goods.

**Example 40**

A mixture was prepared comprising 33 parts dicyandiamide, 100 parts urea, 50 parts orthophosphoric acid (75%), 10 parts guanidine carbonate and 500 parts water, and this applied to the rayon fabric above described by the usual procedure, the curing being done at 340° F. for 6 minutes.

The resulting knitted goods had good flame-resistance.

In regard to the application of this finish to protein fabrics we call attention to the following:

**Example 41**

A mixture was prepared comprising 116 parts dicyandiamide, 289 parts urea, 162 parts guanidine carbonate, 289 parts urea, and 200 parts water. The mixture was applied to a cotton fabric by the usual procedure, and a good flame-resistant finish obtained.
orthophosphoric acid (75%) and 433 parts of water. This was applied to a 100% wool fabric, dried, cured 5 minutes at 340° F., washed and dried.

The resulting wool fabric had good flame-resistance.

**Example 42**

The last procedure was repeated, but in this case a 100% Tussa silk fabric was substituted for the wool.

The resulting silk fabric had good flame-resistance.

**Example 43**

A mixture was prepared comprising 33 parts dicyandiamide, 100 parts urea, 10 parts guanidine carbonate, 50 parts orthophosphoric acid (75%), and 400 parts water. This was applied to a fabric containing 75% spun rayon and 25% aralac using the regular procedure, the curing being done at 300° F. for 4 minutes.

A fabric of good flame-resistance was obtained.

As examples of the use of strong bases only, attention is directed to the following:

**Example 44**

A solution comprising 100 parts amino-guanidine carbonate, 50 parts phosphoric acid (75%), 90 parts water, 26 parts ammonium hydroxide (26%), and 25 parts formaldehyde (37%) was used under the regular procedure. The curing was done at 310° F. for a period of 12 minutes. A fabric of flame-resistant result was obtained.

**Example 45**

A mixture was prepared comprising 360 parts pyrophosphoric acid, 320 parts guanidine carbonate and 750 parts water. This was applied to a cotton fabric using the regular procedure, the curing being done at 340° F. for 5 minutes. The fabric had fair flame-resistance and a low degree of strength.

As examples of the use of free strong and weak bases, not in the form of salts, attention is directed to the following:

**Example 46**

A mixture was prepared comprising 50 parts dicyandiamide, 115 parts urea, 75 parts orthophosphoric acid and 175 parts of a water solution containing 5.1 part of guanidine. This was applied to a cotton fabric by the regular procedure. The time of curing was 5 minutes and the temperature 330° F.

Very durable flame-resistant results were obtained.

**Example 47**

A mixture was prepared comprising 55 parts urea, 53 parts orthophosphoric acid (75%) and 100 parts of a water solution containing 20 parts guanhydurs, and the mixture applied to cotton in the usual manner. The time of curing was 4 minutes and the temperature 330° F.

Very good flame-resistance was obtained.

We have also obtained good results on paper and wood with the process. Here, especially in the case of wood, pressure may be resorted to in applying the solution, or vacuum treatment to remove the air may be used, followed by the application of the solution under pressure, removing excess, drying, if desired, and curing.

Excellent results both with respect to durability and strength are obtained if the cellulose fibers made flame-resistant by this process with phosphoric acid contain one phosphoric acid group for every four pyranose units in the cellulose. That flame-resistance can be obtained with such a small combination is remarkable and due we believe to the fact that nearly all the ingredients of the complex on the fibrous material contribute to the reduction of the flammability. Thus the complexes producing the flame-resistance contain large quantities of nitrogen and phosphorus both of which upon burning create gases or volatile materials which tend to use up the oxygen and smother the flame. With decrease in the ratio of acid group to pyranose units, flame-resistance will correspondingly decrease.

Certain of the materials above given furnish unusual resistance to salt and strong soaping which render the finished product particularly useful for military uniforms which are subjected to extremely severe soaping and handling. In many of the examples given, the end product has a more pronounced capacity for ion exchange than in others, the anion active groups present in the complex having an affinity for cations, such as present in salt water, strong soap solutions, and hard water. By reason of this capacity for ion exchange, the flameproof characteristics, although substantially resistant to water, dry cleaning and ordinary washing, in time decrease somewhat in the presence of salt water and on strong soaps.

We believe that the reduction in flame-resistance caused by these metallic ions is due, first, to the replacement of valuable nitrogen by the metal and, second, to the fact that the addition of the metallic ion to the phosphate radical reduces the ready transformation of this group into oxides of phosphorus so valuable in flame protection.

The resistance to ion exchange and therefore, as described, improved durability to salt and soap solutions may be obtained at the expense of fabric strength by briefly extending the period of curing, say, for example, a cure of from about 5 to about 20 minutes, with a temperature of from about 300° F. to about 350° F., followed by washing in warm water and drying. We prefer to ordinarily retain about 80% to about 90% of tensile strength, although one may go lower (a 30% reduction in strength is about the maximum permissible) and thus obtain greater durability with the same solution and same type of fabric.

Ion exchange resistance may also, and preferably, be obtained with good or superior fabric strength by nitrogen groups which prevent or retard the addition of metallic ions. The ammonium groups, for example, are very easily replaced by a metallic ion while such groupings as guanyl urea, guanidine, biquanoid, melamine and so forth are less easily replaced. Therefore, formulas making use of these chemicals, in sufficient quantities, have superior resistance to ion exchange and a correspondingly higher durability to soaping and cleaning.

As previously described, some of these complex bases are formed during the reaction in the solution and on the cloth during curing. This is especially true where nitrogen containing salts of the acid are used, such as diammonium or mono-ammonium phosphate and hydrilamine phosphate, although changes take place in the presence of more complex nitrogen groupings even when the free phosphoric acid is used as a starting material.
The latter is due to some extent to the fact that whenever phosphoric acid is heated to a high temperature with nitrogen compounds, ammonia is liberated and this plays the part of the ammonia otherwise furnished by the dianmonium phosphate. The ease with which these complex compounds are formed is also to some extent dependent upon the original nitrogen compound used. For example, dicyandiamide is a very reactive compound under these conditions and will react with either phosphoric acid or the ammonium phosphate to form more complex compounds resulting in greater durability of the finish.

In the examples just given it is often desirable to heat the solution during its preparation in order to allow some of these changes to take place. For example, in a formula using dicyandiamide, phosphoric acid, urea and water, the dicyandiamide, acid and some water may be reacted together first at elevated temperatures followed by the addition of the urea and the remaining water to form the finished solution.

The ion exchange may be reduced to some extent by after treatments with materials such as the nitrogen compounds mentioned above, but little seems to be gained by this procedure.

Generally, in the process, the preferred range of curing temperature is from approximately 280°F. to approximately 400°F., and the time of curing from approximately 45 minutes to approximately 1/2 hour. For optimum results, we prefer a temperature of from 320°F. to 360°F. and a time of from 15 minutes to 3 minutes. This is in the conventional apparatus. Where the equipment is large enough and handles the material sufficiently rapidly for commercial purposes, the temperature may be lower and the time longer, as before set forth.

The drying and curing may be combined in one operation so long as the desired curing is obtained.

In the claims, “acid” is used in the sense of including only flame-resistance imparting strong acids capable of reacting with the cellulose and the nitrogen compound under the conditions of the process as previously described, and which, as such, are not excessively volatile nor produce chemicals during the processing which will detrimentally alter the character of the fibers, and the equivalents of such acids, as indicated in the specification. We use “base” to include only organic nitrogen-containing base material, weak, strong or amphoteric, which is at least to some extent water soluble, which, under the conditions of the process, will reduce the acidity and will buffer or moderate the reaction between the cellulose and the acid, and which will enter into the acid-cellulose complex giving nitrogen to the complex and in which the carbon is not so high as to detrimentally lower flame resistance, and the equivalents, as indicated in the specification.

Such material must be employed according to our invention. This, however, does not mean that one may not employ in conjunction therewith other base material or other ingredients, as an additive, so long as the same do not interfere with the desired reactions and end results.

Thus, for example, one may employ strong bases for the purposes of adjusting the pH, providing there is also employed the base material of our invention which will furnish nitrogen to the complex. Where a strong base is used for purposes of adjusting the pH, it should be employed in conjunction with weak bases. Among the strong bases which may be used for so adjusting pH, we mentioned diethylene triamine, triethanolamine, sodium hydroxide, sodium carbonate, and potassium hydroxide.

The term reference has been made primarily to flame-resistant finishes. As previously indicated, where flame-resistance, accompanied by mildew-resistance, is desired, there should be from 1% to 5% of the basic element of the acid (on the basis of using phosphoric acid) and from 25% to 6% nitrogen on the finished cloth. Where mildew-resistance is the primary objective, the percentage of basic element of the acid and of the nitrogen in the finished fabric may be substantially reduced, as small quantities will give results. In general, the acid groups give the mildew-resistance. However, some of the bases, such as phenol guanidine, for example, contribute to mildew-resistance. The acid should be buffered. Insofar as mildew-resistance is concerned, we have found, on the basis of phosphoric acid, 1 phosphoric acid group to 3 pyrazine units, gives very good results. As low as 1 to 16, gives appreciable improvement over the original cloth.

While in the flameproofing processes at present currently used, there is after-glow for an appreciable period of time, with fabrics flameproofed by our process, the after-glow disappears almost immediately on withdrawal of a test piece from the flame.

Referring now to the use of aldehydes, where it is desirable to reduce the swelling of the fabric on being subjected to continued moisture, and using formaldehyde and orthophosphoric acid by way of illustration, the general range for the formaldehyde is from about .2 mol to about 1.5 mols to 1 mol of orthophosphoric acid, the preferred range being .4 mol to 1.0 mol of formaldehyde to 1 mol of phosphoric acid. If the aldehyde is kept very close to the lower limit, care must be exercised in curing as less buffering action takes place. If excessive content of aldehyde is added there is too much buffering action and long curing is necessary.

As additional examples using the aldehydes, we give the following:

Example 48

A solution prepared in the identical manner described in Example 9 was made and consisted of 100 parts of urea, 50 parts of orthophosphoric acid (75%), 7 parts of ammonium hydroxide (28%), 50 parts of formaldehyde (37%) and 50 parts of water.

The solution was water-clear and cotton cloth (herringbone twill) was again impregnated as described in Example 9 and the cloth dried on the tenter frame as described.

One part of the cloth was cured at 345°F. for a period of 3 minutes and 40 seconds, followed by the usual wash in hot water and drying.

Another part of the cloth was cured at 300°F. for a period of 22 minutes, this again being followed by washing in hot water and drying.

The two samples were substantially equally flameproofed and the durability of the finish was likewise substantially the same.

The essential difference between the solutions of Examples 9 and 48 is that in Example 48, 50 parts of formaldehyde were used instead of 10 parts as in Example 9. The increase in the quantity of formaldehyde increases the time required for curing.
A solution was prepared as before, but consisted of 100 parts of urea, 50 parts of orthophosphoric acid (75%), 7 parts ammonium hydroxide (28%), 27 parts formaldehyde (37%) and 55 parts water.

The water-clear solution was applied to cotton fabric and the fabric dried in a tenter as described in the other examples.

The fabric was then cured at 250° F. for a period of 2 hours, followed by the usual washing and drying procedure. The resulting fabric was found to be flameproof and the flameproofing qualities and the durability of the finish were quite satisfactory.

This example again shows that with decrease in the curing temperature a longer period for the cure is required.

**Example 50**

The formula and method of procedure in this example was identical with that described in the previous example, but in this case the cotton cloth was cured at a temperature of 400° F. for a period of 30 seconds, followed by the usual washing and drying procedure.

The finish was both satisfactory and durable. We may use aldehydes other than formaldehyde. For example, a solution consisting of 200 parts of urea, 100 parts of phosphoric acid (75%), 114 parts water, and 15 parts ammonium hydroxide (28%) and 50 parts of glyoxal (30%) gives good results.

As further illustrative, we may use a halogen aldehyde instead of formaldehyde. A solution consisting of 200 parts urea, 100 parts phosphoric acid (75%), 114 parts water, 15 parts ammonium hydroxide (28%) and 75 parts chloral hydrate, gives good results.

We have also used mixtures of aldehydes. For example, a solution consisting of 200 parts urea, 100 parts orthophosphoric acid (75%), 100 parts water, 15 parts ammonium hydroxide (28%), 25 parts formaldehyde (37%) and 25 parts glyoxal (30%) gives good results.

Other aldehydes may be used, such as, for example, acetaldehyde, acrolein and aldel. The aldehyde should be of low molecular weight (a carbon chain of from 1 to 4), reactive with the nitrogen containing compound and desirable also with the cellulose under the conditions of the process.

We have discovered that fabrics treated according to the invention exhibit substantial resistance to creasing. Also the treated fabric has the characteristic of drying very rapidly. To illustrate, the same cloth in the untreated state, when wetted as, for example, by rain, requires a very much longer time to dry than the treated cloth which dries very rapidly. This drying characteristic is advantageous as, for example, in raincoats, towelimg, and bathing garments.

We claim:

1. In the art of producing a complex of acid and nitrogen with fibrous cellulose or protein materials or mixtures thereof to impart durable flame-resistance to such materials, the method of forming said complex which consists in impregnating the fibrous material with an aqueous solution of the reaction product of (1) at least one substantially water soluble inorganic acid compound selected from the class consisting of acids of phosphorus and sulfur which are free of metallic and of organic groups and constituents yielding active oxygen and halogen and which are substantially non-volatile under the conditions of the process, and metal-free salts of such acid compounds decomposable, and the anion of which is volatile, under the conditions of the process, to yield the acid, and (2) at least one non-metallic organic compound basic in the acid solution and soluble therein and which contains nitrogen and has an atomic ratio of carbon to nitrogen not substantially more than the ratio of carbon to nitrogen in acetaldehyde, the amount of acid and the amount of non-metallic nitrogen-containing organic constituent applied to the material being equivalent to that applied by impregnating the material with a solution containing from 6.9% to 30% orthophosphoric acid by weight and containing a non-metallic nitrogen-containing organic constituent at least in amount sufficient to introduce the amount of nitrogen into the complex hereinafter set forth, with a 100% solution pick-up by weight of the fibrous material in the dry state; drying the material; heating the dried material to a temperature ranging from 400° F. to 550° F. for a time ranging from 30 seconds to 120 minutes; and then washing and drying the so heated material, the process being further characterized in that the solution composition is such that the pH of the heated fibrous material before said washing has a value from pH 3 to pH 6, and in that the temperature and time selected in the above ranges and the amount of reaction product applied to the material and the amount of acid and nitrogen present in said reaction product are correlated to form with said material a complex containing an amount of the base element of the acid equivalent to from 1% to 5% phosphorus and to introduce into the said complex from 5% to 6% nitrogen, both by weight of the finally washed and dried material.

2. In the art of producing a complex of acid and nitrogen with cellulose or protein materials or mixtures thereof to impart durable flame-resistance to such materials, the method of forming said complex which consists in preparing a solution from the following ingredients in the proportions given, namely, 60 parts diethylamine, 113 parts urea, 10.3 parts guanidine carbonate, 75 parts orthophosphoric acid (75%) and 158 parts water; impregnating the material therewith with a solution pick-up of substantially 100% by weight of the material in the dry state; drying the material; heating the dried material at 340° F. for a period of 10 minutes; and washing and drying the material.

3. The process of claim 1 in which the temperature range is from 360° F. to 320° F. and the time range from 3 minutes to 15 minutes.

4. The process of claim 1 in which the acid is orthophosphoric.

5. The process of claim 1 in which the acid is sulfamic.

6. The process of claim 1 in which the salt diammonium hydrogen phosphate is employed as the acid substance.

7. The process of claim 1 in which the organic compound is urea.

8. The process of claim 1 in which the basic non-metallic nitrogen-containing organic constituent is a mixture of urea and guanidine.
9. The process of claim 1 in which the basic non-metallic nitrogen-containing organic constituent is a mixture of urea, dicyandiamide and guanidine.

10. The process of claim 1 in which the acid is orthophosphoric and the basic non-metallic nitrogen-containing organic constituent is a mixture of urea, dicyandiamide and guanidine.

11. The process of claim 1 in which the concentration of acid in the solution is equivalent to 6.9% orthophosphoric acid by weight at the temperature 340° F. and the time 5 minutes.

12. The process of claim 1 in which the concentration of acid in the solution is equivalent to 15% orthophosphoric acid by weight, the temperature 400° F., and the time 1 minute.

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WILLIAM P. HALL.

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Certificate of Correction

Patent No. 2,482,755

FLORENCE M. FORD ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 3, line 74, before the word "soaping" insert such a; column 6, line 36, for "isomamine" read melamine; column 7, lines 22 and 23, for "carbohydrazine" read carbohydrazidine; line 38, for "biguadide" read biguanide; column 12, line 12, for "end" read end; column 17, line 47, for "week" read week;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 31st day of January, A. D. 1950.

[Seal]

THOMAS F. MURPHY,

Assistant Commissioner of Patents.