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IMPROVEMENT OF THERMAL STABILITY  
OF TEXTILE FIBERS

FINAL REPORT, JULY 1, 1961 to JUNE 30, 1962  
INCLUDING QUARTERLY PROGRESS REPORT NO. 4  
April 1, 1962 to June 30, 1962

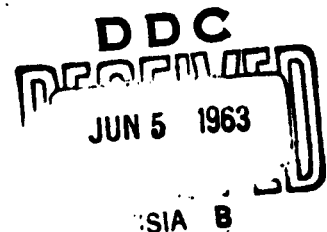
TO

U. S. NAVAL SUPPLY  
RESEARCH AND DEVELOPMENT FACILITY  
BUREAU OF SUPPLY AND ACCOUNTS  
DEPARTMENT OF THE NAVY

Contract No. N140(138)72225B

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POLYTECHNIC INSTITUTE  
OF BROOKLYN



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POLYTECHNIC INSTITUTE OF BROOKLYN

IMPROVEMENT OF THERMAL STABILITY OF TEXTILE FIBERS

Contract No. N140(138)72225B

Final Report, July 1, 1961 to June 30, 1962  
Including Quarterly Progress Report No. 4

April 1, 1962 to June 30, 1962

Introduction

a Background

The work under this contract represents a logical sequence to earlier investigations carried out under Contracts No. N140(132)57745B and No. N140(138)67904B which should be consulted for reference. In brief, valuable synthetic fibers, which suffer though from such disadvantages as poor thermal stability, ready melting, or easy flammability, were to be improved in these respects. Appreciable progress in the case of 6-6 nylon, and to some degree also for dacron, has been made with respect to melt proofing by graft-coating nylon filament or fabric with a thin layer of acrylonitrile. Without greatly impairing the textile properties of the original material, the acrylonitrile sheath apparently contains the melted nylon long enough to enable it to become self-crosslinking under the influence of heat and oxygen. Thus treated fabric becomes thereby effectively infusible, unless when in contact with very hot flames which do not allow sufficient time for crosslinking. The scientific and methodological background, conditions and

results are to be found in the named earlier reports.

In contrast to these encouraging findings, little progress was made with respect to flame proofing. Melt resistant material was effectively unchanged in its burning characteristics. A great number of attempts have led to no outstanding improvement, as also reported in the quoted sources. The main cause seems to be that polyacrylonitrile coating the nylon, is highly resistant to accepting sufficient amounts of flame proofing agents such as halogenated, phosphorous or boron compounds.

With this view in mind, means were looked for to either increase the receptivity of the polyacrylonitrile, or to replace it by another material more amenable to, or possibly being in itself, flame proofing. Good leads were obtained towards the end of the last contract and a suitably adjusted research program was submitted and accepted as the basis of the present investigation.

#### b Nature of the Present Study

The new leads consisted of an observation, a deduction, and a new method. The observation consisted in the fact that difunctional halogen-phosphorous compounds employed in imparting flame resistance were capable of crosslinking nylon by themselves. Thus, if the acrylonitrile were replaced by such phosphorous compounds, less additional flame proofing would be required to obtain improvement. Preliminary work was partly promising, partly showed up new difficulties in that too much

of a di-functional compound would embrittle the fibers, whereas the monofunctional halogen-phosphorous compounds appear to react and combine with the nylon only very slowly. Most of the work to date was spent in overcoming this vexing problem.

The deduction referred to the possibility of making the acrylonitrile sheathing more reactive by copolymerization. In fact, preliminary work showed that up to 50% of the AN could be replaced by vinylacetate without greatly damaging the melt proofing. The vinylacetate, when hydrolyzed to vinyl alcohol, would then be coupled with flame proofing agents by way of the reaction of the hydroxyl function. The second part of this report described our efforts in this direction.

The unexpected difficulties with these our two main approaches led to considerations whether a radical new departure may not be indicated. It was surmised that decisive progress could be made if the grafted coating polymer would itself contain a heavy percentage of chlorine and/or phosphorous atoms. The presence of these, as a rule, renders ordinary free radical grafting rather difficult and suggests the application of graft polycondensation methods instead.

As to our new approach, a fast and convenient method to prepare condensation polymers such as polyamides and polyesters has been developed lately in the form of interfacial polymerization. It consists in allowing the reactants, an acid dichloride and a diamine, etc., to combine at the interface

of two phases, an aqueous and an organic one. We had learned that an interesting application of this method had been tried for the crease proofing of wool and we thought that this procedure might be applicable to our problem if a suitable modification could be found. What had to be tried, basically, was to imbibe the nylon fabric with either an organic solution of acid chloride and react it then with aqueous amine, or vice versa, imbibe the nylon with an aqueous amine and react with the organic and chloride phase. The first variation seemed more promising and will be reported on.

#### Experimental and Results

##### a Halo-phosphorous Reactions

It was shown before that these reactions occurred readily in solution, while only limited yields (about 6-8% weight increase) had thus far been obtained for the heterogeneous reaction. An obvious extension of this phase of the work was to use a swelling agent in order to facilitate diffusion of the reactant into the polymer network and thus increase the reaction yield. A test of the swelling capacity at room temperature for some likely swelling<sup>compound</sup> was carried out and best results were obtained when dimethoxyethane was used (b.p. 83°C.) as solvent in conjunction with the halophosphorous compounds. Nylon cloth showed a weight increase of about 30-40% and exhibited improved initial burning retardation when in contact with flame but, when the flame was sustained, the fibers melt rapidly and eventually

( the cloth propagated the flame.

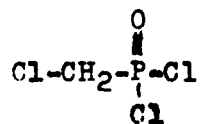
The halo-phosphorous compound reactions with nylon were studied in two basic reaction media, pyridine and high boiling ethers, in order to absorb the halogen acids formed in the reaction. It was found early that, when the nylon fibers were reacted with crosslinking difunctional chloro-phosphorous compounds, the mechanical properties of the fibers became seriously reduced in the range of phosphorous uptake where the phosphorous content becomes high enough to act as a flame retarding agent. It was hoped that the use of monofunctional phosphorous compounds would overcome this problem. Accordingly, the experimental work has been divided into three phases:

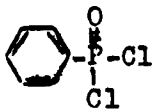
- 1) Crosslinking with difunctional dichloro-phosphorous compounds
- 2) Phosphorylating with monofunctional chloro-phosphorous compounds
- 3) Phosphorylating previously crosslinked fibers.

Although the reaction conditions are very similar for the crosslinking and phosphorylation reactions, no attempt was made to carry them out simultaneously.

Two chloro-phosphorous compounds capable of crosslinking nylon have been used. They are

a Chloromethyl phosphonic dichloride



b Phenylphosphonic Oxydichloride

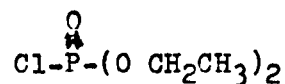
Typically, nylon cloth or fibers were reacted in 20 cc chloromethyl phosphonic dichloride and 70cc of one of the above reaction media. When the latter was pyridine, the reaction rate was greatest at the reflux temperature (115°C.). About 2 - 3% weight increase could be achieved in one hour and this was found to be the lower limit in order to obtain melt proofing of the fibers at temperatures of 300°C. or higher. The mechanical properties are still good with this weight increase and the samples are lightly yellow in color. The fibers do not swell during this reaction nor does there seem to be any unwanted side reactions.

A somewhat different behavior is noticed when the reaction medium is an ether. It became increasingly evident that here the reaction was accompanied by a swelling of the fibers even at the lowest temperatures at which the reactions still occurred. These fibers have a tacky feel and it was not possible to dry them in a heated vacuum oven during extended times, nor was it possible to remove the swelling by immersing the fibers in a variety of non-solvents. It was also noticed that some crimp of the fibers occurred while using dioxane as reaction medium. The fibers could be fully crimped by first reacting in diethylglycoldimethyl ether at low temperatures (~60°-65°C.)

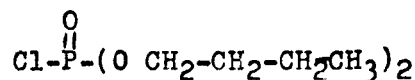
for about one hour and then immersing in refluxing pyridine. Only the case of diethylglycoldimethyl ether was it possible to react chloromethylphosphorous dichloride with the nylon fibers at low temperatures (about 60°C.) without any noticeable swelling. This reaction is slower than in refluxing pyridine and produces a crosslinked fiber that does not drip-melt or melt above 300°C.

Two monofunctional chloro-phosphorous compounds have been used extensively in order to increase the phosphorous content chemically bound to nylon:

Diethylphosphorous Chloride



Dibutyl phosphorous chloride



Both compounds are very similar in their reactions toward nylon whether reacted in pyridine or high boiling ethers. It was found that side reactions deplete the monofunctional phosphorous chloride rather rapidly. This resulted in a limited reaction with the nylon and the maximum weight increase that could be obtained was about 8%. The addition of swelling agents raised the weight increase to about 12-14%, which is still below the accepted value for flame retardation of 15% counted as phosphoric acid. Using reaction media similar to pyridine, such as

2.6 lutidine or dimethylaniline, showed the same disadvantages, even at temperatures below refluxing.

When the reaction medium was changed to ethers, it was again observed that the weight increase was mostly due to swelling. Since the ethers do not act as swelling agents alone, the observed swelling has to be associated with the phosphorylated nylon. In fact, it was found that these ethers are solvents for extensively phosphorylated nylon since the fibers dissolve at sufficiently high reaction temperatures (about 80°-90°C.).

Thirdly, fibers were crosslinked to different degrees in pyridine with chloromethyl phosphonic dichloride and the crosslinked fibers then reacted with monofunctional phosphorous compounds either in ethers or mixtures of ether and pyridine. It was found, contrary to expectations, that even rather severe crosslinking could not prevent subsequent swelling. With increasing amounts of pyridine in the reaction medium the swelling decreased but, on the other hand, side-reaction was enhanced.

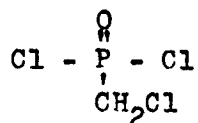
#### c Interfacial Polymerization

In our exploratory work on interfacial polymerization we were relying on the very rapid polycondensation which can be carried out by a fiber immersion process. Further, by first dipping nylon fibers in diacid chloride dissolved in an organic solvent such as methylene chloride, toluene, etc., there exists the probability of creating grafting sites by reacting with end groups or amide groups of the nylon. Thereafter, the fibers containing a controlled amount of diacid chloride were placed into a solution of diamine in water or ethylene glycol. A polymer

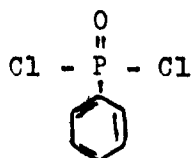
coating is formed at the nylon surface through the diffusion of the amine into the organic phase contained within the fibers.

Specifically, the following compounds have been selected for this study.

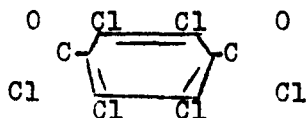
#### Diacid chlorides



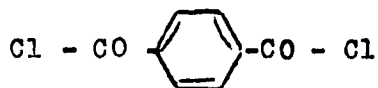
Chloromethyl phosphonic dichloride



Phenylphosphonic Oxydichloride

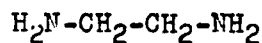


Tetrachloroterephthaloyl dichloride



Terephthaloyl dichloride

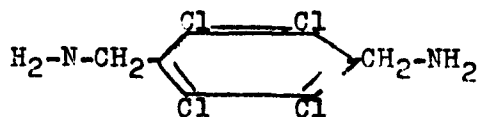
#### Diamines



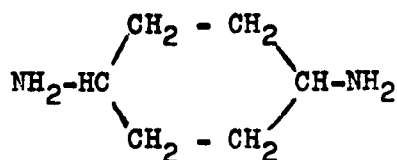
Ethylene diamine



p-phenyl diamine



Tetrachloro-p-xylene a a'-diamine



Piperazine and derivatives

In the case of chloromethyl phosphonic dichloride all attempts to carry out an interfacial polymerization failed. The reaction product was shown to be phosphonium salts with the diamine thus indicating that the above dichloride is too easily hydrolyzed by a rapid diffusion of water from the aqueous phase. Nor was it possible to obtain any polymers by saturating the aqueous phase with a salt (i.e. ammonium sulfate), or by dissolving the diamines in ethylene glycol, to reduce the osmotic mobility.

During the last quarter, work has been continued on the interfacial polymerization technique with emphasis on finding a combination of an acid dichloride and a diamine with good polymer forming (melt proofing) and, if possible, flame retarding properties. From the number of suitable compounds listed above, most combinations were found to be polymer forming. In the case of phenylphosphonic oxydichloride the polymer formation is rather slow, however, especially when condensed with ethylene diamine. Some additional difficulties were encountered with p-phenylene diamine in that it is easily oxidized in basic media. The basicity of the amine solution, on the other hand, is essential in order to neutralize the hydrochloric acid formed in the condensation process. From this and all the other preliminary

( information it was decided to study closely the interfacial polymerization of tetrachloroterephthaloyl dichloride and tetrachloro-p-xylene a-a'-diamine onto nylon alone or in conjunction with phenylphosphonic oxydichloride. By including the latter it was thought that the greater reactivity of this acid chloride would provide more grafting sites on the nylon while the other two compounds exhibited good polymer formation; in addition, their rich chlorine content should enhance flame retardation and crosslinking.

Tetrachloroterephthaloyl dichloride, which had been twice recrystallized from hot ethylacetate, was dissolved at room temperature in three different solvents, toluene, methylene chloride and tetrachloroethane, and diluted to 0.1-m solutions. Similarly 0.1-m solutions of phenylphosphonic oxydichloride were made up in methylene chloride and tetrachloromethane.

Tetrachloro-p-xylene a-a'-diamine being insoluble in water was dissolved in ethylene glycol to a 0.1-m solution under simultaneous stirring and heating to about 60°C. KOH was added to make the solution 0.2-m in alkali. The resulting solution was filtered and had a yellow color.

Initially, the interfacial polymerization on nylon was carried out by immersing cloth first in a diacid chloride solution and then into a diamine solution, but due to the diffuse nature of the reaction unsatisfactory weight increases were obtained by not being able to react over the entire fiber area of the cloth. Instead, nylon filaments were used to get optimum reactive sites

and better reproducibility. After the interfacial polymerization, the fibers were dried in an oven at 125°C., then washed vigorously in water for 4 minutes, dried again and washed again in toluene for 4 minutes to remove any monomer and ungrafted polymer. Finally, the fibers were dried to constant weight.

The experiments were designed to find the optimum conditions for maximum polymer deposition by interfacial polymerization by varying temperature, solvent and composition of the acid dichloride treatment, and the time dependence for the diamine reaction. An important factor not varied was the amount of acid dichloride solution adsorbed on the fibers before being immersed into diamine solution. To achieve such variation would require having the fibers to be taken from the acid dichloride solution through a system of rolls with a variable path length or through a calender. The method employed here was to allow for the fibers an interval of 10 seconds in vertical position before they were dipped into the diamine solution.

The choice of organic solvent was found to play a role in the weight increase on the fibers. Methylene chloride was found to be a more advantageous solvent than toluene which in turn was found better than tetrachloroethane.

In typical runs, immersing the fibers first in the organic acid dichloride solution for 60 seconds at room temperature and then in the diamine solution for 4 minutes, the following weight increases were noted:

| <u>Organic Solvent</u> | <u>% Weight Increase</u> |
|------------------------|--------------------------|
| Methylene chloride     | 8.4%                     |
| Toluene                | 7.0%                     |
| Tetrachloroethane      | 6.3%                     |

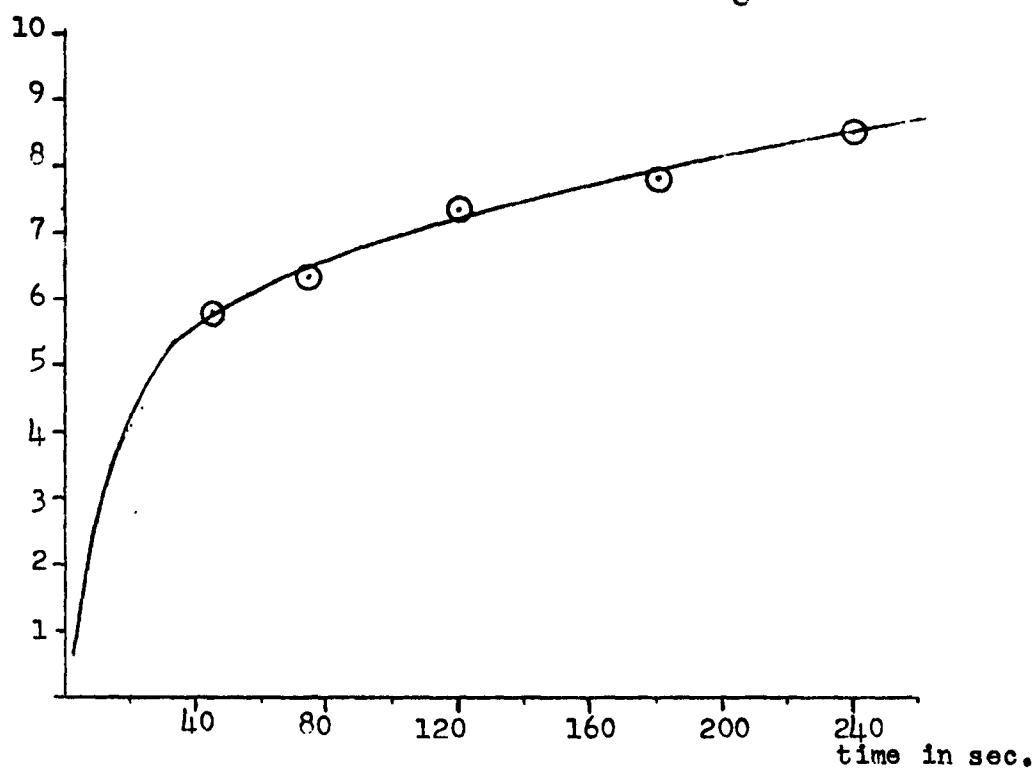
The addition of 20% phenylphosphonic oxydichloride solution did not influence these results. To establish a possible effect of the glass transition temperature, several runs were made by immersing fibers in diacid solution in tetrachloroethane, with or without 20% phenylphosphonic oxydichloride, for 60 seconds at 105°C. which would be above the glass transition of nylon. Before transferring the fibers into the diamine solution they were cooled for 15 seconds in an acid dichloride solution in methylene chloride. No significant weight increases were observed as opposed to room temperature experiments. The average increase using the same time scale as before was 8.7%. The phosphonic dichloride had little or no effect.

The dependence on the time allowed for the uptake of the diamine was checked after the cycle of the acid dichloride dip for 60 seconds in a tetrachloroethane solution at 105°C. and in methylene chloride for 15 seconds, by immersing the fibers in the amine solution for increasing periods. The results are shown in Fig. 1. It is seen that after an initial very rapid rise in weight within about 20 seconds, a slower increase, practically linear with time, begins which after 250 seconds begins to level off. It is tempting to conclude that we witness at first a mixing process which is followed by a slower diffusion.

\*

% uptake

Fig. 1



Percent weight increase of fibers immersed at various times in 0.1m tetrachloro-p-xylene a - a'-diamine solution after constant treatment in a 0.1m tetrachloroterephthaloyl dichloride solution.

By treating the fibers a second time after being washed and dried yields an increase about equal to the first weight pick-up, leading to about 14 - 16% total of total weight increase.

The melting behavior of these fibers is distinctly different from that of untreated nylon fibers. With a weight increase of about 8.5% the fibers melt partially at about 285°C. and there is a tendency to drip while burning. If the fibers were treated by two consecutive interfacial polymerizations with a weight increase of about 14%, the fibers do not melt up to 300°C. and show no tendency to drip. In no case, however, are the burning characteristics significantly retarded.

#### d Co-polymer Grafting and Flame Retardation

Earlier results had shown that up to 50% of the grafted acrylonitrile sheathing could be replaced by vinylacetate without damaging significantly the melt resistant properties of the treated fabric. This suggested the possibility of preparing grafted acrylonitrile coatings by copolymerizing with reactive monomers. The reactive sites thus obtained could then be chemically modified, grafted further, or reacted directly with flame retarding agents.

The initial studies led to the preparation of graft copolymers by coating nylon with polyacrylonitrile-polyvinylacetate copolymer. This was done by irradiating sensitized nylon fabric with U.V. light in a vapor feed consisting of a mixture of acrylonitrile and vinylacetate monomers. The resulting copolymers contained about 35% vinylacetate. The weight increases, based

upon the weight of the untreated fabric, were dependent on the irradiation times in the vapor mixture and were 5 and 8% for 20 and 60 minutes exposure, respectively. Both these weight increases with time and their reproducibility were poorer than for grafts of pure polyacrylonitrile on nylon. The samples containing the heavier grafts were melt resistant when subjected to a slow rate of heating.

In the presence of both, polyacrylonitrile and polyvinylacetate in the graft coatings was ascertained by using sensitized polyethylene film as a model material and irradiating under the same conditions as used for the nylon. The infrared spectra of the irradiated film showed the presence of both polymers. Contrary to expectations, these graft films on polyethylene were resistant to conditions under which pure polyvinyl acetate hydrolyzes to polyvinyl alcohol. Spectral evidence showed that an appreciable number of hydroxyl groups appeared only after treating the films under refluxing with 5% sodium methoxide for 14 hours. It was assumed that the nylon grafts would behave in a similar manner. However, on prolonged hydrolysis the nylon samples lost weight, even dropping to below that of the untreated samples. These results indicated that a more specific method of hydrolysis was needed.

In a new series of experiments samples containing the copolymer grafts were hydrolyzed for 6 hours. The hydrolyzed samples were then treated with tetrabromo-phthalic anhydride in anhydrous nitrobenzene, containing a trace of an acid as catalyst.

The samples were held at 100°C. for 7 hours and increases in weight of about 5% were obtained based on the weight of the untreated copolymer graft. The bromine content was about 4%. Additional treatment of the samples gave no further weight increases. These results were assumed to be due to the formation of polyvinyl tetrabromophthalic acid; no experiments were conducted to prove this point. The melting characteristics of the bromine containing samples were poorer than those of the anhydrolyzed material and the burning was not retarded when treated with the flame of a match.

To avoid undesired side reactions of nylon hydrolysis, attempts were made to graft vinylacetate homopolymer to nylon coated with polyacrylonitrile. The subsequent hydrolysis of the graft acetate homopolymer should proceed as the hydrolysis of pure polyvinylacetate.

Samples of nylon fabric grafted with polyacrylonitrile were resensitized and irradiated with U.V. light in presence of pure vinylacetate monomer vapor. No increase in weight of the sample was observed, indicating that no grafting occurred.

The situation was not improved when acrylonitrile monomer was added to vinylacetate monomer. Even so, vapor feeds high in vinylacetate monomer gave much less grafting per unit time than compositions containing the original 30% acetate monomer.

To overcome this impasse, solution methods of grafting to nylon surfaces were re-investigated. The nylon fabric was irradiated for 1/2 hour each side with wave lengths of light of

about 3300 Å in dimethylformamide acrylonitrile-dye solutions, or 20% aqueous acrylamide-dye solutions. The activating dye used was the sodium salt of anthraquinone-2,7-disulfonic acid and its concentration was  $10^{-3}M$ . After removing the homopolymer by boiling in the appropriate solvents, little grafted material was left and the melting characteristics of the treated and untreated nylon were almost the same.

Additional studies of grafting of chemically reactive copolymers of acrylonitrile to nylon were conducted employing acryloyl chloride,  $CH_2 = CH - \overset{O}{\underset{||}{C}} - Cl$ , as a reactive comonomer. While the acid chloride is difficult to use because of its moisture sensitivity it was hoped that some acid chloride sites could be preserved under anhydrous conditions and used as sites for a diamine phosphonium chloride graft.

Samples of sensitized nylon fabric and of polyethylene films were irradiated with U.V. light in the presence of a monomer vapor feed supplied by boiling a solution containing 6 parts of acrylonitrile and 20 parts of acryloyl chloride by volume. Cuprous chloride was used as inhibitor in the monomers. The samples showed weight increase of about 8 and 18% for irradiation times of 30 and 60 minutes, respectively. These results are not clear cut since appreciable homopolymer formed during the period of irradiation. The samples were placed quickly into a solution of 2,3,5,6-tetrachloro-p-xylene - a, a'-diamine, dried for a short time and then placed into an aqueous solution of tetrakis (hydroxymethyl) phosphonium chloride. The diamine-

tetrakis treatments were repeated a total of three times. The coatings were found not to be grafted but were physically held and did not reduce the burning of the material. Also, the melting characteristics of the treated material were not appreciably improved.

Additional experiments were conducted in which attempts were made to improve the flame resistant properties of previously crosslinked nylon fabric. The fabric had been crosslinked with  $\text{Cl}_2(\text{O})\text{PCH}_2\text{Cl}$ , using dioxane or pyridine as solvent, but dioxane caused considerable swelling of the nylon. Fire retarding agents were then imbedded within portions of the swelled crosslinked, matrix by greating with 10% phosphoric acid in methanol, or 18% HET acid-dioxane solutions. In all cases the textile properties of the treated materials were poor, and the burning resistance not greatly improved.

During the last quarter, the work with grafting and crosslinking continued. Earlier studies had shown that divinyl benzene coatings could contain molten nylon when tested at a slow rate of heating. Although the treated sample burned readily, heavy coatings of poly divinyl benzene did prevent the dripping of the material. Unfortunately, these heavy coatings resulted in very stiff materials. The incorporation of HET acid in these coatings gave improved flame resistance, but then the melt resistance was reduced greatly.

These studies with divinyl benzene were resumed by employing some more recently available flame retarding agents.

The nylon fabric was cleaned by extracting with hot "Perclene", perchloroethylene. The fabric was soaked until thoroughly wet in a reagent of the following composition: 10 cc divinyl benzene-vinyl benzene mixture; 3 cc acrylonitrile; 3 cc Phosgard B - 52-R; 0.3 gm 2,3,5,6-tetrachloroterephthaloyl chloride; 0.5 gm sodium carbonate (insoluble); 0.5 gm benzoyl peroxide and 3 drops of Atlan ARLACEL 85 surfactant (acrylonitrile 13%; Phosgard B-52-30%) and dried in an air oven at 102°C. until the odor of divinyl benzene disappeared. The fabric was treated a total of three times. The final product was flexible but harsh to touch and discolored. When tested with the flame of a match the sample burned slowly at first without melting but finally pulled from the holder.

In order to test the flame resistance of the coating itself, a portion of the same reagent was polymerized at 120°C. for 16 hours. When subjected to the flame of a bunsen burner the product burned but immediately extinguished itself upon removal of the flame. In additional investigations, the fabric was treated with the above reagent and subsequently with diamine and tetrakis (hydroxymethyl) phosphonium chloride. The fabric was then dipped into chloral,  $\text{Cl}_3\text{-C-C-H}$ , allowed to stand and later dried in an air oven. When treated with the flame of a match, the material burned but without dripping.

In a final series of experiments, fabric treated with this reagent was dipped into a dioxane solution of 2,3,5,6-tetrachloro-p-xylene- $\alpha$ ,  $\alpha'$ -diamine and then into an aqueous

solution of tetrakis (hydroxymethyl) phosphonium chloride followed by heating at 120°C. Unfortunately, these treatments resulted in physical coatings that were easily removed. The coating could be retained by retreating the material with the reagent. When tested with the flame of a match the material burned without dripping.

### Discussion

It will be seen from the foregoing that, although an appreciable amount of additional understanding regarding graft processes on nylon was obtained and progress was made with respect to details of potential melt- and flame-proofing procedures, the real breakthrough has yet to be made.

More specifically, we have now delineated the best reaction conditions for the crosslinking of nylon surfaces with phenyl-phosphonic and chloro-phosphonic dichlorides and ascertained that the mechanical properties remain unimpaired by the grafting while a good degree of melt proofing can be achieved. With respect to the latter, this new procedure is equivalent in effectiveness to our older development of melt proofing by grafting with acrylonitrile. It is also technically simpler, but has the disadvantage of requiring a longer reaction time.

Efforts at simultaneous flame proofing, as stated, were still not successful. The main hurdle in the way of achieving this by means of one or the other form of phosphorylation seems to be the fact that phosphorylated nylon becomes soluble, or at least swellable, in the media in which the reaction has to be

carried out. In view of the meager information available on nylon derivatives this could not be foreseen, but presents in itself an interesting (albeit in our context not useful) result. A search for finding new types of solvent for which this may not be true should go on.

Our preliminary work on interfacial polymerization fulfilled a substantial part of our expectations. Limited, though our data are, they suffice to show that this method could become a practical one, since coatings sufficient for melt proofing could be obtained in relatively short time. In fact, the technological development of this method may be simpler than that of acrylonitrile grafting, though not potentially as simple as the phosphorous dichloride method for simple crosslinking and melt proofing. Why we would recommend continued work on interfacial polymerization none the less is that notwithstanding our failure to obtain flame retardation, the chemicals used by us hold the promise of eventual flame retardance as a good possibility. If time had permitted, some combination of the phosphorous crosslink and interfacial polymerization would have been tried, with a good chance of success.

In connection with our attempts to graft a flame proofing agent on our acrylonitrile-vinylacetate primary graft copolymer, it was quite unexpected to find that the copolymeric acetate would hydrolyze with such difficulty that appreciable nylon hydrolysis occurred at the same time. It was also unexpected that a second stage graft of homopolymer vinylacetate would not "take" on a

( primary homoacrylonitrile, or even copolymer. This throws an interesting sidelight on cooperative effects in polymer side group reactivity which is of some value to the present study, but not immediately helpful.

The grafting of divinylbenzene polymers on nylon led also to the expected crosslinking and melt retardation, though only for impractically heavy coatings. Inclusion of flame retarders brought little success, presumably because insufficient quantities were chemically anchored. However, the triple treatment of divinylbenzene copolymer coated with tetrachlorodiamine plus phosphonium chloride, followed by copolymer coating seemed quite successful. There was no time to ascertain to which extent the textile properties of nylon were impaired, nor how critical the various reaction steps were.

#### Further Work

With respect to further work, one should first make certain that no readily accessible variety of our approaches has been overlooked which might yet lead to a success along envisaged lines. Secondly, some of the copolymer work should be continued with a view to a second stage grafting by means of ester or amide exchange reactions. If this should fail, copolymerization with allyl methacrylate or amino ethyl methacrylate should be tried in order to provide secondary grafting sites on which a flame proofing agent could be anchored.

( Our work on interfacial polymerization, especially of diacid chlorides and diamides which contain flame retarding atoms, should be continued in such a manner that simultaneous grafting

occurs, and the combination of divinylbenzene grafting with poly-chloro-amine-phosphonium dichloride treatment be further explored.

While the effort to be expended in executing these programs may yet be appreciable, eventual success is more than likely to be obtained. The resulting impregnated standard fibers may not be superior to basically new fibers such as DuPont's HT nylon, but while the latter will remain a limited speciality, an impregnated large scale commercial fiber should have the advantage of wider application and of the backing of a highly developed technology.

### Conclusions

In conclusion, in our search for improvements on, or alternatives to, our acrylonitrile melt retarding process, we have embarked on three different approaches.

The first, trying to crosslink with halo-phosphorous compounds, and thus to combine melt and flame retardation, lead to results which hold excellent promise for an alternative process of meltproofing, but which yet have not been found practical for flameproofing.

For the second approach of coating by interfacial polymerization, time was not sufficient to elaborate all the many angles of this group of reactions. We were able to establish, though, that the basic method can be applied on a laboratory scale and does lead to meltproofing. An elaboration of this approach with a view of achieving simultaneous flame retardation is highly indicated.

Finally, the various attempts of reactivating melt-

(retarding coatings for the anchorage of flameretarding agents gave, in general, disappointing results. Promising leads uncovered were the copolymerization of acrylonitrile with methacryloylchloride, though the subsequent steps of anchoring a suitable chemical to the active acid chloride site has not been worked out. The repeated divinylbenzene copolymer - and diamine diacid treatments, is also as yet in the early experimental stage.

The shortcomings of the present status suggest further work as intimated in the thus named section. Possibilities of carrying existing knowledge through developmental stages to the level of an applicable process are briefly sketched in the Appendix.

#### Appendix

Referring to various previous Status Reports on the feasibility of melt proofing nylon fabrics, we wish to give in the following a brief description of how we believe the results accumulated to date could be carried into the developmental stage.

##### I. Acrylonitrile Melt Retardation

( We have stated that a suitably ultraviolet activated nylon fabric, when bathed in refluxing acrylonitrile vapor, will within about 10 to 15 minutes acquire a sufficient coating so as to effectively prevent melt-dripping of the material except in hot flames. We have also found that the speed and weight of coating can be improved by sensitizing the nylon first by means of U.V. absorbents. It remains now to describe briefly in which way we imagine that practical applications of these results could be explored.

As a first requirement, nylon fabric would have either to be obtained in a pure, unfinished state or would have to be purified suitably so as to present a reasonably uncontaminated surface.

The next step would involve finding the most suitable conditions of sensitizer application. It will be appreciated that this work has been of an exploratory and largely basic nature and that any exhaustive or final study of optimum utilization conditions could not fall within the frame of this contract. Thus, the approach in Report #2, Contract No. N140(138)67904B has to be taken as a first approximation. Benzophenone appears to be so far the most suitable sensitizer but obviously the search would have to be extended and a number of U.V.-absorbers known in the photographic or pharmaceutical industry will have to be studied. In view of the simple coating and testing procedures which we have developed, this should be an uncomplicated routing study, as would be that of finding the most suitable concentrations of the sensitizer solution and of the corresponding dipping and drying times of the soaked nylon fabric.

Similarly we have ascertained the broad spectral range by which nylon and sensitizers will be activated efficiently, but further work will be necessary with U.V. lamps of a variety of spectral ranges and intensities to ascertain the most suitable practical conditions. As above, using the same tests, this evaluation, too, should be a straightforward routing study.

Presuming that the optimum conditions of sensitization and exposure would thereby have been fixed, a machinery would have

( to be developed which, either by a batch process, or in a continuous manner would allow the four steps of dipping, drying, sensitization and monomer vapor bathing to be carried out at a reasonable speed. Presuming that an exposure of the sensitized nylon of about 4 to 5 minutes would be required, and based on a continuous coating process of a speed of about 250 feet per minute, the following continuous arrangement could be visualized.

The nylon fabric will be run through a dip bath of a length which will give the required time, presumably 30 seconds, at elevated temperature. The fabric will then run through a battery of infrared dryers to reduce the water content to about 10%. Alternatively, a tunnel dryer could be employed which can achieve the same results within the order of 30 seconds in tunnel lengths of approximately 15 feet. The nylon would then pass for about 2 minutes (exact time depending on the preconditioning) past a battery of U.V. tubes of a length of the width of the fabric in an enclosed chamber at distances yet to be ascertained but presumably of about 3 inches. From here, without access to the air, the cloth would enter a second tunnel where it would be exposed to the acrylonitrile vapor in the dark at temperature slightly above the boiling point of AN (pressure application might be interesting but would have to be worked out). In order to allow for a sufficient reaction time at the assumed speed, the tunnel would be designed to be 6 feet in height and about 20 feet in length. Spacing the carrying rolls at 3 inches interval, the cloth length in the tunnel would be approximately 960 feet, or the passage time would be about

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4 minutes in accordance with present estimates of realistic reaction times. The finished fabric would then be dried in vacuum oven at 125°C for several hours to enhance an initial slight cross linking of the outer acrylonitrile sheath.

It will be seen that there is nothing impractical, or involving great engineering difficulties in this process. The above estimate would allow coating of 15,000 feet per hour, a very sizable operation, but scaling down to any desired extent of production would be easy. Last not least, a batch process modeled along the lines of our present step process could be readily visualized, but would actually be less economical than the continuous process. In any case, a pilot plant would have to be built first, not only to learn more about processing variables, but also to prepare a sufficient amount of cloth for testing and end-use evaluation. No cost estimate can possibly be made until a plant design has been prepared, but it is not anticipated that the cost of a batch process pilot plant would exceed \$8,000., or that of the continuous process a cost of \$15,000. Apart from this, small make-shift trial equipment to produce about 10 square feet of material/hr could probably be set up for about \$2,000. cost in materials plus working time.

Melt proofing of nylon cloth by our phosphorylation process could be arranged along the lines of the small scale batch process, at about the same expense. The inter-facial polymerization method is in its infancy, but it is understood that crease proofing of wool is contemplated by this process on a commercial scale, so that the method should become adaptable also to a melt proofing process based on chemistry that we have explored.