THERMALLY STABLE PHOSPHONITRILE COMPOSITIONS

George M. Nichols

E. I. du Pont de Nemours and Co., Inc.
Explosives Department
EASTERN LABORATORY
Gibbstown, New Jersey

ABSTRACT

Phosphonitrilic chloride polymers stabilized against high-temperature polymerization by bonding to various metal halides have been prepared. Reactions of $SbCl_3$, $SbCl_5$, $AlCl_3$, $AlBr_3$, BCl_3, BF_3, $TiCl_4$, $ZnCl_2$, $FeCl_3$, CuCl, and TlCl with PCl_5 and NH_4Cl gave thermally stable compositions which are liquid from room temperature or below up to 1000°F. or higher, pyrolytically stable to 1000°F., and sensitive to hydrolysis to varying degrees. Their exact structure has not been rigorously established.

Several liquid aryloxy phosphonitriles prepared are thermally stable to approximately 750°F. and have pour points below room temperature. They are hydrolytically stable and have very low vapor pressures.

INTRODUCTION

The two most widely studied and well-defined inorganic homologous series are the siloxanes $(R_2SiO)_n$ and the phosphonitrilic chlorides $(PNCl_2)_n$. The former series has received the greatest attention because of the wide range of useful products based on the siloxane backbone. Utility of phosphonitrilic chlorides and derivatives has been impaired by their tendency to polymerize or decompose at elevated temperatures. If this tendency could be overcome, the phosphonitriles would be valuable materials for a variety of purposes including high-temperature fluid applications.

This investigation has been entirely within the area of phosphonitrile chemistry and, in part, represents an extension of studies reported at an earlier Contractor's Conference, May 26-28, 1959 (Ref. 1). The objective of this research has been the synthesis and evaluation of primarily inorganic polymer liquids with potential utility as lubricants, greases, and hydraulic fluids at temperatures up to 1000°F.

Progress toward the objectives has been made in two particular areas of phosphonitrile chemistry as discussed below. The first is that of phosphonitrilic chloride polymers stabilized against polymerization by bonding to various metal halides, these products being designated as $(PNCl_2)_n$/metal halide. The second is that of aryloxy phosphonitriles.

DISCUSSION

$(PNCl_2)_n/SbCl_3$

In an attempt to form a copolymer of phosphorous and antimony nitrilic chlorides by the reaction

$$nPCl_5 + nSbCl_5 + 2nNH_4Cl \longrightarrow \left(\begin{matrix} Cl & Cl \\ | & | \\ P{=}N{-}Sb{=}N \\ | & | \\ Cl & Cl \end{matrix}\right)_n + 8nHCl$$

a liquid phosphonitrilic chloride product containing antimony was obtained that displayed several striking differences from cyclic $(PNCl_2)_n$ polymers. It was soluble only in polar solvents, was very sensitive to hydrolysis, and most important, it did not polymerize on heating to 430°C. In view of the significant effect of antimony in inhibiting polymerization and thereby extending the liquid range of the product, the system was studied in greater detail. It was found that essentially the same products could be obtained more simply by using $SbCl_3$ in place of $SbCl_5$. When the molar concentrations of PCl_5 and $SbCl_3$ in the reaction mixtures were varied from 10 to 1 through 1 to 1, the proportion of liquid product increased progressively from 60% in the 10 to 1 case to 100% liquid at a PCl_5 to $SbCl_3$ ratio of 2 to 1. Elemental analyses and molecular weights of these crude liquids varied with the PCl_5 to $SbCl_3$ ratio, indicating that different products were obtained in each case. The liquids varied in color from brown to black and all were sensitive to moisture.

Several components of the $(PNCl_2)_n/SbCl_3$ crude liquid products were isolated and identified by partial distillation at reduced pressure. $SbCl_3$ was one of the main components removed by distillation, the amount ranging from essentially none in the 10 to 1 case to nearly 50% of the total liquid product in the 1 to 1 case. Small amounts of $(PNCl_2)_n$ trimer, tetramer, and oil were also separated. After removal of all volatile components, the physical and chemical properties of the final liquid products from all of the $(PNCl_2)_n/SbCl_3$ preparations were practically identical. They are soluble only in polar solvents such as methylene chloride and nitrobenzene, and insoluble in nonpolar solvents such as benzene and petroleum ether. They are very sensitive to hydrolysis, being decomposed immediately on contact with water. Their appearance is the same except that the products from reactions involving high PCl_5 to $SbCl_3$ ratios are more viscous than those where the ratio is low.

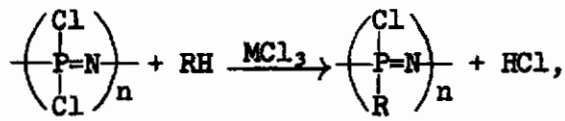
The final liquid from a preparation involving a PCl_5 to $SbCl_3$ ratio of unity boiled above 347°C./0.38 mm. and could be heated to 560°C. in an open tube before polymerizing. Elemental analysis gave an approximate empirical formula of $P_6N_5SbCl_{18}(CH_5)$ as compared with the approximate empirical formula $P_9N_8SbCl_{26}(C_4H_4)$ found for the liquid portion of the product from a reaction involving a PCl_5 to $SbCl_3$ ratio of 10 to 1. The latter product had the same resistance to polymerization at high temperatures as the former.

A more thorough investigation of the lower boiling components of the crude liquid products prepared in sym-tetrachloroethane was accomplished by vapor-phase chromatography (V.P.C.). The following components were isolated and identified: trichloroethylene, tetrachloroethylene, 1,1,2,3,4,4-hexachlorobutane,

sym-tetrachloroethane, antimony trichloride, phosphorous oxychloride, and phosphonitrilic chloride trimer and tetramer. The presence of several additional components in very small concentration was also demonstrated by V.P.C. These were not completely identified but they were found to contain carbon, hydrogen, and chlorine. In some cases peaks were found which were attributed to $(PNCl_2)_n$ pentamer, hexamer, and heptamer. These peaks were assigned by comparison with results obtained for $(PNCl_2)_n$ trimer, tetramer, pentamer, hexamer, and heptamer which could be satisfactorily separated from a normal $(PNCl_2)_n$ liquid by V.P.C. on a silicone grease on "Celite" column at 320°C. In no case was a definite $(PNCl_2)_n/SbCl_3$ component isolated by V.P.C. Adsorption column chromatography confirmed the V.P.C. work but did not lead to identification of other species.

The results demonstrated the instability of sym-tetrachloroethane as a solvent under the conditions used since trichloroethylene, tetrachloroethylene, and 1,1,2,3,4,4-hexachlorobutane definitely are products resulting from the decomposition of sym-tetrachloroethane. It is probable that several of the unidentified minor components are chlorinated hydrocarbons resulting from solvent decomposition.

The discovery that the sym-tetrachloroethane solvent undergoes decomposition in the reaction mixture appears to be significant to the understanding of the instability of ordinary $(PNCl_2)_n$ polymers prepared by the method of Schenk and Römer (Ref. 2). From the nature of the decomposition products isolated and identified, it is apparent that chloroalkyl radicals are present during reaction in significant concentrations and may undergo interchange with the chlorines in the phosphonitrilic chloride polymers. It is also possible that the presence of $SbCl_3$ (or other metal chlorides as discussed later) catalyzes reactions of the following type:



wherein R is $-CCl_2CHCl_2$. Elemental analysis of $(PNCl_2)_n/MCl_3$ liquids prepared in sym-tetrachloroethane confirmed the presence of carbon and hydrogen, and more chlorine than could be accounted for by any reasonable phosphonitrilic chloride structure.

The presence of chloroalkyl groups randomly attached to phosphorous in the $PNCl_2$-type polymers should lead to an inhomogeneous, dark colored product.

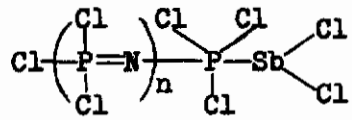
Previous work in this Laboratory (Ref. 3) showed that dark $(PNCl_2)_n$ liquids prepared in sym-tetrachloroethane (with or without $SbCl_3$) could be lightened considerably by treatment with chlorine. If, through decomposition of the solvent, a number of chloroalkyl groups become attached to phosphorous in the $(PNCl_2)_n$ chains or cycles, chlorination would then replace these groups with Cl leaving a uniform perchlorinated product.

On the basis of the above evidence for breakdown and subsequent reaction of sym-tetrachloroethane during phosphonitrilic chloride preparations, 1,2,4-trichlorobenzene (TCB) was evaluated as a less reactive solvent and showed the following advantages: (1) the fluids were clear yellow in color rather than

very dark, (2) the fluids did not become black on heating to 400°C., (3) the fluids appeared to be more homogeneous, and (4) product work-up was greatly facilitated. These comparisons are based on equivalent reaction times and temperatures.

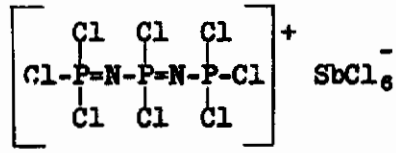
It is apparent that the reaction of PCl_5, NH_4Cl, and $SbCl_3$ does not usually lead to molecular species containing the same P to Sb ratio as in the reaction mixture. In the 10 to 1 case, the liquid portion of the product contains species with P to Sb ratios of approximately 9 to 1. As the molar concentration of $SbCl_3$ is increased, the P to Sb ratio in the crude liquid product follows directly, but this is accomplished by only a small reduction in the P to Sb ratio in the $(PNCl_2)_n/SbCl_3$ species plus solution of unreacted $SbCl_3$ in these species. Thus when the PCl_5 to $SbCl_3$ ratio in the reaction mixture is unity, the crude liquid product is approximately 50% by weight unreacted $SbCl_3$ plus $(PNCl_2)_n/SbCl_3$ compounds having an average elemental composition corresponding to a P to Sb ratio of 6 to 1.

The $(PNCl_2)_n/SbCl_3$ compositions have solubility and hydrolytic properties similar to those of the $(PNCl_2)_n \cdot PCl_5$ polymers which are assumed to be linear in structure (Ref. 4). The infrared spectra of the antimony-containing liquids are similar to those of medium weight $(PNCl_2)_n$ cyclic polymers. On the basis of elemental analysis, molecular weight, and physical and chemical properties, it is suggested that the $(PNCl_2)_n/SbCl_3$ compounds are linear $(PNCl_2)_n$ chains end-capped with the elements of $PSbCl_8$ as follows:



For n = 8 this would give an empirical formula of $P_9N_8SbCl_{22}$ which differs from that actually found for one of the $(PNCl_2)_n/SbCl_3$ oils discussed earlier by omission of the elements $C_4H_4Cl_4$. If it is assumed that two of the chlorines in the above structure have been replaced during reaction by $-CHClCHCl_2$ groups, the formula would then become $P_9N_8SbCl_{28}C_4H_4$ which is in agreement with the elemental analysis of the $(PNCl_2)_n/SbCl_3$ liquid prepared in sym-tetrachloroethane.

Preparations of $(PNCl_2)_n/SbCl_3$ compositions in TCB have led to solid products exclusively. The reactions involved PCl_5 to $SbCl_3$ ratios ranging from 1 to 1 to 10 to 1. These results indicate that the $(PNCl_2)_n/SbCl_3$ products obtained when sym-tetrachloroethane is used as solvent are liquids rather than solids because of a small number of chloroalkyl groups randomly incorporated in the polymer. One of the $(PNCl_2)_n/SbCl_3$ products (38% of the total product) from a preparation in TCB involving a $PCl_5/SbCl_3$ ratio of 5 to 1 was a white, poorly crystalline solid melting at 235-250°C. The remaining 62% of the product was a straw-colored solid melting at 60-76°C. Both of these solids have similar infrared spectra which are consistent with a phosphonitrilic chloride structure. Elemental analysis of the higher melting material gave an approximate empirical formula of $P_3N_2SbCl_{14}$. Thus it is quite possible that the compound has the following structure



analogous to the P_3NCl_{12} compound reported by Becke-Goehring and Lehr (Ref. 5) for which the structure $(Cl_3P{=}N{-}PCl_3)^+PCl_6^-$ was given.

$(PNCl_2)_n/AlCl_3$

It was found that when $AlCl_3$ was included in the reaction mixture for the preparation of $(PNCl_2)_n$ polymers, the liquid portion of the product was resistant to polymerization at elevated temperatures much the same as when $SbCl_3$ or $SbCl_5$ were employed. This result is very reasonable in view of the similarity of $SbCl_3$ and $AlCl_3$ as Lewis acids.

A series of reactions of PCl_5 with NH_4Cl in sym-tetrachloroethane was carried out in the presence of $AlCl_3$ with PCl_5 to $AlCl_3$ ratios of 10 to 1, 5 to 1, and 2 to 1. In each case, reaction proceeded smoothly. The yields were 63.4 g. oil and 59.2 g. solid, 107.2 g. oil and 32.2 g. solid, and 114.9 g. oil and 80.9 g. solid, respectively, based on one mole of PCl_5. The relative amounts of liquid and solid products in these preparations were nearly the same as when $SbCl_3$ was used. One marked difference between the two cases is that unreacted $SbCl_3$ remained in solution whereas $AlCl_3$ not incorporated in the fluid crystallized out in some complex form. These reactions will go rapidly at 95°C. once initiated by heating to about 110°C. Furthermore, they are endothermic and are essentially complete in 30 minutes at 95°C.

The $(PNCl_2)_n/AlCl_3$ liquids ranged from nearly colorless to yellow-brown and were very moisture-sensitive. If these fluids were agitated in the presence of moisture, they became cloudy and lost their stability toward polymerization.

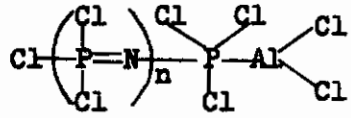
The solid portion of the product obtained with PCl_5 to $AlCl_3$ ratios of 10 to 1 and 5 to 1 was off-white in color and was found to be mostly $(PNCl_2)_n$ trimer and tetramer. The liquid portions of the products in these two cases were too high in molecular weight to be distilled. In the 2 to 1 case, however, the solid product was brown and violently moisture sensitive. On heating and subsequent distillation of this solid mixture, a light brown fluid was collected at ~245°C./0.1 mm. (m.p. ≃ 27°C.). Distillation of the liquid product from the case where the PCl_5 to $AlCl_3$ ratio was 2 to 1 yielded a fraction boiling at 420°C./1.1 mm. (pour point = -55°C.). These two products represent the only $(PNCl_2)_n$/metal halide compositions which have been successfully distilled.

Chemical analysis of the lower boiling fraction gave an empirical formula of P_2NAlCl_8 while that of the higher boiling fraction was $P_4N_3AlCl_{12}$. Both compounds are polar and soluble in polar solvents such as nitrobenzene but are insoluble in nonpolar solvents such as benzene. Both compounds undergo hydrolysis vigorously in water.

The infrared spectrum of the higher boiling fraction had one very strong absorption band at 1270 $cm.^{-1}$ which is midway between that for $(PNCl_2)_n$ trimer and tetramer (Ref. 6). This band is not far removed from the 1240 $cm.^{-1}$ band attributed to linear $(PNCl_2)_{8-9}\cdot PCl_5$ (Ref. 6). The $(PNCl_2)_n/AlCl_3$ compound also had weak bands at 865 $cm.^{-1}$ and 765 $cm.^{-1}$ which are consistent with a $(PNCl_2)_n$-type structure (Ref. 7). If the sample was allowed to contact atmospheric moisture, an hydrolysis band appeared at 3100 $cm.^{-1}$. The lower boiling $(PNCl_2)_n/AlCl_3$ fraction had strong absorption bands at 1330 $cm.^{-1}$, 1175 $cm.^{-1}$, and 810 $cm.^{-1}$. The first two bands are in the region of phosphorous-nitrogen stretching

frequencies in $(PNCl_2)_n$ polymers. The 810 cm.$^{-1}$ band is also in a region where $(PNCl_2)_n$ polymers absorb, but has not been definitely assigned to a particular group.

The following structure is proposed for the two $(PNCl_2)_n/AlCl_3$ compounds discussed above:



where n = 1 and 3, respectively. This structure would be polar and water sensitive and is consistent with the observed infrared spectra. It is exactly analogous to that proposed earlier for the $(PNCl_2)_n/SbCl_3$ compounds. Other ionic or covalent structures are possible but a rigorous structure assignment must await the results of N.M.R. studies and a more complete investigation of chemical properties.

John and Moeller (Ref. 8) report the preparation of a compound having an empirical formula of P_2NBr_7. It has the same solubility characteristics and hydrolytic instability as the two $(PNCl_2)_n/AlCl_3$ compounds, and they suggest that their compound is a $PNBr_2 \cdot PBr_5$ adduct. Preparation of the corresponding P_2NCl_7 compound is reported by Groeneveld, et al. (Ref. 9). The general class of assumed linear $(PNCl_2)_n$ molecules end-capped with the elements of PCl_5 also have similar solubility and hydrolytic properties (Ref. 4). A $(Cl_3P{=}N{-}PCl_3)^+AlCl_4^-$ compound analogous to $(Cl_3P{=}N{-}PCl_3)^+PCl_6^-$ has not been obtained in the present work.

The relative yields of the two distillable $(PNCl_2)_n/AlCl_3$ compounds varied with the relative mole ratios of PCl_5, NH_4Cl, and $AlCl_3$ in the reaction mixture. If a PCl_5 to $AlCl_3$ mole ratio of 2 to 1 was used, the product was predominantly the higher boiling component provided NH_4Cl was present in molar excess of PCl_5. When the molar amount of PCl_5 exceeded that of NH_4Cl, the yield of the lower boiling compound was increased.

A higher molecular weight product obtained from the reaction of NH_4Cl, PCl_5, and $AlCl_3$ (mole ratios 1.6 to 1.0 to 0.1, respectively) in sym-tetrachloroethane solvent had an elemental analysis closely corresponding to the structure shown earlier for $(PNCl_2)_n/AlCl_3$ compounds where n = 7.5 (i.e., a mixture of n = 7 and n = 8) and two chlorines per molecule were replaced by $CHCl_2\text{-}CCl_2\text{-}$ groups.

$(PNCl_2)_n/AlBr_3$

Aluminum bromide was found to react analogously to $AlCl_3$ when included in the reaction mixture of PCl_5 and NH_4Cl using TCB as solvent. With a PCl_5 to $AlBr_3$ ratio of 5 to 1, a red liquid, stable to polymerization at approximately 500°C., was obtained. It was very fluid at room temperature, had a pour point of -49°C., and was very moisture sensitive. Decreasing the PCl_5 to $AlBr_3$ ratio should lead to distillable products but this system appears to offer no advantages over the $AlCl_3$ system.

$(PNCl_2)_n/BCl_3$

The presence of BCl_3 during the preparation of $(PNCl_2)_n$ polymers in TCB also led to a liquid product stable to polymerization at elevated temperatures. The fluids were pale yellow and extremely moisture sensitive. Exposure to moisture led to a white precipitate and loss of polymerization stability.

All attempts to prepare a polymerization-stable $(PNCl_2)_n/BCl_3$ liquid in sym-tetrachloroethane failed. The products polymerized at approximately the same temperature as for ordinary $(PNCl_2)_n$ polymers (280°C. in one case).

Samples were heated to 400°C. in open tubes to remove volatile components before testing in evacuated sealed tubes at higher temperatures. Ten-hour tests were made at 500°C. and 538°C. After the tests the samples were still fluid at room temperature but contained white crystals suspended throughout.

When the $(PNCl_2)_n/BCl_3$ products were heated above 400°C. at atmospheric pressure, vigorous gas evolution and white solid formation occurred up to about 550°C. where polymerization to a dark brown elastomer occurred. At this point only about 30% of the original sample volume remained. These results and those from tests in sealed systems suggest that the decomposition is an equilibrium process. Apparently so long as the system is confined decomposition can proceed only to an equilibrium value on heating with perhaps partial reversal toward the original state on cooling.

Elemental analysis of a $(PNCl_2)_n/BCl_3$ oil (pour point = -44°C.) prepared from a reaction involving a PCl_5 to BCl_3 ratio of 5 to 1 gave the empirical formula $P_2N_2BCl_8$. A definite molecular structure was not established for this material, but the species involved does have an equivalent number of P and N atoms. In all other $(PNCl_2)_n$/metal halide compositions studied, except for the $(PNCl_2)_n/BF_3$ case, there is one more P than N per metal atom. The infrared spectrum of the $(PNCl_2)_n/BCl_3$ liquids has a major band in the region of PN stretching frequencies in $(PNCl_2)_n$ polymers.

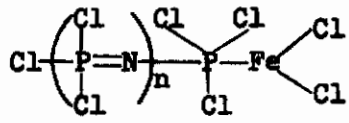
$(PNCl_2)_n/BF_3$

Boron trifluoride had the same effect as BCl_3 in increasing the polymerization stability of the product over that of the normal $(PNCl_2)_n$ cyclic polymers. The method of preparing $(PNCl_2)_n/BF_3$ fluids was the same as that used for BCl_3. It is assumed that the structures of the products are essentially the same. Elemental analyses are consistent with this assumption. The pour point of one of these liquids was -52°C.

$(PNCl_2)_n/FeCl_3$

Ferric chloride reacted with PCl_5 and NH_4Cl to give a high yield of dark liquid product with a pour point of -46°C. The material could be heated to 670°C. in an open tube without polymerization, even though some decomposition occurred. It was slightly soluble in benzene, soluble in nitrobenzene, and insoluble in water although it hydrolyzed slowly therein. The physical and chemical properties and infrared spectrum of this $(PNCl_2)_n/FeCl_3$ liquid indicated that it was similar in structure to other $(PNCl_2)_n$/metal halides. Elemental analysis gave an approximate empirical formula of $P_7N_5Fe_2Cl_{22}$ which could result from a nearly equimolar

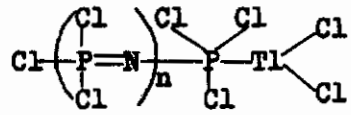
mixture of two polymers having the following structure.



where n = 2 and 3.

$(PNCl_2)_n/TlCl$

Thallous chloride interacted with PCl_5 and NH_4Cl (mole ratios of 1 to 5 to 5, respectively) in TCB solvent to give a good yield of a light brown liquid which was stable to polymerization above 450°C. It had a pour point of -50°C., boiled above 450°C./1.0 mm., was soluble in nitrobenzene, insoluble in benzene, and reacted with water to form an unidentified liquid immiscible with water. Elemental analysis gave an approximate empirical formula of $P_4N_3TlCl_{13}$ which is close to $P_4N_3TlCl_{12}$ obtained by replacing Fe by Tl in the structure given above for $(PNCl_2)_n/FeCl_3$ and assuming that thallium was oxidized to the +3 state, viz.



where n = 3. Its infrared spectrum is very similar to that of the other metal halide-stabilized $(PNCl_2)_n$ polymers. An attractive feature of the $(PNCl_2)_n/TlCl$ liquid was its failure to deteriorate rapidly in air.

$(PNCl_2)_n/SnCl_4$, CuCl, and $TiCl_4$

Reaction of PCl_5 and NH_4Cl in the presence of $SnCl_4$ did not lead to a product with greater resistance to polymerization than ordinary cyclic $(PNCl_2)_n$ polymers. This result may be attributed to formation of the stable $PCl_5 \cdot SnCl_4$ complex which precipitated from the reaction mixture, thus preventing the Sn from undergoing any further reaction. In order to retain part of the Sn in solution during reaction, triphenyltin chloride was used in place of $SnCl_4$ in the reaction of PCl_5 and NH_4Cl in TCB solvent. The products obtained included benzene, chlorobenzene, and a brown liquid $(PNCl_2)_n$ polymer presumably end-capped with $SnCl_3$. The latter product was insoluble in benzene, soluble in nitrobenzene, hydrolyzed slowly in water, had an infrared spectrum similar to other $(PNCl_2)_n$/metal halide compositions, and did not polymerize when heated to 520°C./1 atm. The yield of tin derivative was low, and there is no evidence to indicate that the $(PNCl_2)_n/SnCl_4$ system offers any advantages over $(PNCl_2)_n$/metal halides previously prepared.

When cuprous chloride was reacted with PCl_5 and NH_4Cl in TCB solvent, a very dark brown oil was obtained in low yield. It was stable to polymerization at 400°C., readily oxidized by air, soluble in acetone, and insoluble in benzene. It was insoluble in but reacted with nitrobenzene and water. It had an infrared spectrum similar to that of other $(PNCl_2)_n$/metal halides. Since the $(PNCl_2)_n/CuCl$ system did not have desirable characteristics, no further work with the system was done.

Reaction of PCl_5 and NH_4Cl in the presence of $TiCl_4$ was much slower than with the other compounds previously described. This may be due to formation of a $PCl_5 \cdot TiCl_4$ complex similar to but less stable than that from PCl_5 and $SnCl_4$. The all-liquid product (pour point = -26°C.) from a preparation involving a PCl_5 to $TiCl_4$ ratio of 5 to 1 was very dark brown and upon long standing at room temperature partly crystallized. A sample of the product was heated at atmospheric pressure with the following results. At 400°C. the sample was somewhat darkened but very little gas evolution occurred. Moderate boiling took place at 475°C., and at 500°C. there was vigorous boiling with deposition of yellow solids along the cooler portions of the system. After continuing the heating to 526°C., the sample was cooled to room temperature and remained as a very dark fluid. When tested for 10 hours at 538°C. in an evacuated sealed "Pyrex" tube the $(PNCl_2)_n$/$TiCl_4$ product was stable to polymerization.

$(PNCl_2)_n/ZnCl_2$

Pale yellow, viscous liquid products were obtained from the interaction of NH_4Cl, PCl_5, and $ZnCl_2$ in TCB. Reactions were essentially complete in one hour as determined by HCl evolution. When cool, the reaction mixtures separated into two layers; the upper solvent layers contained by-product $(PNCl_2)_n$ trimer and tetramer and the lower layer was the desired fluid product plus a small amount of solvent. This is the only case studied where a $(PNCl_2)_n$/metal halide fluid separated from the solvent in this manner. Essentially all of the products obtained were liquids containing only a small amount of volatile components. The fluids could not be distilled at 500°C./0.5 mm., thus indicating a high molecular weight. During the process of heating to 500°C. some unidentified black solid material formed in the samples. This was removed by filtration, leaving the product as a pale yellow fluid. These fluids had remarkable pyrolytic stability as judged by tests in evacuated sealed "Pyrex" tubes; for example, 10 hours at 600°C. produced no change in appearance, viscosity, nor infrared spectrum. A sample heated in an open tube to 610°C. did not polymerize, but some decomposition led to deposits of unidentified white solids on the cooler portions of the tube.

The $(PNCl_2)_n/ZnCl_2$ fluids were less sensitive to atmospheric moisture than most of the other $(PNCl_2)_n$/metal halide compositions investigated. They reacted slowly with water, as compared to the vigorous reaction of the $AlCl_3$, BCl_3, BF_3, and $SbCl_3$ compositions.

Elemental analysis of the liquid obtained from a reaction involving a PCl_5 to $ZnCl_2$ ratio of 5 to 1 gave an empirical formula of $P_7N_5Zn_2Cl_{20}$. Its molecular weight was determined as 1140 which is consistent with 1128 for the above empirical formula. Although a definite structure cannot be assigned from these data, it is almost certain that each molecule contains two zinc atoms. Its infrared spectrum has a very strong band at 1270 $cm.^{-1}$ and a smaller band at 760 $cm.^{-1}$, both of which are consistent with $(PNCl_2)_n$ polymers, especially the linear $(PNCl_2)_n \cdot PCl_5$ series.

The result of variations in mole ratios of $PCl_5/NH_4Cl/ZnCl_2$ on the yield and pour point of the resulting products is shown below.

Mole Ratios $PCl_5/NH_4Cl/ZnCl_2$	Liquid Product Wt. (g.)	Pour Point (°C.)
10/10/1	20.0	-15
5/7/1	61.5	- 5
4/2/1	96.3	- 3
2/2/1	151.6	0
1/1/1	105.0	30

It appears that the molecular weight of the product increases as the $ZnCl_2$ to PCl_5 ratio in the reaction mixture is raised, causing a corresponding increase in viscosity and pour point. This may be the result of forming a phosphonitrilic chloride-zinc copolymer.

Nonbonding Metal Halides

Preparations of phosphonitrilic chloride polymers from PCl_5 and NH_4Cl in TCB solvent were carried out in the presence of LiCl, phenylmercuric chloride, $MgCl_2$, $CdCl_2$, AgCl, and $PbCl_2$. There was no evidence that any of these halides became incorporated in the phosphonitrilic chloride products. The materials obtained polymerized at or below 300°C. in each case. A reaction including $SiCl_4$ was inconclusive.

LiCl

When PCl_5 and NH_4Cl were reacted in TCB in the presence of LiCl (PCl_5 to LiCl mole ratio of 5 to 1) a small percentage of the product was obtained as a dark viscous liquid which did not polymerize at approximately 500°C. when initially heated. However, on reheating, it polymerized at 300°C. Elemental analysis of the oil showed no lithium and gave the empirical formula $PNCl_2$. This is reasonable since LiCl would not be expected to react similarly to the Lewis acids discussed earlier. The temporary resistance to polymerization at elevated temperature is not understood. The rate of gas evolution during the preparation was slower than when LiCl was not present.

Preparations of $(PNCl_2)_n$ in the presence of LiCl have been carried out under a variety of conditions but the results have not led to a satisfactory understanding of the effect of the LiCl. Although the results have not been very reproducible, common features of these reactions are the slow evolution of HCl and the fact that these phosphonitrilic chloride products have improved polymerization stability over ordinary $(PNCl_2)_n$ polymers.

Conditions for Formation of $(PNCl_2)_n$/Metal Halides

The results of all reactions between PCl_5, NH_4Cl, and various metal halides fall into a pattern which may be defined in terms of electronegativity. When the metallic element in the metal halide has an electronegativity value (Ref. 10) below 1.2, e.g., Li (1.0), Hg (1.0), Cd (1.1), and Mg (1.2), bonding to $(PNCl_2)_n$ does not occur. Halides of all the elements investigated having electronegativities between 1.2 and 2.0, e.g., Zn (1.2-1.5), Tl (1.3-1.5), Al (1.5), Ti (1.6), Sn (1.6-1.8), Sb (1.8), Cu (1.8), and B (2.0), were found to bond to a $(PNCl_2)_n$ moiety, thereby stabilizing it against polymerization at elevated temperatures. Elements studied that may have electronegativities greater than 2.0 are

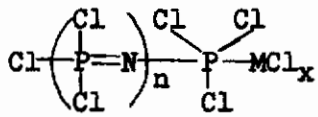
Pb (1.6-2.4), Ag (1.8-3.2), and As (2.0-2.2). Neither $PbCl_2$, AgCl, nor $AsCl_3$ imparted increased polymerization stability to the phosphonitrilic chlorides prepared in their presence.

There are a number of untried metal halides which fall into the class where the metal portion has an electronegativity between 1.2 and 2.0. It is expected that many of these would also bond to $(PNCl_2)_n$ groups. The boundary conditions for formation of $(PNCl_2)_n$/metal halides should not be a function alone of the electronegativity of the metallic, or more electropositive, portion of the metal halide, but should also depend on the relative electronegativities of the metal and halogen. In other words, the degree of ionic character of the bonding in the metal halide must be considered. Thus, highly ionic fluorides would not be expected to bond to $(PNCl_2)_n$ chains, but would be more likely to react with $(PNCl_2)_n$ products formed from PCl_5 and NH_4Cl to produce partially fluorinated phosphonitrilic polymers.

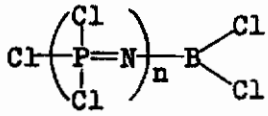
Properties of $(PNCl_2)_n$/Metal Halide Compositions

The similarity of the various $(PNCl_2)_n$/metal halide products suggests that they have similar structures. Although single molecular species could be isolated only in the $AlCl_3$ case, the elemental analyses of the other products indicates that P, N, and the "metal" always occur in ratios of n to n-1 to 1, respectively, where n may be 2 through 9, except for the BCl_3 and BF_3 cases in which the ratio of P to N is more nearly unity. It is therefore assumed that the boron halides react with PCl_5 and NH_4Cl in a slightly different manner. The $(PNCl_2)_n$/boron halide compositions tend to decompose when heated in open tubes at a faster rate than the other metal halide compositions. This effect may be the result of a different type of bonding.

An explanation of the difference between boron and the other elements under consideration may result from a comparison of their electronegativities. The electronegativity of B (2.0) is very close to that of P (2.1), whereas electronegativities of the other "metals" are significantly lower. Thus boron may replace phosphorous at one end of the $(PNCl_2)_n$ chain in the structure.

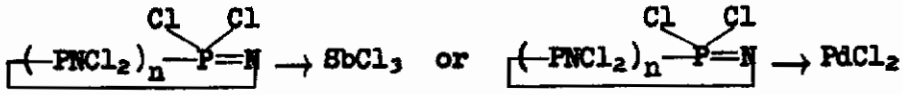


(where x is 1 less than the normal valency of M) so that the following structure is obtained for the $(PNCl_2)_n/BCl_3$ species



The above argument is speculative and further study will be needed before rigorous structural formulas can be assigned.

No reaction was observed when phosphonitrilic chloride trimer was heated with $SbCl_3$, $SnCl_4$, $PdCl_2$, or $CuCl_2$, indicating that cyclic complexes of the type



are not important in cases where high pyrolytic stability was found.

The hydrolytic stability of the $(PNCl_2)_n$/metal halide products varies approximately as the hydrolytic stability of the corresponding metal halide itself varies. The $(PNCl_2)_n$/metal halide products obtained with $SbCl_5$, $SbCl_3$, $AlCl_3$, $AlBr_3$, $TiCl_4$, BCl_3, and BF_3 are all vigorously hydrolyzed by water. Zinc chloride and $(PNCl_2)_n$/$ZnCl_2$ are both less reactive with water. This correlation indicates that the initial site of hydrolysis is the metal halide portion of the $(PNCl_2)_n$/metal halide molecule.

A comparison of liquid ranges of various metal halide stabilized phosphonitrilic chloride polymers is given in Table I. The results of thermal stability tests of $(PNCl_2)_n$/metal halide compositions in evacuated sealed "Pyrex" tubes are summarized in Table II. Viscosities at several temperatures for certain $(PNCl_2)_n$/metal halides are listed in Table III.

Aryloxy Derivatives of $(PNCl_2)_n$ Polymers

The chlorine atoms in phosphonitrilic chloride polymers can be readily replaced by alkoxy groups by the reaction of $(PNCl_2)_n$ with a sodium or potassium alkoxide (Ref. 11). Unfortunately, the alkoxy phosphonitriles are unstable at elevated temperatures, and chemically reactive. The preparation and properties of several aryloxy phosphonitriles have been described (Ref. 12, 13, 14). Their thermal and chemical stability was reported to be good but only in a qualitative manner.

The preparation of aryloxy phosphonitriles was reinvestigated and it was found that phenoxy and substituted phenoxy derivatives of $(PNCl_2)_n$ polymers could be obtained in yields of 70% or higher by reaction of $(PNCl_2)_n$ with the potassium salt of a phenol or substituted phenol in xylene at the reflux temperature. By this procedure phenoxy, o- and p-biphenyloxy, o- and p-chlorophenoxy, m- and p-phenoxyphenoxy, p-benzenesulfonylphenoxy, and m-trifluoromethylphenoxy phosphonitriles were prepared. The boiling points and melting or pour points of these compounds are given in Table IV.

Hexaphenoxytriphosphonitrile is a white crystalline solid melting at 115.0-115.5°C. and boiling at 290°C./0.14 mm. Octaphenoxytetraphosphonitrile was obtained as a white crystalline solid melting at 84.0-85.0°C. and boiling at 340°C./0.44 mm. It had a strong tendency to supercool to a viscous liquid at 25°C. and crystallized only on long standing or agitation. Based on the freezing properties of the trimer and tetramer, it is probable that the pentameric and higher phosphonitrilic phenoxide polymers would be noncrystalline or have very low melting points. As the trimeric and tetrameric phosphonitrilic phenoxide could be readily distilled at reduced pressure, it is reasonable to expect that some of the higher polymers could also be purified by distillation.

Two possible routes to liquid aryloxy phosphonitriles appeared possible: (1) synthesis of completely phenoxy derivatives of $(PNCl_2)_n$ polymers where n is 5 or higher, or where n is mixed, e.g., n = 3, 4, 5, 6, ··· and

(2) synthesis of unsymmetrical triphosphonitriles, e.g., mixed phenoxy and substituted phenoxy derivatives. The former approach was tested by making a phenoxy derivative of a $(PNCl_2)_n$ liquid having an average n value of approximately 7. The product was a very viscous orange liquid with a pour point near 28°C. Fractionation of this product was not attempted, but the results indicated that high fluidity could be expected only for n values near 5. The second approach was then investigated in some detail.

Several derivatives of $(PNCl_2)_3$ in which all six chlorines were replaced by identical substituted phenoxy groups were made in order to ascertain the desirability of different substituted phenols as desymmetrizing agents for phenoxy phosphonitriles. Hexa(o-biphenylyloxy)triphosphonitrile was obtained as a brown, noncrystalline, solid product with a pour point of about 70°C. It was stable to 5% aqueous KOH and became black on heating to 430°C. The sample could not be purified by either crystallization or distillation.

Hexa-m-phenoxyphenoxytriphosphonitrile and hexa-p-phenoxyphenoxytriphosphonitrile were noncrystalline, tacky solids at 25°C. with pour point values near 50°C. The colorless meta compound was found to change little during 6 hours at 400°C. under a dry, oxygen-free, nitrogen atmosphere. The para compound as prepared was light brown and decomposed rapidly at 400°C. The difference in stability of these two materials is attributed to impurities in the para isomer and not to the different position of substitution. No attempt was made to distill either of these high boiling materials.

A very high thermal stability has been reported (Ref. 15) for bis(o-chlorophenyl)-4-biphenylyl phosphate. Thus the o-chlorophenoxy group was investigated by preparing pentaphenoxy-mono(o-chlorophenoxy)triphosphonitrile. This compound melts at 106.5-107.5°C. and boils at 305°C./0.21 mm. Its thermal stability is slightly less than that of hexaphenoxytriphosphonitrile; hence the o-chlorophenoxy group is not considered a desirable substituent in aryloxy phosphonitriles.

Hexa(p-chlorophenoxy)triphosphonitrile (m.p. = 155-156°C.) was prepared and found to have a lower limit of thermal stability than pentaphenoxy-mono(o-chlorophenoxy)triphosphonitrile. This is the expected result of increasing the number of chlorine to phenyl bonds.

The above reactions showed that the potassium salts of chlorophenols, phenylphenols, and phenoxyphenols all react with $(PNCl_2)_3$ at approximately the same rate as does potassium phenoxide. Thus, mixtures of phenol and these substituted phenols should give phosphonitrile products having a statistical distribution of aryloxy substituents.

Reaction of a mixture of potassium phenoxide and sodium o-biphenylyl oxide in 5 to 1 mole ratio with $(PNCl_2)_3$ gave a pale yellow, viscous liquid which was obtained by distillation at 320 to 337°C./0.6 mm. It had a pour point slightly below room temperature and could be heated to 400°C. without discoloration. However, after 10 hours at 427°C. in an evacuated sealed "Pyrex" tube, it became a black solid. The major portion of the sample was assumed to be pentaphenoxy-mono(o-biphenylyloxy)triphosphonitrile.

Since it is reasonable to expect the meta- and para-biphenylyloxy groups to have higher thermal stability than the ortho-biphenylyloxy group, a phosphonitrilic

derivative involving a combination of p-biphenylyloxy and phenoxy groups was prepared. This product was a white crystalline solid melting at 96-98°C. and boiling at ~313°C./0.16 mm. The increased symmetry of the p-biphenylyloxy group over that of the o-biphenylyloxy was apparently sufficient to give a crystalline compound. Results of elemental analysis were consistent with the proposed composition of the desired product, viz., pentaphenoxy-mono(p-biphenylyloxy)triphosphonitrile.

A mixture of aryloxy phosphonitriles consisting of approximately 80% pentaphenoxy-mono(m-phenoxyphenoxy)triphosphonitrile, and 10% each of hexaphenoxytriphosphonitrile and tetraphenoxy-di(m-phenoxyphenoxy)triphosphonitrile (designated as Mixture I) was prepared in good yield from reaction of $(PNCl_2)_3$ with a mixture of phenol and m-phenoxyphenol (in 5 to 1 mole ratio) and KOH. Mixture I is a colorless, viscous liquid having a pour point of 10°C. and boiling between 316 and 345°C./0.18 mm.

A 200-g. sample of Mixture I was evaluated by ASD as a possible high temperature fluid candidate; the results are given in Table V. When compared to the polyphenyl ethers, one of the best classes of high temperature fluids presently available, Mixture I has several advantages such as low evaporative loss, high flash and fire points, and good viscosity properties at high temperatures, all of which are associated with the high molecular weight and correspondingly low vapor pressure of this phosphonitrile composition. Improvements in low temperature viscosity characteristics and stability to oxidation and pyrolysis at elevated temperatures would greatly increase the utility of aryloxy phosphonitriles such as Mixture I.

The para-substituted counterpart of Mixture I, consisting of approximately 80% pentaphenoxy-mono(p-phenoxyphenoxy)triphosphonitrile and 10% each of hexaphenoxytriphosphonitrile and tetraphenoxy-di(p-phenoxyphenoxy)triphosphonitrile (designated Mixture II) was prepared by a two-step procedure from $(PNCl_2)_3$. First, interaction of phenol and p-chlorophenol, in 5 to 1 mole ratio, with $(PNCl_2)_3$ yielded a mixture with a main component of pentaphenoxy-mono(p-chlorophenoxy)triphosphonitrile and minor portions of hexaphenoxytriphosphonitrile and tetraphenoxy-di(p-chlorophenoxy)triphosphonitrile. Second, this product was treated with potassium phenoxide using copper powder catalyst at 250°C. to give the desired Mixture II. Use of p-bromophenol in the first step was found to work as well. Mixture II has approximately the same physical and chemical properties as Mixture I. It is interesting that the para-substituted material is not crystalline.

Thermal stability tests of other phenoxyphenoxy phosphonitriles indicated that the meta-phenoxyphenoxy group might be more stable at elevated temperatures than the para-phenoxyphenoxy group, but Mixture II was found to have approximately the same thermal stability as Mixture I when tested in evacuated sealed "Pyrex" tubes at 400°C.

A phosphonitrile incorporating the p-benzenesulfonylphenoxy group was made by reaction of equimolar quantities of hexaphenoxytriphosphonitrile and benzenesulfonyl chloride. Analysis indicates that the desired pentaphenoxy-p-benzenesulfonylphenoxytriphosphonitrile was obtained. It had a high pour point (30°C.) and poor thermal stability; thus, the p-benzenesulfonylphenoxy group was ruled out as a useful desymmetrizing group for aryloxy phosphonitriles.

Diphenyl-tetrachlorotriphosphonitrile was prepared by the method of Bode and Bach (Ref. 16) and reacted with potassium phenoxide to give diphenyl-tetraphenoxy-triphosphonitrile (both phenyl groups are assumed to be bonded to the same phosphorous) as a white crystalline solid, m.p. = 97-98°C. No attempt was made to distill the compound although this should be possible since it does not decompose rapidly below 400°C.

Trifluoromethylphenoxy Phosphonitriles

An investigation of the m-trifluoromethylphenoxy group has led to very interesting phosphonitrile products. Reaction of $(PNCl_2)_3$ with m-hydroxybenzotrifluoride and KOH in xylene under reflux gave a 71% yield of hexa(m-trifluoromethylphenoxy)triphosphonitrile a colorless liquid having a pour point of -5°C. and a boiling point of 250°C./0.2 mm. Hg. Replacement of $(PNCl_2)_3$ by $(PNCl_2)_4$ in the above reaction gave octa(m-trifluoromethylphenoxy)tetraphosphonitrile a white crystalline solid melting at 54-55°C. and boiling at 280°C./0.20 mm. It readily supercools as a colorless liquid having a pour point of -10°C. The m-trifluoromethylphenoxy phosphonitriles are analogous to the chlorophosphonitriles in that the tetramer is more crystalline than the trimer. The situation is reversed for phenoxyphosphonitriles.

A mixture of $[PN(m\text{-}CF_3C_6H_4O)_2]_n$ polymers (where n = 3, 4, 5, 6, and probably higher) was obtained by reaction of a $(PNCl_2)_n$ liquid sample (n = 3, 4, 5, 6 ····) with m-hydroxybenzotrifluoride and KOH in p-xylene. The product was separated into fractions ranging in boiling point from 250 to 375°C./0.07 mm. Preliminary property determinations indicate that trimer, tetramer, pentamer, hexamer, and perhaps heptamer were thus distilled.

Reaction of $(PNCl_2)_3$ with phenol and m-hydroxybenzotrifluoride (mole ratio of 2 to 1) and KOH in xylene gave a 70% yield of colorless liquid having a pour point of -2°C. This material was distilled between 252 and 270°C./0.2 mm. and is assumed to be a mixture of triphosphonitriles having approximately a statistical distribution of phenoxy and m-trifluoromethylphenoxy groups (the rate of reaction of m-trifluoromethylphenol and KOH with $(PNCl_2)_3$ appears to be approximately the same as for phenol and KOH). A mixed phenoxy and m-trifluoromethylphenoxy derivative of a mixture of phosphonitrile trimer (~85%) and tetramer (~15%) where the phenoxy and m-trifluoromethylphenoxy groups are statistically distributed in the ratio of 2 to 1, respectively, on the trimeric and tetrameric phosphonitrile rings was also made.

All of the m-trifluoromethylphenoxy phosphonitriles discussed above darkened on heating to 400°C. for 10 hours in evacuated sealed "Pyrex" tubes. However, there were no solids formed and little change in viscosity occurred. This stability is somewhat surprising since the CF_3 group greatly lowers thermal stability when incorporated in polyphenyl ethers (Ref. 17).

Relative Properties of Aryloxy Phosphonitriles

Comparison of the properties of the aryloxy phosphonitriles has been made and the results of thermal stability tests in evacuated sealed "Pyrex" tubes are given in Table VI. (Hexaphenyltriphosphonitrile was included for comparison.) The highest stability was found for hexaphenyltriphosphonitrile. Next, the phenoxy, p-biphenylyloxy, m- and p-phenoxyphenoxy, and m-trifluoromethylphenoxy

phosphonitrile derivatives all appear to have approximately the same thermal stability. The o-biphenylyloxy, chlorophenoxy, and benzenesulfonylphenoxy derivatives were of lower stability and consequently of less interest.

The low temperature viscosity and pour point are generally high for molecules with molecular weights as high as the aryloxy phosphonitriles. Thus it is important to utilize any factors that might lead to greater fluidity at low temperatures without sacrificing thermal stability. Table VII lists the pour points of several of the aryloxy phosphonitriles. The benzenesulfonylphenoxy group leads to the highest increase in pour point. This effect is presumably due to the highly dipolar nature of the sulfone linkage causing a certain amount of molecular association. The biphenylyloxy group imparts a higher viscosity than the phenoxyphenoxy group because of the inflexibility of the phenyl to phenyl linkage. This effect is exemplified by the vast difference in fluidity of polyphenyls and polyphenyl ethers. Hexaphenoxytriphosphonitrile can be easily supercooled below its melting point while hexaphenyltriphosphonitrile cannot. The most striking effect on the pour point resulted from the introduction of the m-trifluoromethylphenoxy group. The pour point of hexa-m-trifluoromethylphenoxytriphosphonitrile is 15°C. lower than that of hexaphenoxytriphosphonitrile.

All of the aryloxy phosphonitriles prepared have approximately the same hydrolytic stability, i.e., they are stable to hot 5% aqueous KOH. Furthermore, they have low vapor pressures, generally boiling above 300°C. at 1.0 mm. Hg. The trifluoromethylphenoxy derivatives have the highest vapor pressures (hexa-m-trifluoromethylphenoxytriphosphonitrile boils at 250°C./0.2 mm. Hg) which is characteristic of fluorocarbons.

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TABLE I

Comparison of Liquid Ranges
of $(PNCl_2)_n$/Metal Halides

Compound	Pour Point (°C.)	Boiling Point (°C./mm. Hg)
$(PNCl_2)_n/SbCl_3$	~80 (m.p.)	> 500/760
$(PNCl_2)_n/SbCl_3$*	< 0	> 560/760
$(PNCl_2)_n/AlCl_3$*	< 0	> 588/760
P_2NAlCl_8*	~27 (m.p.)	245/0.1
$P_4N_3AlCl_{12}$*	-55	420/1.1
$(PNCl_2)_n/AlBr_3$	-49	> 500/760
$(PNCl_2)_n/BCl_3$	-44	> 550/760
$(PNCl_2)_n/BF_3$	-52	> 500/760
$(PNCl_2)_n/TiCl_4$	-26	> 526/760
$(PNCl_2)_n/FeCl_3$	-46	> 670/760
$(PNCl_2)_n/TlCl_3$	-50	> 450/1.0
$(PNCl_2)_n/ZnCl_2$	- 5	> 500/0.5
$(PNCl_2)_n/SnCl_4$	< 25	> 520/760
$(PNCl_2)_n/CuCl$	< 25	> 400/760

* Prepared in sym-tetrachloroethane solvent; all other compounds were prepared in 1,2,4-trichlorobenzene.

TABLE II

Thermal Stability of $(PNCl_2)_n$/Metal Halides in Evacuated Sealed "Pyrex" Tubes

Compound	Temp. (°C.)	Time (hrs.)	Result
$(PNCl_2)_n$ liquid	400	0.1	Black polymerized rubber.
$(PNCl_2)_n/SbCl_3$	538	10	No color change; fluid; small amount of dark solid formed.
$(PNCl_2)_n/AlCl_3$	538	10	No color change; fluid; small amount of dark solid formed.
$(PNCl_2)_n/BCl_3$	538	10	No darkening; fluid; white crystals slowly forming at 25°C.
$(PNCl_2)_n/BCl_3$	600	10	Color changed from pale yellow to pale greenish yellow; rubber.
$(PNCl_2)_n/BF_3$	538	10	No darkening; fluid; some white crystals formed at 25°C.
$(PNCl_2)_n/TiCl_4$	538	10	Color changed slightly from brown to greenish brown; fluid which crystallized on long standing at 25°C.
$(PNCl_2)_n/ZnCl_2$	600	10	No color change; fluid at 25°C.

TABLE III

Viscosities of $(PNCl_2)_n$/Metal Halides

Compound	Viscosity in cs. at 0°F.	77°F.	100°F.	210°F.	400°F.	700°F.
$(PNCl_2)_n/AlCl_3$	169.8	30.7	20.8	5.87	1.88	0.73
$(PNCl_2)_n/ZnCl_2$		2433	906	65.3	9.44	
$(PNCl_2)_n/BCl_3$		46.2	29.7	7.45		
$(PNCl_2)_n/BF_3$		29.7	22.9	6.46		
$(PNCl_2)_n/FeCl_3$		30.2	20.2	5.76		
$(PNCl_2)_n/TlCl_3$		28.6	18.0	4.91		

TABLE IV

Comparison of Liquid Ranges of New Aryloxy Phosphonitriles

Compound	Pour Point (°C.)	b.p. (°C./mm. Hg)
$P_3N_3(C_6H_5O)_5(m\text{-}C_6H_5OC_6H_4O)_1$	10	328-330/0.30
Mixture I (see text)	10	315-362/0.35
Mixture II (see text)	10	315-362/0.35
$P_3N_3(m\text{-}C_6H_5OC_6H_4O)_6$	50	-
$P_3N_3(p\text{-}C_6H_5OC_6H_4O)_6$	50	-
$P_3N_3(o\text{-}C_6H_5C_6H_4O)_6$	70	-
$P_3N_3(C_6H_5O)_4(C_6H_5)_2$	100 (m.p.)	-
$P_3N_3(C_6H_5O)_5(o\text{-}ClC_6H_4O)_1$	108 (m.p.)	305/0.21
$P_3N_3(C_6H_5O)_5(p\text{-}C_6H_5C_6H_4O)_1$	100 (m.p.)	360/0.60
$P_3N_3(C_6H_5O)_5(o\text{-}C_6H_5C_6H_4O)_1$	23	335/0.65
$P_3N_3(C_6H_5O)_{\sim4}(m\text{-}CF_3C_6H_4O)_{\sim2}$	-2	252-270/0.20
$P_3N_3(m\text{-}CF_3C_6H_4O)_6$	-5	250/0.20
$P_4N_4(m\text{-}CF_3C_6H_4O)_8$	56 (m.p.)	280/0.20
$P_3N_3(C_6H_5O)_5(p\text{-}C_6H_5SO_2C_6H_4O)_1$	30	365/0.23

TABLE V

Results of ASD Evaluation of Mixture I

(Major Component: Pentaphenoxy-m(phenoxyphenoxy)triphosphonitrile)

1. Pour point (°F.) = +60

2. Flash point (°F.) = 640

3. Fire point (°F.) - did not obtain (appeared to boil at 765°F. to 770°F.)

4. Viscosity (cs.) °F. at 100 - 1598
   210 - 29.8
   400 - 3.34
   700 - 0.917

5. Shell-4-ball wear - conducted at Wyandotte at 400°F., 1 hr., 1200 r.p.m.
   40 kg. = 1.0 mm. wear scar
   MIL-L-9236 base stock under same conditions = 1.0 mm. wear scar

6. Thermal - DTA 730°F.
   - Isoteniscope 790°F. (rerun by Monsanto)

7. Oxidation stability (10 cc.) at 500°F., 6 hrs., 1 liter air/hr.
   Acid value - no change
   Viscosity change = +22 cs. from original
   Color change = (to slight pink from clear)
   Oxidation stability is good. However, ethers exhibit no change at all in this test.

8. Properties of a grease utilizing 10% carbon black thickener
   a. Unworked penetration 368
   b. Dropping point above 700°F.
   c. Evaporation (22 hrs. at 600°F.) 48.4%
   d. Separation (30 hrs. at 600°F.) 62.1%

TABLE VI

Thermal Stability of Aryloxy Phosphonitriles in Evacuated Sealed "Pyrex" Tubes

Compound	Temp. (°C.)	Time (hrs.)	Result
$P_3N_3(C_6H_5O)_6$	400	10	Slight darkening; I.R. indicates some formation of $P_4N_4(C_6H_5O)_8$.
$P_4N_4(C_6H_5O)_8$	400	10	Slight darkening; I.R. indicates some formation of $P_3N_3(C_6H_5O)_6$.
$P_3N_3(p\text{-}ClC_6H_4)_6$	400	1	Became very dark brown.
$P_3N_3(C_6H_5O)_5(o\text{-}ClC_6H_4O)_1$	400	10	Became dark brown; large increase in viscosity.
$P_3N_3(C_6H_5O)_5(o\text{-}C_6H_5C_6H_4O)_1$	400	10	Became dark green; very large increase in viscosity.
$P_3N_3(C_6H_5O)_5(p\text{-}C_6H_5C_6H_4O)_1$	400	10	Slight darkening; tacky and non-crystalline at 25°C.
$P_3N_3(C_6H_5O)_5(p\text{-}C_6H_5SO_2C_6H_4O)_1$	400	1	Became black.
$P_3N_3(C_6H_5O)_4(C_6H_5)_2$	400	10	Became a dark brown, noncrystalline solid.
$P_3N_3(C_6H_5O)_5(m\text{-}C_6H_5OC_6H_4O)_1$	400	10	Slight darkening; I.R. indicates some formation of tetrameric phosphonitrile; 67% increase in viscosity at 210°F.
$P_3N_3(C_6H_5O)_5(p\text{-}C_6H_5OC_6H_4O)_1$	400	10	Slight darkening; I.R. indicates some formation of tetrameric phosphonitrile.
$P_3N_3(C_6H_5O)_4(m\text{-}CF_3C_6H_4O)_2$	400	10	Became brown; I.R. indicates some formation of tetrameric phosphonitrile; 12% increase in viscosity at 210°F.
$P_3N_3(m\text{-}CF_3C_6H_4O)_6$	400	10	Became brown; I.R. indicates some formation of tetrameric phosphonitrile; 1% increase in viscosity at 210°F.
$P_4N_4(m\text{-}CF_3C_6H_4O)_8$	400	10	Became brown; I.R. shows formation of some trimeric phosphonitrile; 12% decrease in viscosity at 210°F.
$P_3N_3(C_6H_5)_6$	400	10	No change.

TABLE VII

Pour Points of Aryloxy Phosphonitriles

Compound	Pour Point (°C.)
$P_3N_3(C_6H_5O)_6$	10 (supercooled)
$P_3N_3(C_6H_5O)_5(m\text{-}C_6H_5OC_6H_4O)_1$	10
$P_3N_3(C_6H_5O)_5(p\text{-}C_6H_5OC_6H_4O)_1$	10
$P_3N_3(m\text{-}C_6H_5OC_6H_4O)_6$	50
$P_3N_3(p\text{-}C_6H_5OC_6H_4O)_6$	50
$P_3N_3(o\text{-}C_6H_5C_6H_4O)_6$	70
$P_3N_3(C_6H_5O)_5(p\text{-}C_6H_5SO_2C_6H_4O)_1$	30
$P_3N_3(C_6H_5O)_4(m\text{-}CF_3C_6H_4O)_2$	-2
$P_3N_3(m\text{-}CF_3C_6H_4O)_6$	-5
$P_4N_4(m\text{-}CF_3C_6H_4O)_8$	-10 (supercooled)