TECHNICAL REPORT
67-2-CM

DEVELOPMENT OF AN INORGANIC PHOTOTROPIC SYSTEM FOR FLASHBLINDNESS PROTECTION

by
Alvin M. Marks

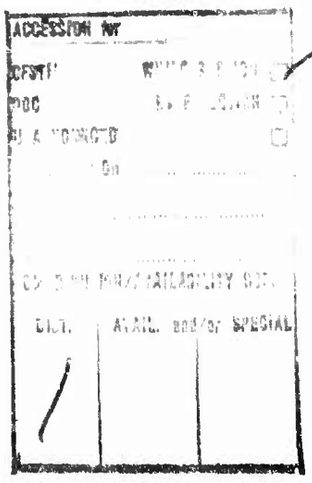
Marks Polarized Corporation
Whitestone, N. Y.

Contract No. DA-19-129-AMC-158(N) 0.1.9122

July 1966

UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760

Clothing and Organic Materials Division
C&OM-22



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Abbreviations

PMA	Phosphomolybdic acid
PVMA	Phosphovanadomolybdic acid
PTA	Phosphotungstic acid
STA	Silicotungstic acid
SMA	Silicomolybdic acid
PVA	Phosphovanadic acid
B-90	Polyvinyl butyral, Shawinigan Resins Co.
D-331	Partially hydrolyzed polyvinyl acetate, Shawinigan Resins Co.

ABSTRACT

This report presents the details of a study made to determine the feasibility of using films containing one or more hereopoly acids for possible protection against flashblindness. Phosphomolybdic, phosphovanadomolybdic, phosphotungstic, silicotungstic, and silicomolybdic acids are evaluated.

Methods for the preparation and purification of heteropoly acids in general are given. Also given are details for the preparation and purification of specific compounds: potassium-arseno-12-molybdate, phospho-18-molybdic acid, arseno-12-molybdic acid, purpureophospho-12-vanadic acid, and borotungstic acid. Mixtures of phosphomolybdic and phosphotungstic heteropoly acids with simple and isopoly ions were separated by paper chromatography and identified by ultraviolet light and by spray techniques.

Films for evaluating the photochromic response were prepared by centrifugally spinning a thin film of acid-resin solution on a polyester substrate and evaporating the solvent. Photochromic response and capabilities were determined by 1) exposing the films to a xenon flash, an ultraviolet lamp, and a xenon-mercury arc; and 2) measuring the optical transmission or density before and after exposure. The response of several films, particularly phosphomolybdic acid in polyvinyl acetate (which changed from an optical density of 0.07 to a density of 3.4), indicates that further research in this area is warranted. Also, since several of the films were somewhat heat sensitive, a study of different resins is indicated.

I. Introduction

Several years ago, the photosensitivity of the Group VIA elements chromium, molybdenum, and tungsten suggested their use in a photothermotropic device that would protect from flashblindness and thermal radiation. Subsequently, the Marks Polarized Corporation [1] studied films containing certain of the molybdenum and tungsten heteropoly acids and found that they became opaque upon exposure to an intense light source. This prompted them to determine which acid-resin combinations would yield the most opaque films.

The present work was initiated to determine the feasibility of using the most promising of these films to protect against flashblindness. Satisfactory flashblindness protection requires the film to have:

1) Transmission of at least 80 percent in the visible portion of the spectrum before exposure to a flash of light, with extremely little or no deviation or distortion of the image-forming rays;

2) Optical density of "4" within approximately 50 microseconds after exposure to radiation that is similar to the first pulse of a nuclear weapon;

3) Storage capability at temperatures between -65°F and +125°F for at least six months; and

4) Operational capability at temperatures ranging from -65°F to +115°F.

II. Background

The chemistry of molybdenum and tungsten is complicated by the existence of several oxidation states (+ 1, 2, 3, 4, 5, and 6), isopoly anions, and heteropoly anions. The lower oxidation states are reducing agents and are fairly readily oxidized to + 6, the most stable state of both elements. A number of reducing agents can convert simple molybdate ion (MoO_4^{-2}) to "molybdenum blue" ($Mo_8O_{23}.xH_2O$) and the corresponding tungstate ion (WO_4^{-2}) to "tungsten blue" ($W_8O_{23}.xH_2O$).

At elevated temperatures, the alkali metal tungstates are reduced to metallic-appearing highly colored conducting solids called "bronzes", such as $M_x(WO_3)_y$ where M is an alkali metal. These bronzes have a defect structure in the crystal lattice where missing sodium ions are probably compensated for by tungsten atoms in the + 6 state. The color and conductivity of these bronzes are attributed to the presence of two oxidation states of tungsten and to mobile electrons in the lattice.

A characteristic property of molybdenum and tungsten is the formation of isopoly and heteropoly acids. The isopoly acids are those that contain a single anhydride, whereas the heteropoly acids are usually composed of two different anhydrides, one containing boron, silicon, phosphorus, or arsenic, and the other containing tungsten or molybdenum. There is some controversy over the exact structures of heteropoly acids. One explanation of the structural relationship of the units comprising them has been offered by Keggin[2] and is consistent with the X-ray diffraction data. The suggested arrangement is centered about an XO_4 tetrahedron (where X is B, P, Si, V, or Ti). Each corner of the tetrahedron is shared by three octahedra (MoO_6 or WO_6). The four sets of 3 octahedra (Mo_3O_{10} or W_3O_{10}) are also linked by shared corners, giving $(XMo_{12}O_{40})^{8-n}$ groups (n is the oxidation number of X). Spaces in the crystal structure are then occupied by water. However, this crystal structure, which has been established for some heteropoly acids, does not help us understand the solutions of acids.

The ionic species in solution are dependent, at least in part, on the pH of the solution. Jander et al[3] investigated solutions of isopoly acids by measuring diffusion coefficients and conductivities as a function of pH. Their data suggest the following pH-dependent isopoly acid scheme (pH is shown over arrows):

$$MoO_4^{-2} \underset{}{\overset{(6.5)}{\rightleftharpoons}} Mo_3O_{11}^{-4} \overset{(4.5)}{\rightleftharpoons} HMo_6O_{21}^{-5} \overset{(2.9\text{-}1.5)}{\rightleftharpoons}$$

$$H_3Mo_6O_{21}^{-3} \overset{(1.25)}{\rightleftharpoons} H_7Mo_{12}O_{41}^{-3} \overset{(1.0)}{\rightleftharpoons}$$

$$H_7Mo_{24}O_{78}^{-5} \overset{(1.0)}{\rightleftharpoons} MoO_3 \text{ (aqueous)}$$

Tungstate and vanadate systems have given similar results. The literature is not clear as to the exact characterization of heteropoly and isopoly acid species. Different formulas are often used to describe the same material. Therefore, to prepare the acids and to guarantee reproducible results for any application, care must be exercised in their preparation, purification, identification, and use.

III. Preparation of Heteropoly Acids and Heteropoly Acid Salts

A. General Methods of Preparation

1. Drechsel's Method[4,a]

This method involves formation of the ether addition product, its isolation, and the subsequent crystallization of the free acid.

A concentrated aqueous solution of the heteropoly acid together with approximately one-third its volume of ether is placed in a separatory funnel and shaken to saturate the solution with the ether. Small additions of ice-cold concentrated hydrochloric acid (HCl) are made with swirling. The funnel is cooled with flowing tap water immediately after each addition, for the liquids should not become warm. The free acid combines with the ether to give an addition compound which separates as heavy, oily drops. A third layer also forms and is collected, after clarification. The reaction is complete when the further addition of concentrated HCl yields no more droplets of the addition product. The oily fraction is isolated and mixed with an equal quantity of water. The ether is removed by bubbling a clean, dry stream of air through the two solutions. The acid can be induced to crystallize from the aqueous solution in a desiccator over concentrated sulfuric acid (H_2SO_4). However, once the crystallization begins, the H_2SO_4 should be replaced by solid potassium hydroxide (KOH) to remove the remaining water and the HCl.

2. Ion-Exchange Method[4,b]

The advantage of this method is the high degree of purity that can be attained in the final product. The starting material is a purified water soluble salt of a heteropoly acid. Because of the strongly acidic nature of the heteropoly acid and its susceptibility to reducing agents, a cationic ion exchange resin is indicated, preferably one containing sulfonic acid groups.

The details of the preparation are dependent upon the individual character of the heteropoly acid. Preliminary experiments to optimize conditions are desirable. One should observe the following rules: 1) the exchange capacity should normally be about 2 milliequivalents/cm^3 of resin; 2) the solution placed on the column should have the highest concentration possible; and 3) the solution flow rate should be between 2 and 5 cm^3/minute. The solution of free heteropoly acid obtained from the column can be concentrated as desired and, if required, the acid can be induced to crystallize in a desiccator.

If the required starting salt cannot be synthesized from the constituents, it can be obtained by supersaturating a moderately concentrated solution of its acid with metal chloride. The yield is better and the product purer if a molar equivalent of metal carbonate is added. It is best to proceed with caution in adding the carbonate since any excess will tend to decompose the heteropoly anion.

3. Freeze-Drying Method

The procedure previously used in the drying of heteropoly acids often leads to partial or complete reduction of the acid. The literature recommends uniform drying with sulfuric acid (H_2SO_4) in a desiccator. We found that, in the case of arsenomolybdic acid and phosphovanadic acid, vacuum desiccation using H_2SO_4 as the desiccant will cause reduction of the acid. Since water molecules occupy positions in the polyhedron between the peripheral anions and, by hydrogen bonding, help to stabilize the structure, we can speculate that severe desiccation would result in the loss of these molecules and would render the heteropoly acid susceptible to facile reduction. Therefore, it would be desirable to have a drying method that would yield a dry crystalline material without removing the water so essential to the crystal structure. We believe that the freeze-drying technique meets this requirement.

Freeze-drying involves freezing the material and then subjecting it to a high vacuum (micron or fractional micron range) while it is connected to a condenser or cold trap that is maintained at a very low temperature (-80°C). Under these conditions, the sample is dehydrated via sublimation of the ice present. Apparently, structurally bound water is not labile under these conditions.

A solution of acid to be freeze-dried is concentrated as much as possible, using low heat ($< 40°C$) methods exclusively. The concentrated solution is placed in the sample container of the freeze-dryer and frozen in an acetone-dry-ice bath in a Dewar flask. When the contents are frozen, the sample holder is connected to the vacuum pump and the vacuum trap is cooled with a mixture of acetone and dry ice. It is not necessary to continue chilling the sample at this stage since it is cooled by sublimation of the ice. In fact, the temperature of the acid may be taken as an indication of the completion of the drying process. When the acid is dry, its temperature will approach ambient. It is important that the supply of dry ice in the cooling mixture surrounding the vacuum trap be replenished periodically.

B. Preparation and Purification of Specific Acids and Salts

1. Potassium Arseno-12-Molybdate(4,c)

Twenty-three grams of molybdenum trioxide (MoO_3) is dissolved in a solution of 18 g potassium hydroxide (KOH) in 100 ml of water. A solution of 1.47 g of arsenic pentoxide (As_2O_5) in 50 ml of water (a small amount of ammonium hydroxide (NH_4OH) is necessary to facilitate solution) is added to the MoO_3 solution and the mixture is warmed at 70°C for one hour to remove the ammonia. The solution is cooled in an ice-water bath, then 21 ml of concentrated ice-cold nitric acid (HNO_3) is quickly added and the solution stirred. The solution turns yellow and a small quantity of yellow precipitate is deposited. The solution is heated at 70°C for 30 minutes and cooled overnight in a refrigerator at 5°C. The yellow precipitate of potassium arseno-12-molybdate is collected by filtration and dried in a desiccator.

2. Phospho-18-Molybdic Acid

This acid was prepared as follows, exactly as described by Killeffer and Linz(5):

One hundred grams of sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$) is dissolved in about 450 ml of water, then 15 ml of 85% phosphoric acid (H_3PO_4) and 80 ml of concentrated hydrochloric acid (HCl) are added. The mixture is refluxed for 8 hours, then cooled and 100 g of powdered ammonium chloride (NH_4Cl) is stirred in. The crystalline precipitate is allowed to settle and is filtered on a Buchner funnel. It should be sucked as dry as possible. The precipitate is redissolved in an equal weight of water. A part of the precipitate (ammonium phospho-24-molybdate) remains undissolved, so it is again filtered through hardened paper. Enough NH_4Cl to make a 20 percent solution is added to the perfectly clear solution. If the solution is not stirred, the ammonium phospho-18-molybdate will form larger crystals than if the solution is stirred. After the solution stands for from 4 to 8 hours, the crystals are filtered on a Buchner funnel and are sucked as dry as possible. They are redissolved in just enough water and the solution is evaporated under vacuum at 40°C until crystals again begin to form. (The solution cannot be evaporated with the aid of a free flame, steam bath, or excessive heat because the ammonium salt is transformed into the insoluble yellow precipitate of the 2:24 series at 60-70°C.) The crystal-liquid mixture is cooled slowly to 5-6°C, then is transferred to a Buchner funnel and the crystals sucked as dry as possible. After the suction is discontinued, the crystals are covered with a large excess of dry ether. To insure mixing, they are stirred and then allowed to stand for a few minutes before being sucked. The crystals are then air dried on a

watch glass for about an hour. Quick drying is necessary to prevent the formation of a yellow precipitate such as occurs during slow drying. The orange crystals obtained are of the composition $3(NH_4)_2O \cdot P_2O_5 \cdot 18MoO_3 \cdot 11H_2O$ and should give a clear solution in water.

The free phospho-18-molybdic acid can be prepared from the salt as follows:

Fifty grams of ammonium phospho-18-molybdate is dissolved in 100 ml of water and 60 ml of concentrated HCl is added. The mixture is extracted by shaking with ether in a separatory funnel and then is cooled. This procedure is repeated twice. The combined ether extracts are placed in a tall beaker. Forty ml of water is then added and the ether evaporated with an air stream. The residual solution is concentrated by drying it over sulfuric acid (H_2SO_4). (Like the ammonium salt, the free 2:18 acid is transformed into the 2:24 acid at high temperatures.) Orange prisms of the composition $3H_2O \cdot P_2O_5 \cdot 18MoO_3 \cdot 11H_2O$ are obtained. The solution should give no precipitate with NH_4Cl.

3. Arseno-12-Molybdic Acid

One gram of arsenic pentoxide(As_2O_5) is dissolved in 50 ml of water with the aid of a small amount of sodium hydroxide (NaOH). The turbid solution is heated to 70°C and 25.2 g of sodium molybdate dihydrate ($Na_2MoO_4.2H_2O$) is added. The solution is stirred at 70°C for one-half hour and then cooled to about 5°C. Twenty ml of cold concentrated nitric acid (HNO_3) (sp gr = 1.42) is slowly added, with mixing and cooling. The white precipitate that sometimes forms during the first addition redissolves on further addition of the acid, yielding a clear yellow solution.

The cooled yellow solution is placed in a separatory funnel and one-third its volume of ether is added. The contents of the funnel are swirled and the layers are allowed to separate. An oily layer heavier than either the aqueous or ether layer may appear at this point. This oily layer (containing the ether addition product) will form if the concentration of HNO_3 in the aqueous layer is too low. Additional HNO_3 should be added until all the oily layer has dissolved in the ether phase. The ether layer is then transferred to another vessel, a small quantity of water is added, and a stream of filtered dry air is passed through the system. This removes the ether from the addition product and effects the solution of the arsenomolybdic acid in the water. Crystallization of the acid may be attempted from either the aqueous solution or the ether addition product by desiccation over sulfuric acid (H_2SO_4).

Crystallization proceeds well until yellow-orange crystals are formed. This is a critical phase. In most cases, after this crystallization but before complete dryness, the crystals are reduced to the "molybdenum blue". It is inadvisable to dry the ether solution prior to crystallization because drying at this stage seems to leave the resulting crystals more susceptible to reduction. In either case, it is possible to add an oxidizing agent, for example HNO_3 or hydrogen peroxide (H_2O_2), to the partially reduced acid and continue drying. The yellow color is regenerated and eventually the crystals become dry.

Arsenomolybdic acid can also be prepared by removing the partially reduced acid from the desiccator and treating it with H_2O_2 to obtain the unreduced form (yellow). The moist crystalline mass is then placed in the sample container of the freeze dryer and dried as described above (A.3). The yellow mass obtained is then ground to a powder. This material is rather unstable and should be stored in the freezer compartment of a refrigerator, ideally in a closed container under oxygen.

4. Purpureo Phospho-12-Vanadic Acid[4,d]

a. Vanadium Pentoxide Method: A slurry of 68.2 g of vanadium pentoxide (V_2O_5) in 150 ml of water containing 44.8 g of disodium phosphate (Na_2HPO_4) is brought to pH 11 by the slow addition of sodium hydroxide (NaOH). The solution is warmed to 70°C for one-half hour and then cooled. Concentrated nitric acid (HNO_3) is added slowly, with cooling, until pH 6 is reached. Any sediment present is filtered from the system and a quantity of acetone equal to one-fifth the filtrate volume is added to the filtrate. The solution is placed in a refrigerator overnight. The precipitated sodium salt of the acid is removed by filtration and dried in a desiccator. The dry salt is converted to the acid by Drechsel's method[4a,6], (also see A.1., above).

The manner in which this acid is dried is apparently quite critical. If the acid is placed in a vacuum desiccator over sulfuric acid (H_2SO_4), color changes occur. The brown-red colored mass becomes flecked with yellow and then a green-black reduction product appears. This sequence may be reversed by treatment with hydrogen peroxide (H_2O_2). Samples of the acid have been freeze-dried successfully.

b. Ammonium Metavanadate Method: Vanadium pentoxide (V_2O_5) is added to a solution of concentrated ammonium hydroxide (NH_4OH), the addition of which causes a hissing sound. Presumably this indicates that a reaction is taking place. The suspension is stirred for several hours, using a non-metallic stirrer. During this period, the color of

the suspended material changes from brown to grey-white. The insoluble ammonium metavanadate may be filtered off and the filtrate evaporated without heat to recover the small quantity of dissolved salt. As long as a hissing sound occurs with the last addition of vanadium pentoxide, no pentoxide will be present in the product.

A slurry of 96 g of ammonium metavanadate is prepared in 300 ml of water containing 43 g of sodium dihydrogen phosphate (NaH_2PO_4). If diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) is used, 45 g will be required. The slurry is stirred mechanically while 76.5 ml of concentrated nitric acid (HNO_3) is added slowly. Each addition of acid produces a transient red color until the pH of the slurry is low enough to produce the phosphovanadic acid. At this pH, the depth of the red color of the solution increases with the further addition of nitric acid. The suspended material also begins to turn red. Stirring is continued for several hours and is followed by cooling in a refrigerator overnight. The precipitate is filtered from the red supernatant liquid and is dissolved in a minimum quantity of water. This solution, which probably contains a mixture of the ammonium and sodium salts of the heteropoly acid in addition to the free acid, is passed through a Dowex 50W-X4 ion-exchange column. The column effluent may be concentrated under vacuum at less than 40°C. During the concentration process, red crystals of the acid are precipitated. When the volume of the crystal-solution mixture is one-fifth of the original solution volume, the suspension is refrigerated overnight to precipitate the rest of the acid.

The red filtrate from the first filtration may be concentrated to yield more precipitate or it may be treated with acetone to yield a yellow precipitate. This yellow precipitate gives a red solution when dissolved in water and is apparently another crystalline hydrate of phosphovanadic acid. Yellow crystals are also formed during the drying of the acid. Comments concerning the critical nature of the drying process mentioned in the vanadium pentoxide method also apply here.

5. Borotungstic Acid[7,8]

Thirty to fifty grams of commercial barium borotungstate is dissolved in a minimum quantity of water and any insoluble material removed by filtration. The filtrate is slowly passed through a column 1-1/2 inches in diameter and 14 inches long containing Dowex 50W-X4 ion exchange resin in the acid form. The rate of flow is regulated at about 1 drop per second. The pH of the effluent is below 2 for most of the operation and begins to approach 5 slowly as the borotungstic acid content decreases. The column effluent (1-2 liters) containing the borotungstic acid is gently concentrated under vacuum at 20-40°C and the liquid residue is freeze-dried. The grey-white mass obtained is then ground to a powder.

IV. Chromatographic Analysis of Heteropoly Acids

A. Theory

Paper chromatography for heteropoly acids involves the partition of the material to be examined between the two liquid phases of the chromatographic system. One phase, richer in water, is stationary and is bound to the cellulose matrix; the other phase, poorer in water, moves along the length of the paper by capillary action. Samples that are very soluble in the moving phase tend to move with it and will be found at the solvent front. Samples that are not soluble in the moving phase remain at the origin. Samples of intermediate character move to a point between the origin and the solvent front. The separation achieved is related to the partition coefficients of the substances being separated.

Other factors must be considered as well. For example, the paper may not be inert with respect to the sample. Some materials may be adsorbed on the paper while others may undergo ion exchange with the polar constituents or impurities in the paper. The presence of adsorption phenomena is indicated by the failure of n-butanol, a solvent for heteropoly acids, to move either phospho-12-molybdic or phospho-12-tungstic acid from the origin.

B. Preliminary Results

The results of initial chromatographic studies indicate that pure organic solvent mixtures do not move phosphomolybdic acid (PMA) and phosphotungstic acid (PTA) from the origin. Other solvent compositions, such as those shown in Table I, were then investigated. The addition of acetic or perchloric acid does not change the mobility, whereas nitric acid will confer mobility upon a portion of the material. The addition of water to the organic solvent systems increases the mobility of the material and yields a streak in practically all cases. The use of salt solution in place of water tends to increase the amount of material that is mobile. When a salt solution and nitric acid are added to the organic solvent systems, mobility increases but some material remains at the origin while the more mobile material moves with the solvent front.

C. Problem of Adsorption

To improve sample mobility, consideration was given to the problem of adsorption of the heteropoly acid on the paper. It was surmised that coating the paper surface with a neutral material would interfere with the bonding between the acid and the paper and permit the acid to move with the liquid phase. Dow Corning Silicone 200 fluids were examined for this purpose. It was apparent that the silicone coating on the paper should be non-volatile and uniform and this necessitated the use of the 50 centistokes (cs) fluid (which has the lowest viscosity of the nonvolatile silicone fluids). Experiments

TABLE I

Examples of Solvent Mixtures Evaluated in

Chromatographic Separations

Prior to the Use of Silicone-Coated Paper

Solvent Composition (in milliliters)

Solvent	n-Butanol	HOAc	H_2O	$HClO_4$	1M NaCl	2-Propanol	HNO_3
1	90	10	10	-	-	-	-
3D	80	4	-	6	-	-	-
2F	80	10	5	0.1	5	-	-
3J	-	-	8	-	10	80	2
6K	-	-	15	-	15	70	0.5
6M	-	-	-	-	30	70	1.5

TABLE II

Solvent Compositions for Chromatography

on Silicone-Coated Paper

Solvent Mixture	Water	2-Propanol	Nitric Acid
15	100.0	20	4
20	100.0	25	4
22	100.0	30	3
25	100.0	30	4
28	100.0	35	4
30	100.0	35	2
31*	10.0	90	4
32*	20.0	80	4

*Prepared by simply mixing the components. (The others were prepared by mixing the alcohol with water and adding 100 ml of this mixture to the nitric acid.)

showed that spots of heteropoly acid applied to paper strips dipped in the 50 cs silicone fluid move off the paper with the solvent front. On undipped strips, the spots smear while the solvent front runs off the paper. To reduce the amount of silicone on the paper, the coating was deposited from a toluene solution. Experiments were carried out to determine the optimum concentration of the silicone in the dip, using silicone concentrations of 5, 10, 15 and 20 percent (v/v). The results indicated that the silicone fluid deposited from all of these solutions markedly increased the mobility of the acid tested. This was determined by measuring the amount of acid moved a constant distance along the paper strip. The 20 percent dip was chosen for future work because maximum concentration of acid in a spot is desired to facilitate detection and this dip showed a somewhat greater mobility of acid than the other concentrations of silicone.

D. Solvent Mixtures

In a further attempt to improve sample mobility and to maintain the integrity of the spot, several solvent mixtures were investigated. These mixtures, which are water solutions of nitric acid and 2-propanol, are given in Table II. The purpose of the nitric acid in the solvent is twofold: it insures the presence of only one acidic species of heteropoly anion, and it guards against the possible reduction of the acid during the course of chromatography. The alcohol, (2-propanol chosen because of its relative oxidation stability), was included to restrict both the flow of solvent along the paper and the movement of heteropoly acid in the mobile phase. The R_f values for phosphotungstic acids in these mixtures are shown in Table III (the R_f is the ratio of the distance traversed by a compound to the distance traversed by the solvent).

E. Paper Chromatography of Mo, P, W Anions

In addition to the study of phosphotungstic and phosphomolybdic acids (Table III), tungstate, molybdate, and phosphate anions were chromatographed with several of the solvent mixtures listed in Table II. The R_f values for the ions with these solvents are given in Table IV. The second phosphate determination (last entry in Table IV) was made on undipped paper. While the R_f's of the dipped and undipped phosphate determinations are similar, it should be noted that the distance of solvent travel on undipped versus dipped paper was 1.6:1 for mixture 25 and 2.3:1 for mixtures 31 and 32. This may help to explain the differences in the R_f values tabulated for the phosphate anion.

Solutions of both the tungstate and molybdate ion appeared to contain considerable quantities of the isopoly anion. This conclusion was reached as a result of paper chromatographic studies on each ion. These studies revealed the appearance of a spot along the line of solvent travel and a separate streak much closer to the origin. Since

TABLE III

R_f Values* for Solvent Mixtures with Phosphomolybdic Acid and Phosphotungstic Acid

Solvent	R_f PMA	R_f PTA
15	0.11	0.09
20	0.18	0.27
22	0.32	0.52
25	0.35	0.54
28	0.50	0.73
30	0.57	0.77

*Ratios of distance traversed by a compound to the distance traversed by the solvent.

TABLE IV

R_f Values for Several Anions with Selected Solvent Mixtures

Anion	20	25	28	31	32
Molybdate	0.76	0.65	0.62	--	--
Isopoly Molybdate	0.27	0.01	0.30	--	--
Tungstate	0.39	0.39	--	0	0
Isopoly Tungstate	--	0.05	--	0	0
Phosphate	--	--	--	0.75	0.70
Phosphate*	--	0.88	--	0.78	0.79

*This phosphate determination was made on undipped paper.

the material deposited at the origin was of analytical reagent grade and the average density of the streak was about the same as that of the spot (visual observation with ultraviolet light), the streak was not caused by trace contaminants and, therefore, the chemical composition of the streak and the spot must be identical. Because it is known that materials of higher molecular weight move much more slowly than similar materials of lower molecular weight, the presence of an isopoly anion is indicated. A streak indicates the presence of a range of molecular weights. The separation between the streak and the spot indicates that the isopoly anion was present prior to chromatography, since the production of an isopoly anion from a simple anion during chromatography would result in a spot followed by, and continuous with, a streak, i.e., tailing.

F. Detection of Anions on Paper Chromatograms

The heteropoly, isopoly, and simple anions can be detected by ultraviolet irradiation, with sensitivity ordinarily increased by protracted irradiation. The observable result of this method is the formation of a blue anion reduction product, with the paper substrate serving as the reducing agent. However, this technique fails when silicone-dipped paper is used because contact between the anions and the paper is greatly hindered and several days must pass before the anions have diffused to the paper and can be photoreduced. A spray composed of 8-hydroxyquinoline and kojic acid has been found helpful in the detection of heteropoly and simple anions but not of isopoly anions. With this reagent, a visible yellow complex, which has increased sensitivity to ultraviolet light, is formed. Phosphate is detected by spraying the chromatogram first with ammonium molybdate and then with a sodium sulfite /N-methyl-p-aminophenol sulfate solution. This reagent is quite sensitive; only a very small amount of phosphate need be present to form an easily observed spot of phosphomolybdic acid.

G. Results

At the present time, mixtures of the following components can be resolved (as indicated by a study of the R_f values) and their constituents identified: 1) phosphomolybdic acid (PMA), phosphotungstic acid (PTA), simple molybdate and tungstate ions, and isopoly molybdate and tungstate ions. 2) PMA, PTA, and phosphate ion.

Both phosphate and simple or isopoly anions cannot be identified in mixtures because the latter are converted to heteropoly acids (such as phospho-12-molybdic) in the presence of phosphate ion by the acids in the chromatographic solvent mixtures. Also, the newly formed acids may interfere with the detection of heteropoly acids originally present.

H. Experimental Procedures

1. Separation

Chromatography paper (S&S No 2043-A) is cut into 3 x 14-inch strips and marked about 1 inch from one end with a pencil line across its width. At this line, called the origin, 2 microliters of the sample solution is deposited in a single small spot. (The sample solution consists of the material to be examined dissolved in distilled water in a concentration of 50 mg/ml.) Two samples may be examined on one 3 x 14-inch strip by depositing the materials about 1-1/4 inches apart at the origin. After the water has evaporated, the paper strips are center-folded along their length to help them to stand upright. They are then placed in a glass cylinder so that the margin at the origin is in the solvent. The glass cylinders are 3 inches in diameter and 18 inches long. The tops are beaded and ground so that the contents can be sealed by covering with a glass plate. About 19 ml of solvent is placed in the cylinder to saturate the atmosphere before the paper strips containing the sample spots are inserted. The strips are left in contact with the solvent overnight, removed the following morning, and air dried.

2. Detection Method - Dry

The dry chromatographic strips obtained by the separation procedure are examined with transmitted ultraviolet light, i.e., the light is shone through the paper strips, to determine the extent of migration of the sample.

3. Detection Method - Wet

a. Spray Technique Enough liquid is sprayed onto the dried chromatograms to moisten them thoroughly and uniformly. Where sequential spraying is indicated, the chromatograms are allowed to dry before applying additional spray reagent.

b. Phosphate Detection Spray The dry chromatograms are sprayed with a solution of 5 g of ammonium molybdate in 100 ml of 1 M sulfuric acid, then air dried in a hood. If phosphate is present a yellow spot of PMA will become apparent. This spot can be more easily detected by its ultraviolet absorption. A second spray, composed of 5 g of anhydrous sodium sulfite and 0.5 g of N-methyl-p-aminophenol sulfate (Metol) in 100 ml of water, will make this spot readily visible by reducing the PMA, thereby causing a blue-green color to form.

c. Molybdate and Tungstate Detection Spray The dry chromatograms are sprayed with a solution containing 2 g of 8-hydroxyquinoline and 1 g of kojic acid in 100 ml of ethanol. The anion spots and the background will become yellow upon drying. It is possible to detect the spots by transmitted ultraviolet light but the contrast is poor. Better contrast can be obtained by placing the dried chromatograms in an ammonia atmosphere for one-half hour. The background color will then fade, leaving only the yellow anion spots. This technique also enhances the detectability of the heteropoly acid spots.

I. Future Work

At this point, our progress indicates that we will be able to use chromatographic analysis as had been originally intended, that is, in the characterization of heteropoly acids and the detection of possible anhydride impurities. To characterize a material chromatographically one must know, in addition to the analytical data, its R_f in at least two completely different solvent systems. To detect anhydride impurities in a sample one must develop a sensitive method and determine the most effective sample size. Sufficient sensitivity might be developed through a study of reducing agents that can, independently or when followed by ultraviolet irradiation, generate the blue reduction product of the heteropoly acid. Spots other than those identified as the acid would be impurities. Proper sample size could be investigated with an empirical approach to find the maximum amount of the heteropoly acid sample which can be deposited on the paper without destroying the value of the chromatographic method. (Too large a quantity of material on the paper causes tailing and alters the R_f of a spot.)

V. Film Preparation

A. Discussion

The films evaluated during this program were prepared by centrifugally spinning a thin coating, consisting of the heteropoly acid and a resin in a mixed solvent, onto a very thin polyester substrate, and following this by drying. The apparatus consisted of a turntable spun at an appropriate speed. The desired amount of coating material was placed at the center of the substrate on the turntable and allowed to spread into a uniform film while spinning. This procedure is convenient and yields a film of uniform thickness and of low mass. Increased sensitivity to flash exposure is possible with this technique because the film temperature rises more quickly than in heavier materials and this should contribute to the response speed.

B. Procedure

Solutions of the heteropoly acid and a resin were prepared separately in n-propyl alcohol and methyl alcohol, respectively. The resins used were polyvinyl butyral (Shawinigan B-90) and partially hydrolyzed polyvinyl acetate (Shawinigan D-381). These solutions were mixed in proportions that would produce the desired concentrations of heteropoly acid in the resulting films, as indicated in Table V. The coatings were spun on a 1-mil polyester film (Mylar) substrate at 750 rpm for six seconds, and this was followed by drying.

TABLE V

Film Composition[a] and Response Data for

Films Exposed to Successive Xenon Flashes[b]

Drying Temp. (°F)	Initial Trans.	Trans. After Successive Exposures to Xenon Lamp 1	2	3	4	Footnote
		Film Composition: 10%PMA; 90%D381				
Ambient	0.89	0.89	0.89	0.89	0.89	
100	.89	.88	.88	.88	.88	
125	.89	.89	.89	.87	.87	
150	.83	.80	.79	.79	.78	
		Film Composition: 10%PMA; 90%B90				
Ambient	.87	.87	.86	.84	.82	
100	.88	.88	.87	.86	.84	
125	.77	.77	.77	.72	.72	
150	.79	.79	.74	.73	.73	
		Film Composition: 40%PMA; 60%D381				
100	.87	.85	.81	.77	.7?	
125	.74	.72	.54	.00084	-	c
150	.58	.004	-	-	-	c
		Film Composition: 40%PMA; 60%B90				
100	.87	.80	.75	.43	.15	c
125	.77	.67	.03	.03	-	
150	.67	.55	.20	-	-	c

a Film component symbols are explained on page vi; percentage compositions are by weight.

b Intensity of the flash was 0.5 g-cal/cm^2.

c Film scorched and cracked by last noted exposure.

TABLE V (Cont'd)

Drying Temp. (°F)	Initial Trans.	Trans. After Successive Exposures to Xenon Lamp 1	2	3	4	Footnote
	Film Composition: 40%PMA; 60%D381					
Ambient	0.87	0.86	0.86	0.85	0.82	
100	.89	.85	.85	.82	.80	
125	.58	.57	.51	.38	.25	c
150	.85	.0004	-	-	-	c
	Film Composition: 40%PMA; 60%B90					
Ambient	.85	.85	.003	-	-	c
100	.89	.73	.0017	-	-	c
125	.26	.00015	-	-	-	c
150	.068	.00015	-	-	-	c
	Film Composition: 71%PMA; 29%D381					
Ambient	.32	.025	-	-	-	c
	Film Composition: 71%PMA; 29%B90					
Ambient	.87	.87	.001	-	-	c
Ambient	.87	.78	.00008	-	-	
Ambient	.85	.69	.63	.00005	-	
150	.032	.008	-	-	-	
	Film Composition: 74.5%PMA; 25.5%B90					
Ambient	.35	.75	.0013	-	-	c
Ambient	.87	.77	.0029	-	-	c
Ambient	.82	.68	.62	.20	.0022	c
	Film Composition: 10%PVMA; 90%D381					
Ambient	.85	.83	.83	.83	.82	
100	.85	.85	.85	.85	.82	
125	.85	.85	.85	.82	.82	
150	.83	.83	.79	.79	.79	

c Film scorched and cracked by last noted exposure.

TABLE V (Cont'd)

Drying Temp.(°F)	Initial Trans.	Trans. After Successive Exposures to Xenon Lamp 1	2	3	4	Footnote
	Film Composition: 10%PVMA; 90%B90					
Ambient	0.86	0.86	0.82	0.82	0.81	
100	.85	.82	.80	.80	.79	
125	.82	.82	.82	.82	.82	
150	.82	.82	.32	.82	.78	
	Film Composition: 40%PVMA; 60%D381					
Ambient	.84	.82	.82	.80	.79	
100	.83	.82	.82	.82	.80	
125	.83	.83	.80	.80	.80	
150	.53	.13	.0028	-	-	c
	Film Composition: 40%PVMA; 60%B90					
Ambient	.86	.83	.76	.72	.038	
100	.82	.79	.77	.72	.48	
125	.72	.68	.58	.035	-	
150	.40	.032	-	-	-	
	Film Composition: 60%PVMA; 40%D381					
Ambient	.82	.82	.81	.80	.79	
100	.81	.81	.77	.77	.77	
125	.83	.79	.74	.71	.64	
150	.06	.00005	-	-	-	c
	Film Composition: 60%PVMA; 40%B90					
Ambient	.81	.77	.68	-	-	c
100	.81	.77	.70	.004	-	c
125	.29	.005	-	-	-	c
150	.04	-	-	-	-	c

c Film scorched and cracked by last noted exposure.

TABLE V (Cont'd)

Drying Temp.(°F)	Initial Trans.	Trans. After Successive Exposures to Xenon Lamp 1	2	3	4	Footnote
	Film Composition: 71%PVMA; 29%D381					
Ambient	.77	0.76	0.76	0.62	0.00007	c
100	.77	.75	.73	.73	.69	
125	.68	.68	.61	.00023	-	
150	.0013	-	-	-		c
	Film Composition: 71%PVMA; 29%B90					
Ambient	.77	.72	.00003	-	-	
100	.73	.66	.0037	-	-	c
125	.27	-	-	-	-	c
150	.02	-	-	-	-	c
Ambient	.71	.63	.00004	-	-	
Ambient	.83	.72	.67	.61	.00004	
	Film Composition: 74.5%PVMA; 25.5%B90					
Ambient	.73	.64	.00014	-	-	c
Ambient	.66	.19	.0008	-	-	c
Ambient	.83	.72	.68	.63	.00001	
	Film Composition: 10%PTA; 90%B90					
Ambient	.88	.88	.87	.87	.87	
100	.87	.87	.87	.87	.87	
125	.88	.88	.88	.88	.88	
150	.88	.88	.87	.87	.87	
	Film Composition: 40%PTA; 60%B90					
Ambient	.88	.88	.87	.87	.87	
100	.87	.87	.87	.87	.87	
125	.87	.87	.87	.87	.87	
150	.87	.87	.87	.87	.87	

c Film scorched and cracked by last noted exposure.

TABLE V (Cont'd)

Drying Temp. (°F)	Initial Trans.	Trans. After Successive Exposures to Xenon Lamp 1	2	3	4	Footnote
	Film Composition: 60%PTA; 40%B90					
Ambient	0.86	0.86	0.86	0.86	0.86	
100	.86	.86	.86	.86	.86	
125	.87	.86	.86	.85	.84	
150	.87	.87	.85	.85	.84	
	Film Composition: 71%PTA; 29%B90					
Ambient	.87	.86	.85	.81	.80	
100	.86	.86	.85	.82	.80	
125	.87	.86	.85	.83	.81	
150	.87	.87	.85	.83	.81	
	Film Composition: 75%PTA; 25%B90					
Ambient	.87	.86	.84	.82	.78	
	Film Composition: 10%STA; 90%B90					
Ambient	.82	.82	.82	.82	.82	
100	.76	.76	.76	.76	.76	
125	.76	.76	.76	.76	.76	
150	.83	.83	.82	.82	.82	
	Film Composition: 40%STA; 60%B90					
Ambient	.83	.83	.83	.83	.83	
100	.80	.80	.80	.80	.80	
125	.88	.88	.88	.88	.88	
150	.83	.83	.83	.83	.83	
	Film Composition: 60%STA; 40%B90					
Ambient	.85	.85	.85	.85	.85	
100	.84	.84	.82	.82	.82	
125	.76	.76	.75	.75	.75	
150	.12	.0025	-	-	-	c

c Film scorched and cracked by last noted exposure.

TABLE V (Cont'd)

Drying Temp.(°F)	Initial Trans.	Trans. After Successive Exposures to Xenon Lamp 1	2	3	4	Footnote
	Film Composition: 71%STA; 29%B90					
Ambient	0.83	0.83	0.82	0.82	0.81	
100	.84	.83	.80	.79	.79	
125	.42	.40	.28	-	-	c
150	.045	.00045	-	-	-	c
	Film Composition: 75%STA; 25%B90					
Ambient	.82	.82	.82	.82	.80	
	Film Composition: 10%STA; 90%D381					
Ambient	.84	.84	.84	.84	.84	
100	.84	.84	.84	.83	.83	
125	.89	.89	.89	.89	.89	
150	.88	.88	.88	.88	.88	
	Film Composition: 40%STA; 60%D381					
Ambient	.86	.86	.86	.84	.84	
100	.87	.87	.87	.87	.86	
125	.87	.87	.87	.87	.87	
150	.83	.83	.83	.83	.83	
	Film Composition: 60%STA; 40%D381					
Ambient	.83	.83	.83	.83	.82	
100	.84	.84	.84	.84	.84	
125	.82	.82	.81	.80	.78	
150	.48	-	-	-	-	c
	Film Composition: 71%STA; 29%D381					
Ambient	.85	.85	.84	.82	.82	
100	.82	.82	.82	.81	.81	
125	.72	.72	.70	.70	.68	
150	.20	.015	-	-	-	c, d

c Film scorched and cracked by last noted exposure.
d Film exposed at a distance of 1-3/8 inch from the flash tube. (Other films were exposed at a distance of 10 mm.)

TABLE V (Cont'd)

Drying Temp. (°F)	Initial Trans.	Trans. After Successive Exposures to Xenon Lamp 1	2	3	4	Footnote
	Film Composition: 75% STA; 25% D331					
Ambient	0.32	0.32	0.32	0.82	0.32	
	Film Composition: Sat SMA-B90					
Ambient	.33	.72	.63	.64	.58	
100	.32	.31	.73	.73	.66	
125	.10	-	-	-	-	c
150	.00033	.00033	.00035	.00032	.0003	d
	Film Composition: Sat SMA-D381					
Ambient	.34	.70	.65	.42	.07	c
100	.30	.75	.53	.30	.005	
125	.011	.00025	-	-	-	c
150	.0004	.0004	.00037	.00032	.00028	d

c Film scorched and cracked by last noted exposure.
d Film exposed at a distance of 1-3/8 inch from the flash tube. (Other films were exposed at a distance of 10 mm.)

The films prepared in this manner were given, prior to testing, different and non-cumulative drying treatments as follows: a) at ambient temperature, b) at ambient temperature plus one hour at 100°F, c) 24 hours at 125°F, and d) 12 hours at 150°F. These conditions were used because prior work had indicated that, until heated for a critical time period, heteropoly acid films are not very sensitive to radiation exposure.

VI. Spectral Analysis of Heteropoly Acids and Heteropoly Acid Films

A. Acids

After chromatographic purification, solution spectra of the heteropoly acids were obtained in n-propyl alcohol at a concentration (by weight) of 0.001 percent over the 200-400 mμ range and 1 percent over the 400-2200 mμ range. All the acids examined absorbed strongly in the 200-400 mμ range and weakly, if at all, in the 400-2200 mμ range. One of the strongest absorbers in the 400-2200 mμ region was phosphomolybdic acid, the spectrum of which is shown in Figure 1. The absorption spectra of the acids were also obtained with each of the film-forming resins (B-90 and D-381) added to the solution. For these spectra the concentration of acid in each of the two spectral ranges remained the same while the concentration of the resin was 0.003 and 3 percent, respectively. A typical spectrum of this type is that of silicotungstic acid and B-90 resin in n-propyl alcohol (Fig. 2). All the acid-resin solutions absorbed very strongly at 200-400, weakly at 1400-1500, and strongly at 1900-2000 mμ.

B. Acid Films

Spectra of many films were obtained after the drying operation but before exposure to constant high-intensity light. The absorption intensity varied considerably depending on the method of drying. One exception was a film composed of 71 percent phosphotungstic acid and 29 percent B-90 resin. This film remained clear from about 350 to 2200 mμ without dependence on the drying temperature. A representative absorption sequence is shown in Figure 3 for films containing phosphovanadomolybdic acid. These spectra show very little absorption, from 500 mμ up, for a film dried at ambient temperature, whereas the absorption is much greater for a film dried at 150°F.

No spectra were taken of the films after exposure to a high intensity flash.

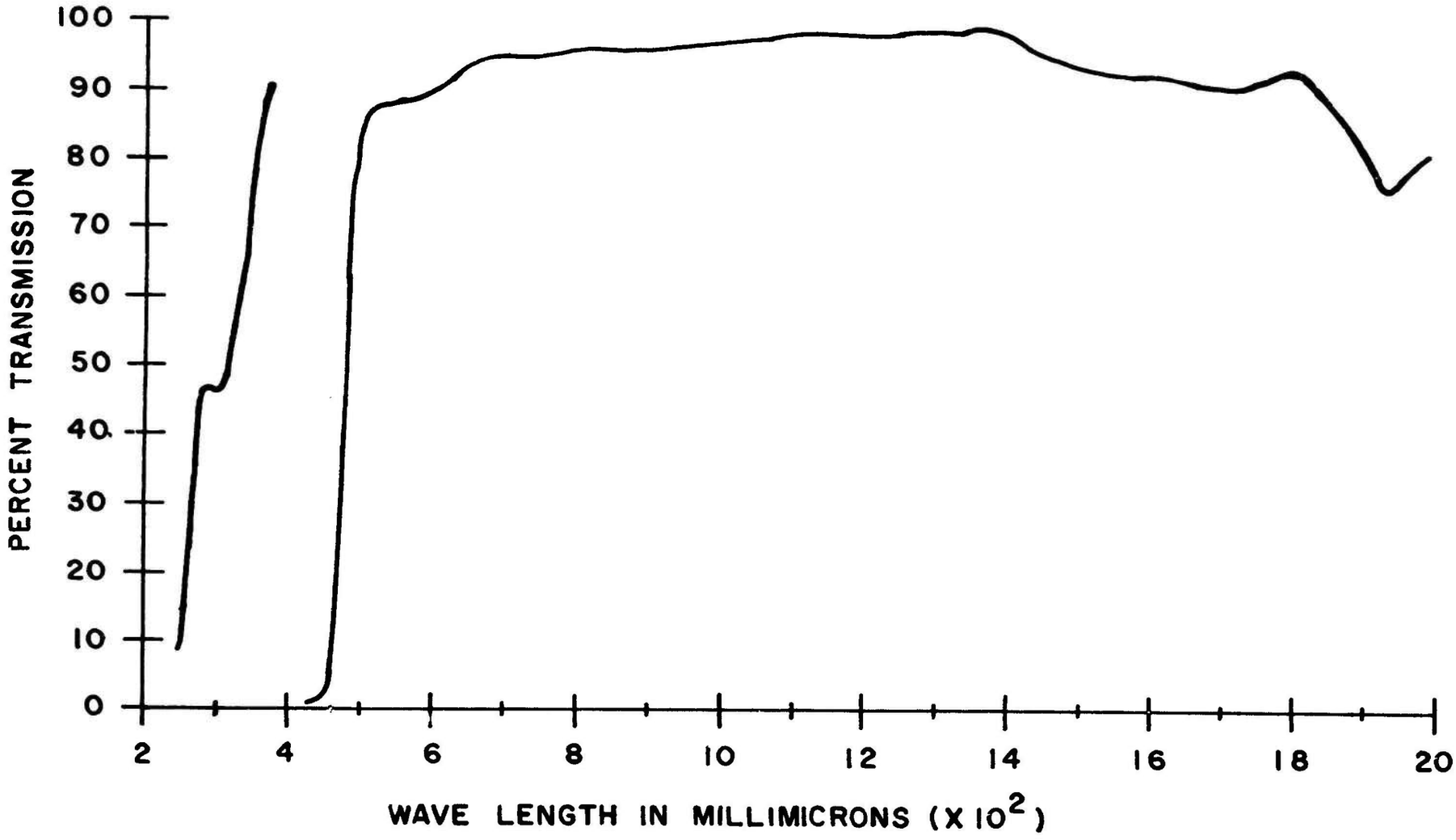

Figure 1. Spectrophotometric Curve of Phosphomolybdic Acid in n-Propyl Alcohol versus n-Propyl Alcohol Reference.

Concentration: for 2-400 mμ, 0.001%
(by wt) for 400-2000 mμ, 1.0%

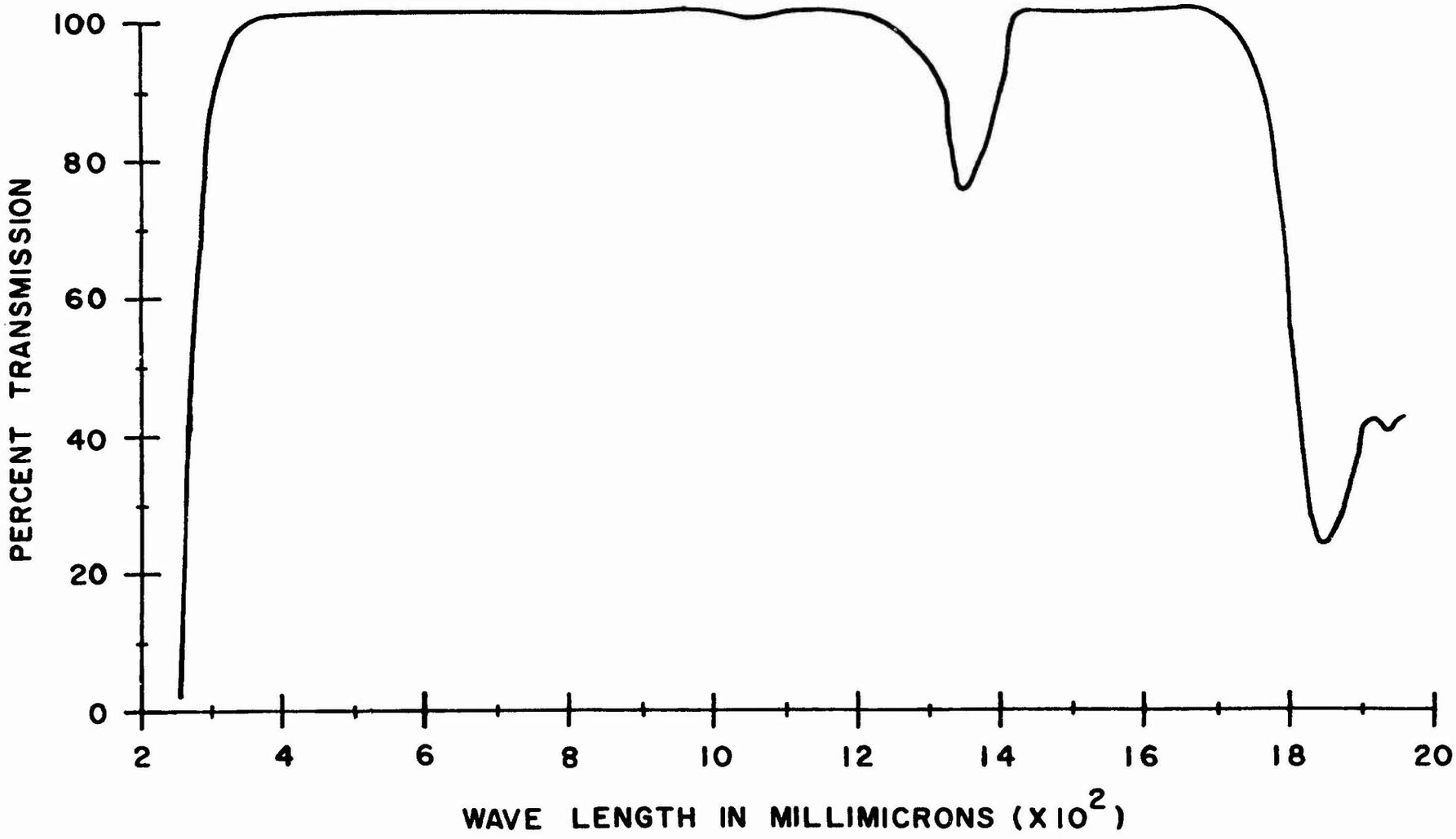

Figure 2. Spectrophotometric Curve of Silicotungstic Acid with B-90 Resin in n-Propyl Alcohol Solution versus n-Propyl Alcohol Reference.

Resin concentration: for 2-400 mμ, 0.003%
(by wt) for 400-2000 mμ, 3.0%

Acid concentration: for 2-400 mμ, 0.001%
(by wt) for 400-2000 mμ, 1.0%

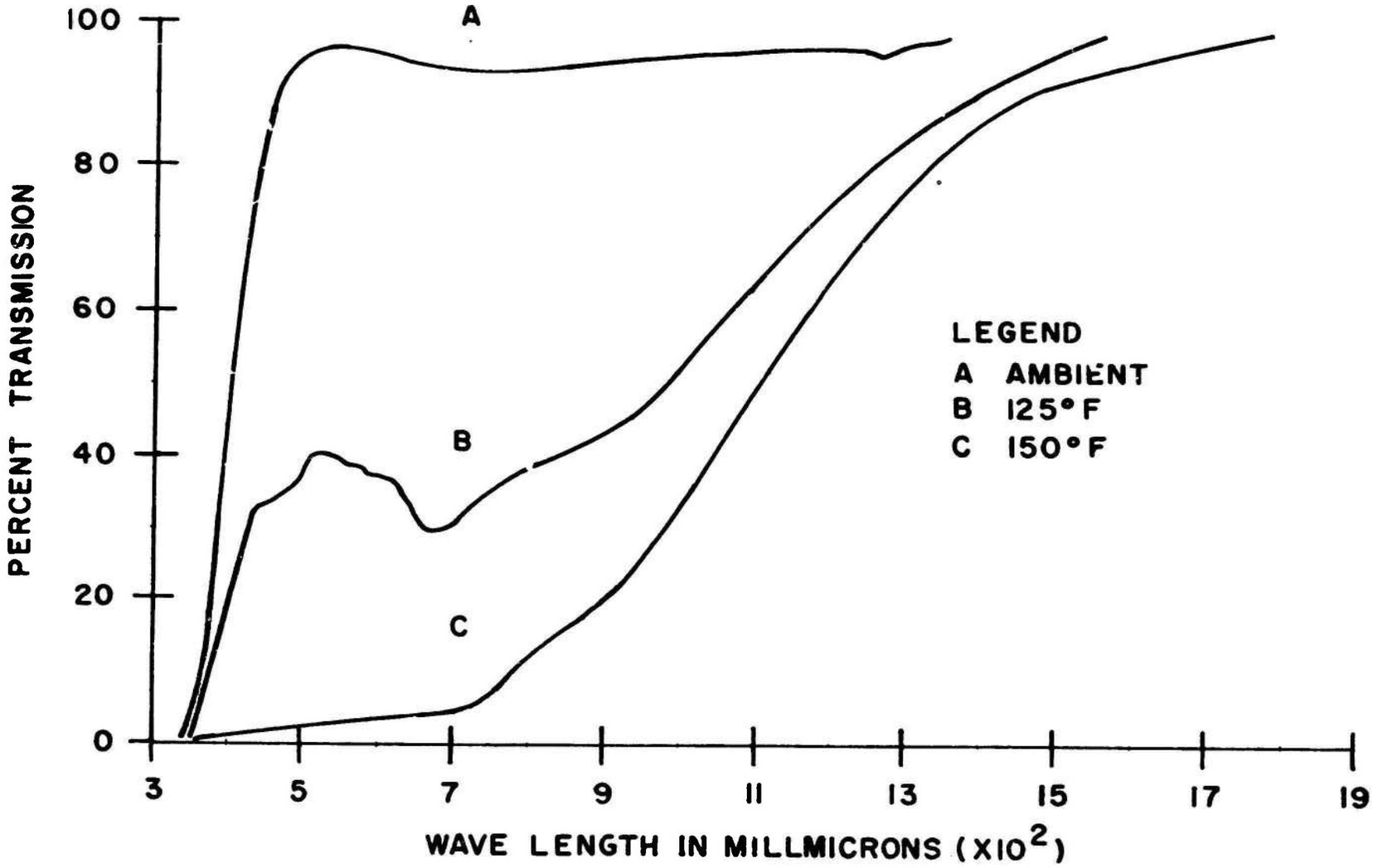

Figure 3. Spectrophotometric Curve of a B-90 Resin - Phosphovanadomolybdic Acid Film on Mylar Substrate versus Mylar Reference.

(The temperatures refer to the heat treatments described in the text.)

VII. Heteropoly Acid Film Test Procedures, Equipment, and Calculations

A. Exposure of Film to "Fluorescent" Ultraviolet Light

The films were placed 1-1/2 inches from a 15-watt tubular fluorescent light bulb (G. E. Astrolite No. FT15T8-BLB) and exposed for one-half hour. The percentage of light transmission of each film was measured before and after exposure. The FT15T8 bulb peaks at 353 mμ and the entire band is nearly symmetrical, having a half-band width of 375A°.

B. Exposure of Film to a Xenon Flash

The films were placed 10 mm from the closest part of the helix of a xenon lamp (G. E. No. FT-403) and exposed to successive flashes. The percentage of light transmission of each film was measured before and after each successive exposure. The flash lamp was operated at 500 watt-seconds and delivered approximately 0.5g - cal/cm^2 to the film. The flash duration was 500 microseconds, with peak intensity reached 1 millisecond after triggering.

The spectral distribution of the xenon flash was measured by the use of fixed filters. The measured energy below 430 mμ, incident upon a surface 10 mm from the lamp helix, was 0.006 g-cal (12% of the total energy), which should be adequate to effect an optical density change in the exposed film. The ultraviolet region is the active region for effecting optical density changes in these materials.

C. Exposure of Film to a Xenon-Mercury Arc (action spectra)

The films were exposed to light from a 1000-watt A.C. xenon-mercury compact arc (Hanovia 537B-9) which was passed through a quartz prism before reaching the sample. The xenon-mercury emits a collimated beam that is dispersed by the prism to provide a spectrum in the ultraviolet and visible regions. This procedure allows for the selection of specific bands. The spectral bands in the dispersed beam were determined by using fluorescent papers and the spectral distribution data provided by the manufacturer. The optical density of the films was measured both before and after exposure. The spectral sensitivity (S), i.e., the film darkening due to exposure to a particular spectral band, was calculated for the films exposed by the following formula:

$$S_\lambda = 2\,(D_2 - D_1) \,/\, (RE_\lambda)\,(BW)\,(1 - T_\lambda)$$

where S is the spectral sensitivity at wavelength λ,

D_2 is the optical density of the test film after exposure to a spectral energy band centered upon wavelength λ,

D_1 is the optical density of the film before exposure,

RE_λ is the relative energy of the source at wavelength λ as given in the manufacturers literature,

BW is the band width of the prism-dispersed source (in millimeters), and

T is the transmittance of the film at wavelength λ.

The spectral sensitivity is thus a measure of the efficiency with which a particular wavelength of radiation produces a visible change in the optical density of an exposed film.

VIII. Heteropoly Acid Film Test Results

A. Films Exposed to Ultraviolet Light

Films containing phosphotungstic (PTA), silicotungstic (STA), silicomolybdic (SMA), or phosphovanadomolybdic (PVMA) acid, in varying concentration and dried under different conditions (see Section V), were exposed to ultraviolet light as described above (Section VII, Part A). The light transmission of films before and after a one-half hour exposure is recorded in Table VI.

The order of ultraviolet sensitivity, which is limited to the 337-370 mu region by the lamp, appears to be SMA = PMA > PVMA = PTA > STA. The data also suggest that, as a rule, the greater the heteropoly acid concentration, the greater the optical density change in the film.

A back reaction, in opposition to the photochemical reaction, is indicated by several instances where the transmittance of a film increased after irradiation. For example, the film containing 40 percent STA and 60 percent B-90 resin and dried at 150°F increased from 81 to 85 percent transmission. Although the time of irradiation is known, it is not known how long after exposure the final transmittance was read. The back reaction may not be a significant factor in the response of these films to a flash, since the transmission increases were small. It is assumed that this reaction is dependent upon the oxygen concentration. In order to prove the significance of the back reaction, the kinetics of the forward and reverse reactions should be studied.

Table VI

Light Transmission Data for Films Exposed to Ultraviolet Radiation from a Fluorescent Lamp*

Film Composition (% by weight)	Drying Temp.(°F)	Initial Trans.	Trans. After 1/2 Hr. Exposure to UV Lamp
10%PTA; 90%B90	Ambient	0.88	0.87
" "	100	.875	.86
" "	125	.875	.865
" "	150	.86	.86
40%PTA; 60%B90	Ambient	.875	.87
" "	100	.875	.86
" "	125	.865	.86
" "	150	.87	.85
60%PTA; 40%B90	Ambient	.87	.84
" "	100	.87	.84
" "	125	.86	.845
" "	150	.87	.83
71%PTA; 29%B90	Ambient	.87	.83
" "	100	.87	.71
" "	125	.86	.78
" "	150	.865	.72
75%PTA; 25%B90	Ambient	.87	.54
10%STA; 90%B90	Ambient	.88	.875
" "	100	.87	.855
" "	125	.83	.82
" "	150	.825	.825
40%STA; 60%B90	Ambient	.87	.865
" "	100	.89	.88
" "	125	.87	.87
" "	150	.81	.85

*FT15T8-BLB, General Electric Company

Table VI (Cont'd)

Film Composition (% by weight)	Drying Temp.(°F)	Initial Trans.	Trans. After 1/2 Hr. Exposure to UV Lamp
60%STA; 40%B90	Ambient	0.86	0.855
" "	100	.88	.86
" "	125	.745	.745
" "	150	.10	.14
71%STA; 29%B90	Ambient	.86	.78
" "	100	.87	.80
" "	125	.45	.45
" "	150	.03	.032
75%STA; 25%B90	Ambient	.38	.76
10%STA; 90%D381	Ambient	.89	.885
" "	100	.89	.39
" "	125	.875	.875
" "	150	.88	.38
40%STA; 60%D381	Ambient	.88	.87
" "	100	.89	.89
" "	125	.87	.87
" "	150	.81	.84
60%STA; 40%D381	Ambient	.87	.87
" "	100	.88	.86
" "	125	.80	.745
" "	150	.53	.55
71%STA; 29%D381	Ambient	.87	.82
" "	100	.88	.815
" "	125	.74	.60
" "	150	.22	.24
75%STA; 25%D381	Ambient	.87	.81
Sat'd SMA-D381	Ambient	.725	.37
" "	100	.73	.36
" "	125	.135	.072
" "	150	.0024	.0017

Table VI (Cont'd)

Film Composition (% by weight)	Drying Temp.(°F)	Initial Trans.	Trans. After 1/2 Hr. Exposure to UV Lamp
Sat'd SMA-B90	Ambient	0.75	0.28
" "	100	.74	.28
" "	125	.023	.016
" "	150	.0012	.0012
10%PMA; 90%D3	Ambient	.89	.86
" "	100	.88	.83
" "	125	.87	.81
" "	150	.86	.80
40%PMA; 60%D381	Ambient	-	-
" "	100	.77	.54
" "	125	.68	.39
" "	150	.60	.43
60%PMA; 40%D381	Ambient	-	-
" "	100	.87	.82
" "	125	.55	.34
" "	150	.14	.11
71%PMA; 29%D381	Ambient	-	-
10%PMA; 90%B90	Ambient	.87	.81
" "	100	.85	.79
" "	125	.78	.72
" "	150	.84	.785
40%PMA; 60%B90	Ambient	-	-
" "	100	.84	.57
" "	125	74	.535
" "	150	.70	.52
60%PMA; 40%B90	Ambient	-	-
" "	100	.74	.38
" "	125	.28	.19
" "	150	.108	.073
71%PMA; 29%B90	Ambient	.745	.30
75%PMA; 25%B90	Ambient	.72	.29

Table VI (Cont'd)

Film Composition (% by weight)	Drying Temp.(°F)	Initial Trans.	Trans. After 1/2 Hr. Exposure to UV Lamp
10%PVMA; 90%D381	Ambient	0.86	0.82
" "	100	.86	.83
" "	125	.86	.81
" "	150	.84	.77
40%PVMA; 60%D381	Ambient	.80	.70
" "	100	.80	.72
" "	125	.80	.69
" "	150	.58	.46
60%PVMA; 40%D381	Ambient	.72	.55
" "	100	.72	.66
" "	125	.71	.47
" "	150	.0048	.0037
71%PVMA; 29%D381	Ambient	.63	.42
" "	100	.625	.44
" "	125	.57	.34
" "	150	-	-
10%PVMA; 90%B90	Ambient	.87	.80
" "	100	.87	.81
" "	125	.87	.81
" "	150	.86	.81
40%PVMA; 60%B90	Ambient	.83	.58
" "	100	.83	.58
" "	125	.78	.55
" "	150	.45	.375
60%PVMA; 40%B90	Ambient	.78	.40
" "	100	.78	.40
" "	125	.35	.23
" "	150	.04	.034
71%PVMA; 29%B90	Ambient	.70	.35
" "	100	.69	.325
" "	125	.30	.15
" "	150	.031	.015
75%PVMA; 25%B90	Ambient	.68	.27

B. Films Exposed to a Xenon Flash

Films of the same composition as those exposed to ultraviolet light were given successive flashes from a Xenon flash tube in the manner described in Section VII B. The optical density data recorded before and after each flash (Table V) reveal that silicotungstic acid and silicomolybdic acid films are comparatively insensitive to the xenon flash. However, the phosphovanadomolybdic acid film containing 70 percent acid in B-90 resin and dried at ambient temperature was sensitive enough to reach a density of 4.1 (0.01% transmission), from a density of 0.11 (77% transmission), during the second flash from the xenon lamp. The most sensitive material was a phosphomolybdic acid film, which opaqued to a density 3.4 (0.04% transmission) from a density of 0.07 (85% transmission) on the first exposure to a xenon flash. But, unfortunately, it was somewhat sensitive to the heat of the flash. This film had been baked at 150°F for 12 hours before testing and contained 40 percent PMA in D-381 resin. A closely related film, prepared with B-90 resin, was much too heat-sensitive to afford comparative data.

The significant information revealed by Table V is that, of the acids reviewed, the phosphomolybdic and phosphovanadomolybdic acids show the most promise of success for development into a device for flashblindness protection.

C. Films Exposed to a Dispersed Xenon-Mercury Arc

Action spectra were obtained of phosphomolybdic, phosphovanadomolybdic, and phosphotungstic acid films using the equipment and procedure described in Section VII, Part C. However, before specific absorption bands in these spectra can be assigned to the heteropoly acids, more specific knowledge of the exact relative energies of the source at each wavelength will have to be obtained. The average relative spectral energy values published by the manufacturer (Hanovia Lamp Division, Engelhard Industries, Inc.) for the lamp used were not adequate for this type of study. For this reason, no meaningful conclusions can be drawn about the behavior of the acids and, therefore, the data obtained are not presented.

IX. Summary and Conclusions

The purpose of this study was to determine the feasibility of using heteropoly acids as the active components of films which darken upon exposure to an intense flash of radiation. A film for nuclear-flash eye protection is assumed to require the following characteristics: initial transmission, 80 percent in visible; image distortion, none; opaquing rate, to a density of 4 in 50 μsec when exposed to a suitable source; stability in storage, no change in properties after 6 months between 125°F and -65°F; and operational temperature range, 115°F to -65°F.

To carry out this study, four acids and one salt were synthesized and four other acids were obtained commercially. It was necessary to work out chromatographic techniques for the purification of all the acids. Potassium arseno-12-molybdate, phospho-18-molybdic acid (PMA), arseno-12-molybdic acid, purpureo phospho-12-vanadic acid, and boro-tungstic acid were synthesized. Phosphovanadomolybdic acid (PVMA), phosphotungstic acid (PTA), silicotungstic acid (STA) and silico-molybdic acid (SMA) were obtained commercially. Five of these acids (PMA, PVMA, PTA, STA, and SMA) were evaluated in films of polyvinyl butyral (B-90) and partially hydrolysed polyvinyl acetate (D-381) resins. The films were examined for heat stability, response to a xenon flash, sensitivity to ultraviolet light, and response to a dispersed xenon-mercury arc. A light transmission change from 85 to .04 percent (optical density 0.07 to 3.4) was achieved in a film of phosphomolybdic acid and polyvinyl acetate in response to the flash, although some heat damage from the flash was observed. Most of the films were heat resistant up to 150°F for at least 12 hours. A few individual films containing phosphovanadomolybdic acid scorched and cracked within 24 hours at 125°F.

The photosensitivity of phosphomolybdic, phosphotungstic, and phosphovanadomolybdic acids was measured for the first time. This was done by using xenon-mercury arc light dispersed through a quartz prism. Although the results are inconclusive because quantitative calibration data were not available during the contract period, phosphomolybdic acid appears to be the most photosensitive. All three acids were shown to be photosensitive to radiation below 400 mμ by this method.

The feasibility of employing films similar to those studied during this program for flashblindness protection is indicated by the following achievements:

1. Films of good optical quality were produced.

2. Film transmittances of 80 percent and higher were attained.

3. Some films became opaque to an optical density of 3.4 from an optical density of 0.07 when exposed to a millisecond xenon flash.

Thus, the feasibility of obtaining a film or coating having good optical qualities, high initial transmittance in the visible, and high opacity when irradiated by a flash has been demonstrated, but a final density of 4 within 50 microseconds and the storage and operational requirements have not yet been achieved.

X. Recommendations

1. Although storage for extended periods at temperatures up to 100°F did not affect any of the films studied, further work at higher and very low temperatures is required to meet the design requirements. During the present contract, long-term storage at different temperatures and tests at the required extremes of climate were not feasible because films having promising design characteristics were not available early enough. However, preliminary affirmative stability data were collected while drying the films at 125°F and even at 150°F for several hours. Further work is particularly recommended on the most promising film compositions: 40 percent phosphomolybdic acid with 60 percent polyvinyl acetate resin, and 71 percent phosphovanadomolybdic acid with 29 percent polyvinyl resin.

2. While the reported density measurement of 3.4 does not meet the design requirement of 4.0, it can readily be shown by the application of the density ratio that heteropoly acid films have a potential for meeting this goal. For example, the density ratio (q), defined as a ratio of the density of the opaqued film (D_2) to the density of the film before exposure (D_1), may be used as a figure of merit in evaluating film response capability. Stated mathematically the density ratio = $q = \frac{D_2}{D_1}$.

The design requirements for a flashblindness protective film include an initial transmittance of 0.80 (0.1 density) and a final transmittance of 0.0001 (4.0)density) and thus a density ratio of 40:

$$q = \frac{D_2}{D_1} = \frac{4.0}{0.1} = 40$$

The density ratio obtained by the polyacid system described in this report (density change from 0.07 to 3.4) is 48.6:

$$q = \frac{D_2}{D_1} = \frac{3.4}{0.07} = 48.6$$

The fact that this polyacid system is capable of achieving a density ratio of 48.6 indicates its potential. If a heavier film of like composition were prepared, thus reducing the initial transmittance from 0.85 to 0.80 (0.07 to 0.10 density), an opacity of 4.86 density might be achieved after exposure to a flash. This would more than meet the design goal.

$$q = \frac{D_2}{D_1} \; ; \; D_2 = q \times D_1 = (48.6)\ (0.10) = 4.86$$

Proof of this concept should be high on the future work agenda.

3. We further recommend a study of the kinetics of the photoreaction and dark reaction of heteropoly acid films, both in the presence and absence of oxygen. This study would be very useful in improving the film response and heat stability that are now lacking.

4. Although several heteropoly acids were prepared, namely potassium arseno-12-molybdate, arseno-12-molybdic acid, purpureo phospho-12-vanadic acid and borotungstic acid, they were not evaluated as films. Extension of this work, including the synthesis of new acids as well as film preparation and evaluation, is recommended. Film-forming resins, other than B-90 and D-381, that seem to warrant evaluation should also be included.

5. Alkali metal salts of heteropoly acids should be evaluated in films. These salts, at elevated temperatures, result in the formation of characteristic bronze compounds that are highly colored and have, to a degree, metal-like properties. They might, therefore, afford a superior reflective surface when irradiated.

6. The design of an actual device into which heteropoly acid films can be incorporated for flashblindness protection is premature at this time because the state of the art is not far enough advanced. However, limited effort toward the choice of an effective design type is warranted.

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13 ABSTRACT

This report presents the details of a study made to determine the feasibility of using films containing one or more heteropoly acids for possible protection against flashblindness. Phosphomolybdic, phosphovanadomolybdic, phosphotungstic, silicotungstic, and silicomolybdic acids are evaluated.

Methods for the preparation and purification of heteropoly acids in general are given. Also given are details for the preparation and purification of specific compounds: potassium-arseno-12-molybdate, phospho-18-molybdic acid, arseno-12-molybdic acid, purpureophospho-12-vanadic acid, and borotungstic acid. Mixtures of phosphomolybdic and phosphotungstic heteropoly acids with simple and isopoly ions were separated by paper chromatography and identified by ultraviolet light and by spray techniques.

Films for evaluating the photochromic response were prepared by centrifugally spinning a thin film of acid-resin solution on a polyester substrate and evaporating the solvent. Photochromic response and capabilities were determined by 1) exposing the films to a xenon flash, an ultraviolet lamp, and a xenon-mercury arc; and 2) measuring the optical transmission or density before and after exposure. The response of several films, particularly phosphomolybdic acid in polyvinyl acetate (which changed from an optical density of 0.07 to a density of 3.4), indicates that further research in this area is warranted. Also, since several of the films were somewhat heat sensitive, a study of different resins is indicated.

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