Chem. Rev. **1998,** *98,* 359−387

A Survey of Applications of Polyoxometalates

Dimitris E. Katsoulis

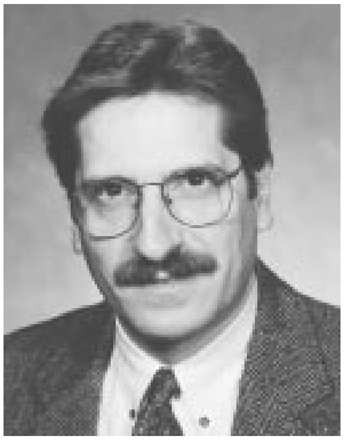
Dow Corning Corporation, Central Research and Development, Midland, Michigan 48686

Received June 2, 1997 (Revised Manuscript Received November 8, 1997)

Contents

I. Introduction

The field of polyoxometalates (POMs), although a mature field, continues to attract significant attention. The number of publications and patents continues to grow. New researchers are entering the field. The scientific communities of fast-growing new economic/technology powers such as Peoples Republic of China and India are becoming important contributors of the total number of worldwide publications on POMs. Figure 1 depicts the growth of the POM literature per year since 1966. In 1996, according to *Chemical Abstracts*, nearly 600 refereed publications and over 120 patents were issued in reference to the POM chemistry and technology. Figure 2 shows the countries where the most research activity exists based on publications, and Figure 3 lists the 10 largest patent assignee countries in the world. Japan issues 40% of the worldwide patent literature followed by the USA with ∼17%. The applications of POMs are based on combinations of so-called "value-adding properties" which are summarized in Table 1.



Dimitris E. Katsoulis was born in Athens, Greece in 1955. He received a B.S. degree in Chemistry from University of Athens in 1977. He subsequently joined the research group of Prof. Michael T. Pope at Georgetown University and obtained a Ph.D. degree in 1985. He continued with a postdoctoral assignment at Georgetown University, and in 1988 he joined the Science and Technology function of Dow Corporation in Midland Michigan. He is currently an Associate Research Scientist in the Rigid Materials Science Expertise Center (Central R&D) in Dow Corning. His research interests include hybrid materials, with focus on siloxane-polyoxometalate compositions, sol−gel chemistry, silsesquioxanes, gel systems, polymer matrix composites, and nanocomposites.

From the above-listed properties, the applications of POMs are centered primarily on their redox properties, photochemical response, ionic charge, conductivity, and ionic weights. The majority of the patent and applied literature is devoted to the applications of the Keggin type heteropolyacids (HPA) and their salts. Primarily $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $H_4SiMo_{12}O_{40}$, and $H_4SiW_{12}O_{40}$ are used as the main examples for many applications. Their popularity can be attributed to a large extent to the enormous volume of literature over several decades that describes their fundamental chemistry and to their commercial availability, which makes them convenient starting materials. Approximately two-thirds of the applied chemistry/technology literature describes applications that are based on these POMs.

S0009-2665(96)00398-6 CCC: $30.00

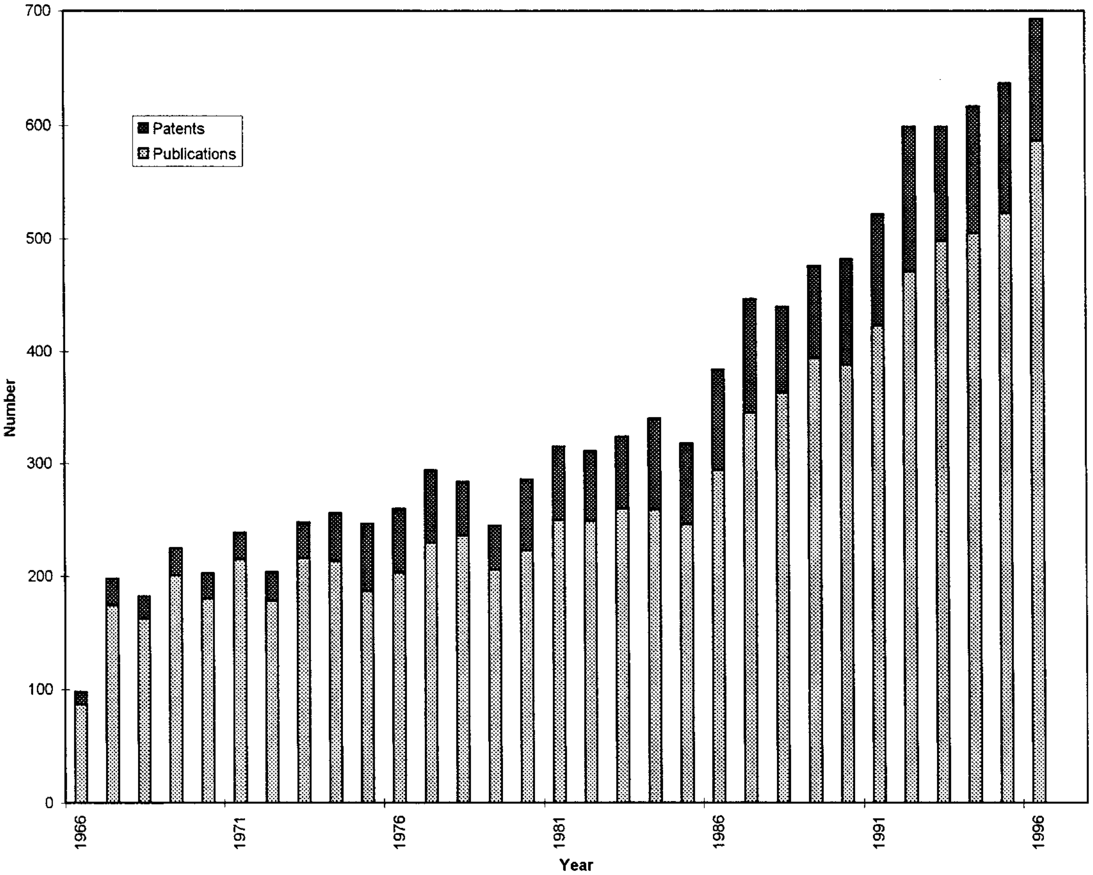


Figure 1. Publication and patent growth on POMs since 1966. Source: *Chemical Abstracts*.

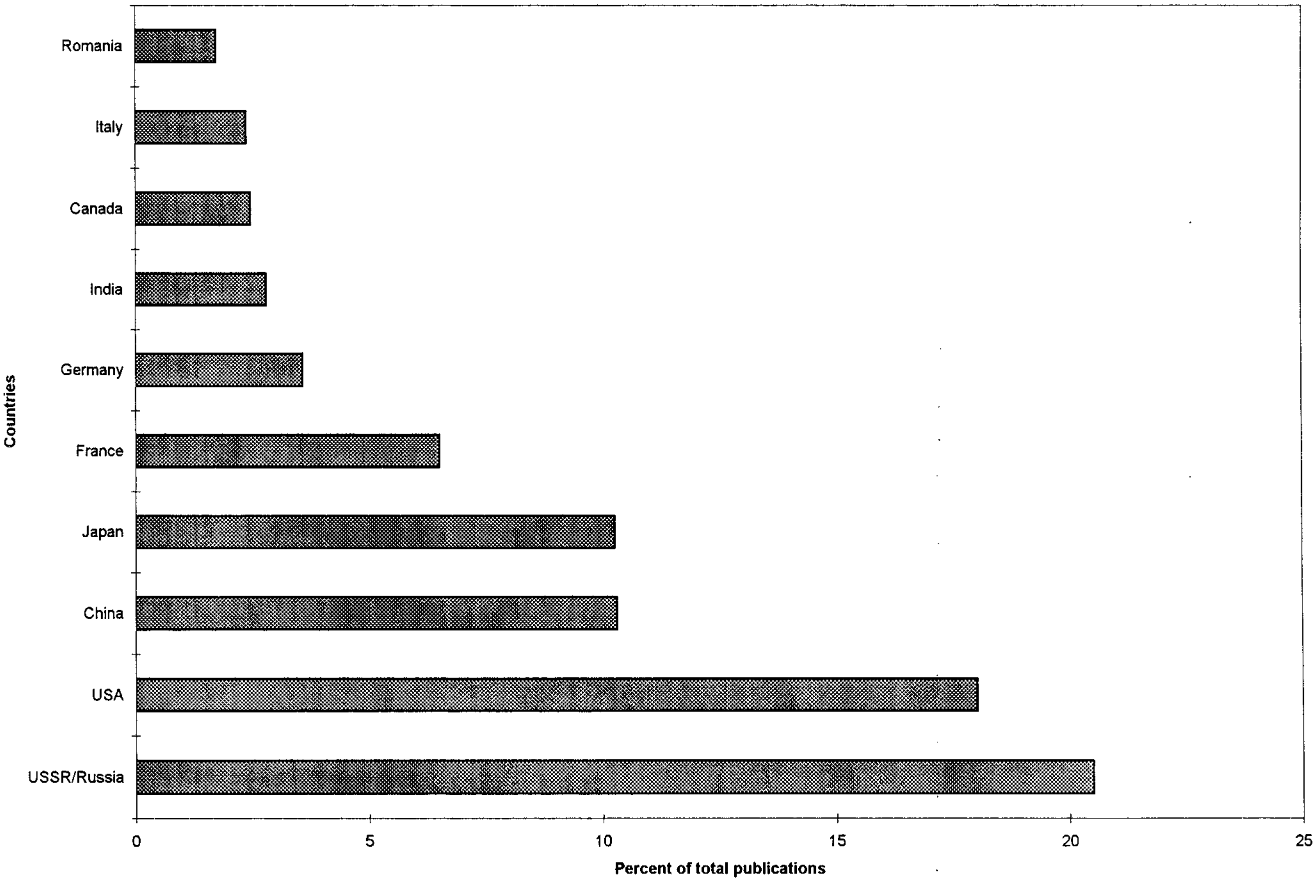


Figure 2. The 10 countries with the largest number of POM publications. Source: *Chemical Abstracts*.

Given the enormous number of POM complexes available and their variability in properties, it is obvious that plenty of room exists for expanding the exploration of the opportunities for these materials.

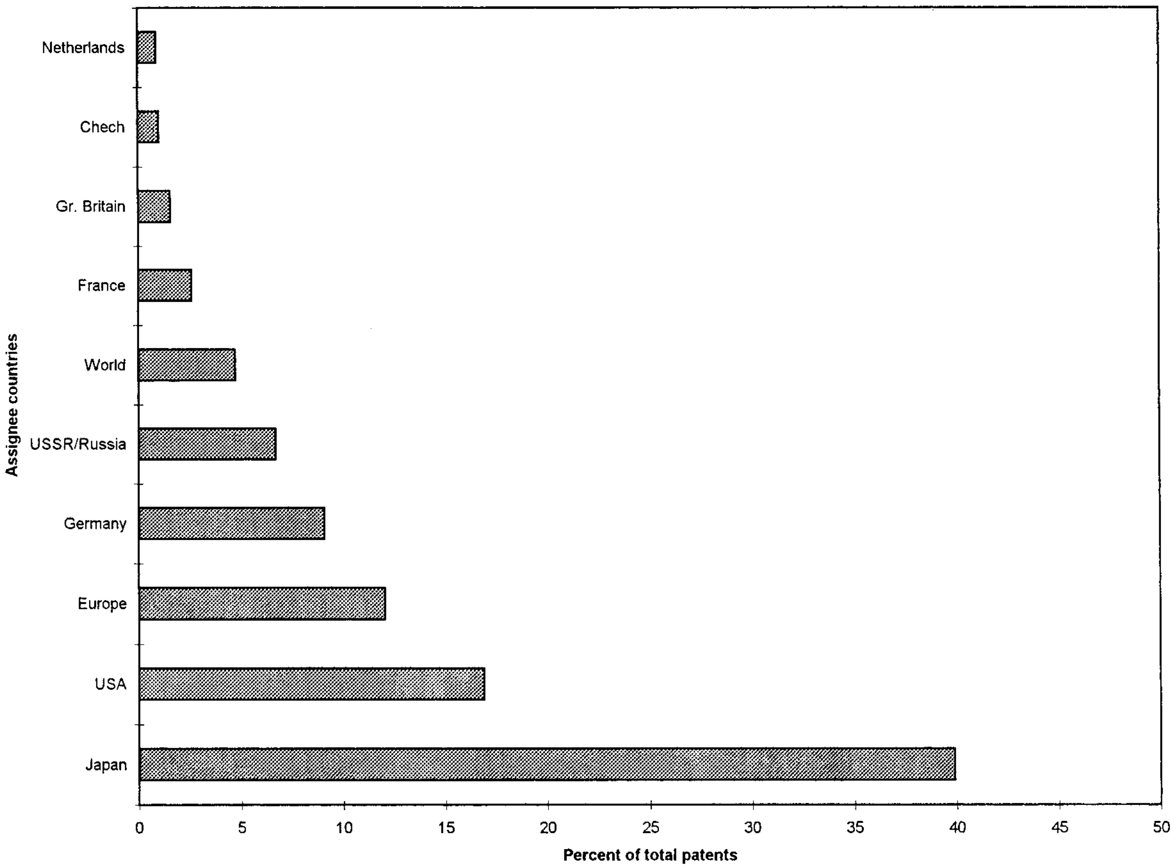


Figure 3. The 10 largest POM patent assignee countries. Source: *Chemical Abstracts*.

Table 1. "Value-Adding Properties"of Polyoxometalates

1.	metal oxide like
2.	stable (H_2O/air, T): *processing advantage*
3.	large size (diameter, 6–25 Å)
4.	discrete size/discrete structure (confined geometric factors)
5.	anions (charge from −3 to −14)
6.	high ionic weight ($10^3 - 10^4$)
7.	fully oxidized compounds/reducible
8.	variable oxidation numbers for the addenda atoms ($E_{1/2} = 0.5$ to -1.0 V vs SCE)
9.	color of oxidized forms different from color of reduced forms
10.	photoreducible
11.	arrhenius acids ($pK_a < 0$)
12.	incorporate over 70 elements and form large number of structures: *processing advantage*
13.	acid forms very soluble in H_2O & other oxygen carrying solvents (ethers, alcohols, ketones); also soluble or transferable into nonpolar solvents: *processing advantage*
14.	hydrolyzable to form deficient structures: *processing advantage*

As the multidisciplinary approach in science keeps increasing, it is just a matter of time before the widening of the scope of this field becomes a reality. One course should always be to weigh the cost factors against the value of the application.

The majority of the applications of POMs are found in the area of catalysis. About 80–85% of patent and applied literature claims or investigates POMs for their catalytic activity. These applications are reviewed in two separate sections in this issue. The remaining 15–20% of the applications can be grouped in the categories of Table 2.

This review, which is based mainly on patent literature and on referee literature of applied research, summarizes the developments in applications of POMs other than catalysis and medicine. It is well-known that claims in patent literature do not necessarily represent commercial successes as well as proven scientific events. Thus patents with specific examples and data were sought for further analysis as being more reliable. Table 3 lists uses of specific POMs from illustrative examples from the patent and refereed literature.

The review is organized in 18 sections on the basis of the material form that POMs are found (or proposed to be) in applications, or on the basis of a particular POM value-adding property (Table 1). Half of the sections that follow describe applications where POMs function within coatings, membranes, or thin films. These include corrosion resistant coatings, POMs in sol–gel matrixes and in conductive and nonconductive polymer membranes, and POMs as surface modifiers of substrates (i.e. carbon electrodes). The remaining sections describe uses of

Table 2. Categories of Applications for POMs (Derived from Patent Literature; Excluding Catalysis and Medicine)

1. coatings
2. analytical chemistry
3. processing radioactive waste
4. separations
5. sorbents of gases
6. membranes
7. sensors
8. dyes/pigments
9. electrooptics
10. electrochemistry/electrodes
11. capacitors
12. dopants in nonconductive polymers
12. dopants in conductive polymers
13. dopants in sol−gel matrixes
14. cation exchangers
15. flammability control
16. bleaching of paper pulp
17. clinical analysis
18. food chemistry

POMs as pigments, toners, wood pulp bleaching agents, reagents for chemical/biochemical analysis and for nuclear waste processing, and some miscellaneous applications.

II. Corrosion Resistant Coatings

Of the most widely used methods to combat corrosion of metal surfaces is the utilization of corrosion inhibitors such as chromates, phosphates, or silicates. Chromates, known as *anodic passivating inhibitors*, cause a large positive shift on the corrosion potential of a metal substrate such as steel during polarization measurements. Mechanistic studies suggest that metal protection is afforded by a combination of adsorption and oxide formation on the steel surface. The main concern with the use of chromate inhibitors is their toxic nature.

Polyoxometalates have relatively low toxicity as compared to chromates; they accept electrons without major changes of their structures and form insoluble salts with large cations. These properties make them attractive as oxidizing and film-forming corrosion inhibitors.

Thus a significant activity is encountered in the applied literature that claims known and unidentified POM compositions as corrosion inhibitors as such and in formulations with suitable delivery systems.

A recent study by Lomakina et al.[1] investigated the corrosion inhibition of POMs for aluminum and its alloys under high-temperature aqueous conditions. Such alloys are considered for use as construction materials in atomic industries, and thus a corrosion inhibitor must exhibit high radiation stability.

The corrosion rates of aluminum alloys (Al−Ni−Fe) as measured by the increase of sample weight (due to formation of hydrous aluminum oxides) as a function of time were reduced significantly in the

Table 3. Applications of Specific POMs from Illustrative Examples in the Patent and Refereed Literature

examples of POMs	application	reference
$H_4PMo_{11}VO_{40}$	modification of carbon electrodes, capacitors	188
$K_xH_{4-x}PMo_{11}VO_{40}$		
$H_5PMo_{10}V_2O_{40}$		
$(NH_4)_6P_2Mo_{18}O_{62}$		
$H_3PMo_{12}O_{40}$		189
$H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$	electrolytic capacitors	217, 218
$H_4SiW_{12}O_{40}$, $H_4SiMo_{12}O_{40}$		
$[C_{16}H_{33}N(CH_3)_3]_xH_{4-x}SiMo_{12}O_{40}$	corrosion resistant coatings, primers	11
$[C_{16}H_{33}N(CH_3)_3]_xH_{4-x}SiW_{12}O_{40}$		
$Na_5H_2PV_6Mo_6O_{42}$	corrosion inhibitor for steel St3 (mild steel)	6
$(NH_4)_{10}H_2W_{12}O_{42}$, $(NH_4)_6P_2W_{12}O_{62}$	corrosion inhibitors of Al alloys	1
$H_nP(Si)M(\equiv Mo,W)_{12}O_{40}$ with phosphosilicate pigments	metal pigments for coatings (automotive, roof, industrial)	23,24
$M_{3/2}PW_{12}O_{40}$ (M = Ni, Co, Cu, Zn)	hardeners in epoxy resins	77
$H_3PMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$	colorants for pigmenting paints, printing inks and plastics	87
$H_4SiMo_{12}O_{40}$,$H_4SiW_{12}O_{40}$	dyes for polyester and polyacrylonitrile fibers	85
$H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$		
$H_5PMo_{10}V_2O_{40}$, $Na_4PVW_{11}O_{40}$, $H_9P_2V_3W_{15}O_{62}$, $Na_6V_{10}O_{28}$	wood pulp bleaching	258, 264
$K_5SiVW_{11}O_{40}$, α-$Na_xH_{5-x}PMo_{10}V_2O_{40}$	wood pulp bleaching	259
α-$Li_xNa_{4-x}SiW_{12}O_{40}$	separation of heavy minerals from light minerals	283
$H_3PW_{12}O_{40}$	electrochromic−ion conducting gels, films, xerogels	38, 39, 52,
$H_3PW_{12}O_{40}$	photochromic coatings for copiers	107, 108
$[C_{16}H_{33}N(CH_3)_3]_6Mo_7O_{24}$, $[(C_4H_9)_4N]_3PW_{12}O_{40}$, $[C_{18}H_{37}N(CH_3)_2C_2H_5]_{10}[H_2W_{12}O_{40}]$	charge-controlling agents in toners	113
$H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $2(M)_2O \cdot P_2O_3 \cdot 5MoO_3 \cdot nH_2O$, M = Na, K, NH_4	hydrophilic treating solution for planographic printing plates	110
$[\text{metformin}]_2HPM(\equiv Mo,W)_{12}O_{40}$	determination of metformin HCl	150−152
$H_4SiW_{12}O_{40}$	treatment of cathode electrodes (vitreous C and graphite)	191
$H_4SiW_{12}O_{40}$	dopant of polyaniline and polypyrrole	244
$H_3PMo_{12}O_{40}$	dopant of poly(*N*-methylpyrrole)	244
$H_6P_2W_{18}O_{62}$	dopant in poly(1-naphthol)	243
$[(C_4H_9)_4N]_4[PW_{11}O_{39}Fe^{III}(OH_2)]$	dopant in polypyrrole	234
$H_4SiW_{12}O_{40}$	Au/*n*-Sb_2S_3 Schottky barrier solar cells	132
$H_4SiW_{12}O_{40}$ disk/SnO_2	electrochromic display device.	176
$H_3PW_{12}O_{40} \cdot nH_2O$	liquid H_2−O_2 fuel cell	180
$PW_{11}O_{39}Fe^{III}(OH_2)^{4-}$	electrode for NO determination	236
$H_3PMo_6W_6O_{40}$	as porous support for the purification of vent air	406
$H_5PV_2Mo_{10}O_{40}$	decontamination of mustard (HD) analogues	416
$(NH_3)_6[H_2W_{12}O_{40}]$, $H_3PW_{12}O_{40}$	flame retardant for aramid fibers	415

presence of isopoly or heteropoly tungstates. For example, an order of magnitude reduction in the corrosion rate of a Al−Ni−Fe alloy in pure water at 250 °C was observed when 100 mg/L $(NH_4)_{10}H_2W_{12}O_{42}$ or $(NH_4)_6P_2W_{18}O_{62}$ were added. Dodecamolybdophosphate, on the other hand, gave worse results and in some cases increased the corrosion rate possibly due to its instability in dilute solutions.

Electrochemical studies of these aluminum alloys in solutions that contained Cl^- and SO_4^{2-} ions in the presence of isopoly- and heteropolytungstates showed a consistent shift of the pitting corrosion potential toward more positive values, this potential being greatly dependent on the type of the added anion. For example, the pitting potential of a Al−Mg−Si alloy at 90 °C with 15 mg/L Cl^-, 50 mg/L SO_4^{2-}, and 100 mg/L $PW_{11}O_{39}Fe^{III}(OH_2)^{4-}$ exhibited a shift of more than 1 V to more positive values. This indicates the increased stability of the protective mixed metal oxide film formed in the presence of the POM.

XPS analysis of sample surfaces showed the formation of W^{5+} and W^{6+} in the oxide film. The peak intensities depended on the time of exposure to the tungstate solution. Reduction of W^{6+} was caused by Al^0 since no W^{5+} signal was observed when the aluminum surface was covered by an oxide film prior to immersion into the tungstate solution. Similar observations were made when polyoxomolybdates were used. Molybdate was incorporated into the film, and some molybdenum atoms were reduced to +5 oxidation state. Depth profile analysis by etching the films with argon showed that tungsten was present throughout the film (thickness, 1−2 μm) with slightly decreasing concentration with depth progression. The nature of the polytungstate in the film is unknown, although it has been hypothesized that alumino-containing polyoxotungstates are formed as part of the protective film.

Pretreatment of aluminum samples in solutions of polytungstates prior to exposure to corrosion experiments induced the formation of thinner hydrated oxide films than the pretreatment of aluminum samples in pure water. Thus the critical thickness leading to cracking and detachment of the film was not reached. (Thin films deform easier to release stresses). A lot of unknowns are obviously remain in this field and deserve further exploration.

Several investigators claimed/described the use of POMs as corrosion inhibitors in other substrates such as zinc and galvanized steel. Wu et al.[2] has reported that $H_3PMo_{12}O_{40}$ is the better passivator for zinc plating among the group of four of the more common Keggin type acids $H_nXM_{12}O_{40}$, (X = P, Si; M = Mo, W). A dense corrosion resistant complex film, $Zn_x(PMo_3)_yO_x$/ZnO/Zn was assumed to form during the passivation process. According to SEM, XPS, AES, IR, and Raman spectroscopy, molybdenum was found in +6, +5, and +4 oxidation states. The ratio of P/Mo was 1:3. The complex characterization was incomplete. A German patent by Buettner[3] claimed the passivation of galvanized steel by the deposition at 80 °C of a corrosion-inhibiting electrically conductive layer consisting of a generic heteropolyacid and/or an isopolyacid, a heteroelement of group IVB, VB, VIB and acetyl acetonate. Conceivably zinc oxide films incorporating the POM are formed and protect the surface.

The oxidizing ability of a heteropolyacid in acidic solutions was utilized in a patent application assigned to Asahi Chemical Industry,[4] where stainless steel showed high corrosion resistance when treated at 100 °C with 10% aqueous H_2SO_4 containing 100 ppm $H_3PMo_{12}O_{40}$ for a short time. In an analogous patent Otsuka Chemical Co. claimed the use of POM acid solutions (Mo, W, V) at 50−5000 ppm for corrosion protection of aluminum alloy engines.[5]

Pikel'nyi et al.[6,7] communicated that the polyoxometalate $Na_5H_2PV_6Mo_6O_{42}$ acted as a corrosion inhibitor for steel St3 (mild steel). Upon electroplating a steel St3 electrode with a thin blue film of POM the corrosion rate of the specimen was found to be almost zero when tested at 40 °C in a 150 mg/L Cl^- + 540 mg/L SO_4^{2-} solution in the presence of the POM for 100 h. Since the reduced POM can be reoxidized by oxygen to its initial form its inhibition property was extended for a prolonged time. Two other molybdovanadophosphates, those of $Na_5H_2PV_3Mo_9O_{42}$ and $Na_5H_2PV_5Mo_7O_{42}$, were found to be poor corrosion inhibitors.

A method for the in situ formation of POMs for the protection of metal surfaces from corrosion was claimed by Bech-Nielsen et al.[8] The method involved the treatment of metals such as zinc, cadmium, silver, and aluminum with a molybdate solution that contained a heteroelement from the ones that are known to form heteropolyanions (i.e. H_3PO_4, SiO_3^{2-}, etc.). The metallic surface was maintained at a potential of −0.6 to −1.8 V vs NHE during the treatment. The corrosion resistance of the treated metals as measured by exposure to hot/humid, salt environment was comparable to those of chromate coatings, without the environmental and toxicological drawbacks associated with the chromate treatment.

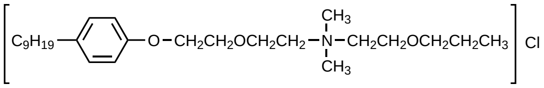
Several patents and publications in applied literature describe compositions and formulations that contain POMs as part of anticorrosive agents.[9−33] They include resin primers, combinations with conventional chromate inhibitors, and other pigment compounds. $H_nXMo_{12}O_{40}$ (X = P, Si) were used in primer formulations (at 0.5−2 wt %) of H_3PO_4 (at about 62 wt %) with phenolic or other synthetic resins and poly(vinylbutyrals) for rustproof coatings of steel.[9] Primer formulations based on silicon-based inorganic binders, Zn powder, and molybdenum compounds (that included POMs) were air-sprayed onto sandblasted steel plates, dried at room temperature for a week, and heated at 800 °C for 2 h. Improved corrosion protection was demonstrated after outdoors exposure for 6 months.[10]

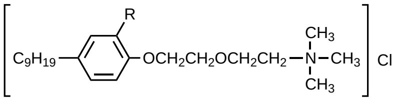
Organic amines is a class of corrosion inhibitors because of their adsorption on the metal surface. Combinations with POMs in the form of organic salts offers potential for synergistic effects from the combination of a cathodic protection and an oxidizing inhibitor. Salts of POMs with organic cations were claimed to exhibit anticorrosive properties. White or slightly opaque salts prepared from reactions of water soluble nonheterocyclic quaternary ammonium cat-

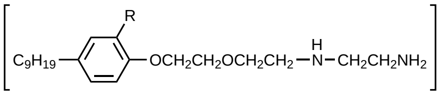
Table 4. Quaternary Ammonium Cationic Surfactants Used to Prepare Corrosion-Resistant Pigments of Heteropolyacids[11]

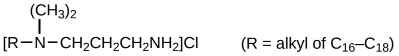
$[C_{16}H_{33}N(CH_3)_3]Cl$

$[C_{12}H_{25}N(CH_3)_3]Cl$

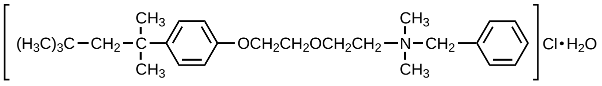


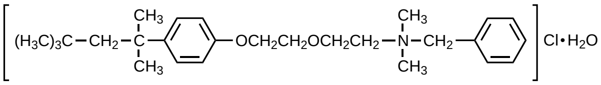






$[R-\overset{(CH_3)_2}{N}-CH_2CH_2CH_2NH_2]Cl$ (R = alkyl of C_{16}–C_{18})





ionic surfactants (i.e., wetting agents, see Table 4) with heteropolyacids of the Keggin type were found to improve the corrosion resistance when applied to metal surfaces from suitable formulations. Due to their light color appearance, these complexes were sought as advantageous primers over the colored known primers which are based on red lead, iron oxides and which require multiple overcoats of paint.[11,12]

Tetraalkylammonium salts of 1:4 organoarsenate molybdenum polyoxoanions with general formula $[R_4N]_2\{[R^1As(OH)O_2]Mo_4O_{13}H\}$ (where R^1 = amino-, hydroxy-, or methoxy-substituted aryl group) were reacted with dicarboxylic acid halides in the presence of a trialkylamine acid scavenger to produce polymeric resins that when used as coatings on carbon steel improved its corrosion resistance.[13]

Examples of combination coatings of POM acids with chromate base formulations that functioned as corrosion inhibitors primarily for steel were described in a series of Japanese patents assigned to Nippon Steel Corp.[14−22] The formulations often included other strong acids such as H_3PO_4 or HF and organic resin matrixes such as urethanated epoxy ester resins, hydrophilic polyamide resins, SiO_2 powder polyethylene wax, etc. The patents offered no characterization of POMs in these systems.

Jenkins et al.[23,24] claimed the use of heteropolyacids [preferentially $H_nP(Si)M(\equiv Mo,W)_{12}O_{40}$,] **(I)**, in combination with certain types of phosphosilicate pigment compounds **(II)**, for the passivation of metal particles of Al and Zn from hydrogen evolution upon exposure to water. Slurries of Al or Zn particles were heated in glycol ether or nitroparaffin/water solvents with combinations of **I** and **II** at 0.1−10% levels for several hours. The preferred temperature range was between 20 and 100 °C. After filtration, pastes were produced that upon exposure to water showed significantly reduced levels of hydrogen. Presumably the heteropolyacids oxidized the surface of the metal particles, and their anions together with the phosphosilicate anions formed neutral Al or Zn salt coatings that prevented the remaining metal particles from reacting with water. The metal pigment pastes were claimed to be suitable for use in water-based coatings without loss of adhesion or degradation of optical properties. Examples included general industrial coatings, roof coatings, and automotive coatings.

Recently, phosphomolybdate pigments were demonstrated to be suitable alternatives to lead- and chromate-corrosion inhibitors by using newer test methods that simulated outdoor exposure.[32]

From the literature examples one can speculate that combinations of the oxidative character of the various POMs, with their ability to form complexes within the metal oxide surface of the substrates contribute to the mechanism of corrosion protection. Significant research effort is needed to validate/elaborate on this and other hypotheses, identify the nature of the adsorbed POMs and mixed oxides in the coatings, access their corrosion inhibition effects, and increase the understanding of the science so that the utilization of POMs can be optimized and increased.

III. POMs as Additives in Sol−Gel Inorganic Matrixes

The recent explosive growth of sol−gel science and technology offers several examples of utilization of POMs as additives in inorganic or organic matrixes. The number of examples is not as large as one might have anticipated based on the advantages that POMs offer in the ease of incorporation into sol−gel matrixes and on their rich combinations of properties such as ion conductivity, photochromicity, and electrochromicity. This trend is changing, and more material scientists are investigating the interactions of POMs with organic and inorganic matrixes. The high solubility of heteropolyacids in water is a drawback since it renders them unstable under humid conditions, and thus various hydrophobic hosts are required to preserve their value-adding properties. As one might expect the primary application of these composite systems is in coatings where attributes such as optical properties, adhesion, hardness and abrasion resistance are desirable. Common inorganic matrixes are usually derivatives of Al, Si, Ge, Ti, or Zr alkoxides and to a lesser degree derivatives of Sn, Pb, or Nb alkoxides.

Through a sol−gel approach Judeinstein and Schmidt[34] trapped POM anions such as $PW_{12}O_{40}{}^{3-}$, $SiW_{12}O_{40}{}^{4-}$, or $W_{10}O_{32}{}^{4-}$ into gel matrixes. Conductive materials with electrochromic and photochromic properties were obtained.

In a series of patents by Minami,[35−37] assigned to Nisshin Steel Co., Ltd., siloxane coatings on steel substrates were prepared by the hydrolysis/condensation of alkoxysilanes and/or silanols in the presence of POM acids (e.g. $H_4SiMo_{12}O_{40}$) that function as catalysts for the process. The coated steel plates were heated at 140−400 °C to cure. The siloxane coatings showed good adhesion, and because of their low surface tension/water repellency they exhibited self-cleaning characteristics. We and others have used the acid catalysis properties of POMs in conjunction with their photochromic, electrochromic, and ion conductive properties to produce composite siloxane materials through the sol−gel approach.[37−40]

Substances of high electrical conductivity have the potential to function as effective antistatic agents. POMs are among the many compounds that have been claimed to function as such. Their function is based on the synergy between their hygroscopic and ionic character. Asuka et al.[41−46] patented siloxane−POM acid (Keggin type) networks as coatings with antireflective and antistatic properties. The coatings were the products of hydrolysis/condensation reaction of tetrafunctional/trifunctional alkoxysilanes [e.g. $Si(OEt)_4$, $MeSi(OEt)_3$, $Y_nSi(OR)_{4-n}$ where Y = organic group other than Et]. Variable concentration levels of POMs were used. The coatings exhibited good adhesion, transparency, abrasion resistance, hardness, and (low) resistivity. Similar coatings have been used on various substrates such as on acrylic resins,[43] poly(ethylene terephthalate) (PET) films,[45] glass cathode-ray tubes,[47] polycarbonates,[48] poly(methylmethacrylates),[49,50] diethylene glycol bis (allyl carbonate) polymer,[51] etc. Double-layered coatings were also described by Asuka et al.[48] consisting of an innermost electrically conductive high refractive layer that contained the POM acid embedded into a siloxane matrix and an outermost siloxane coating of low refractive index. These coatings when applied to polycarbonate substrates exhibited a reflection ratio of 2.3%, pencil hardness 2H, and static voltage 2.3 kV.

In a report by Orel et al.,[52] stable insoluble $H_3PW_{12}O_{40}$/titania gels were prepared and characterized with regard to their electrochromic and ion conducting properties. Titania gels exhibit electrochromicity, and POMs exhibit ionic conductivity. Homogeneous, amorphous films of excellent optical quality were easily produced by dip-coating techniques. Optical density changes (from blue to colorless) were sufficient to obtain an exploitable electrochromic effect. The films exhibited ionic conductivity in the range of 10^{-4} S/cm. The combination of mixed electrochromicity and ionic conductivity was demonstrated in a semiliquid electrochromic cell based on $H_3PW_{12}O_{40}$/titania gel and an Ag film counter electrode with a reversible response.

The applications envisioned for the POM-doped gels are in solid-state electrochromic displays and windows for reliable light control for buildings and automobiles.

Stangar et al.[53,54] studied the properties of titanium oxide gels and xerogels doped with $H_3PW_{12}O_{40}$ (7 mol %). Gels were prepared by the sol−gel method and films by dip-coating. They exhibited electrochromicity and ionic conductivity ($\sigma = 1.7 \times 10^{-4}$ S/cm). The electrochromism was studied in the form of a deposited film in an electrolytic cell. In the electrolytic cell the color change from transparent to blue was accompanied with effective inserted charges up to 35 mC/cm^2, giving rise to $H_xPW_{12}{}^{y+}O_{40}{}^{3-}$ where $x = 4.7$ and $y = 5.6$. Ex situ near grazing incident angle (NGIA) reflection spectroscopy showed a decrease of the intensity of the longitudinal optical modes that correspond to the intratriad $\nu W{-}O_c{-}W$ and intertriad $\nu W{-}O_b{-}W$ vibrations of the Keggin ions while the terminal $\nu W{-}O_d$ modes remained unaffected. The changes are associated with a proton insertion during the application of the potential.

A semiliquid electrochromic cell was constructed to demonstrate the electrochromic/ion conductive properties of the $H_3PW_{12}O_{40}/TiO_2$ gels. Also the electrochromism of solid films ($H_3PW_{12}O_{40}/TiO_2$) was shown by in situ UV−visible transmittance in an all solid-state device with $H_3PW_{12}O_{40}/TiO_2/H_3PO_4$ doped poly(vinyl alcohol)/Sb:SnO_2 configuration.

Tanahashi et al.[55] patented a double-layer capacitor that contained a gel electrolyte doped with a heteropolyacid. The gel matrix was prepared by the sol−gel method and consisted of SiO_2, Al_2O_3, and/or TiO_2. The doped gel was mixed with activated carbon to form the polarized (cathode) electrode. The anode was prepared from an activated carbon also. The capacitor showed low inner resistance, low leak current, and high withstand voltage.

Satake et al.[56] claimed HPA doped into sol−gel produced matrixes for their proton conductive properties. The amorphous matrixes were oxides of elements such as B or Al, Si, Ge, Sn, P, Ti, or Zr. Ayusawa and Kondo[57] claimed the same doped oxides as solid electrolytes for fuel cells.

Nakajima et al.[58] patented a photochromic recording material consisting of a coating layer of (γ-glycidoxypropyl)trimethoxysilane/$H_4SiW_{12}O_{40}$ on a polyacrylate plate cured at 80 °C and covered with another polyacrylate plate. Information was recorded by irradiation with light and erased by removing the second polyacrylate plate and exposing the coated surface to air or oxygen.

Other examples of gel, film, and xerogel hosts of POMs that were tested in optoelectronic devices are described by Tell et al.,[59,60] Mohapatra et al.,[61] Tatsumisago et al.,[62] and Orel et al.[63]

Katsoulis et al. recently prepared and characterized model silane−POM compounds as well as siloxane−POM materials using an adaptation of Knoth's precedure[64] of reacting lacunary POM with di-, tri-, and monochloro or -alkoxysilanes.[65−67] Well-characterized monomers, oligomers, and polymers have been prepared in that manner, maintaining stoichiometric and architectural control. This methodology offers higher degree of control over the more traditional sol−gel approach. It was demonstrated that these hybrid materials exhibited important properties such as film formation, UV absorbency, electrochromicity, modest conductivity, low loss tangent, and memory capability.

It is reasonable to suggest another approach for making sol−gel/POM systems. An in situ preparation of POM structures in sol−gel matrixes from metal ester precursors such as $WO(OEt)_4$ or $VO(OBu^t)_3$, etc. This method could result in homogeneous composite materials with multifunctional and useful properties.

IV. POMs as Additives in Organic Nonconductive Matrixes

Several accounts exist where the POMs are incorporated in organic nonconductive matrixes to form composite materials. The polymer matrixes provide the mechanical integrity and processability, and the POMs are usually claimed to provide optoelectronic benefits. Substantiation of the claims is very difficult in most cases since comparative studies are scarce. Like the inorganic matrixes described above, organic resins such as alkyl resins have been claimed as carriers of POM acids and antistatic film formers.[68,69] Suzuki claimed an electrochromic display that consists of a POM acid (5 wt %) dispersed in a gel state resin (butyl alcohol/polyvinylbutyl alcohol).[70] The gel was applied on an indium 203 transparent electrode, and a stainless opposing electrode was attached to the resin layer. Electrochromic response was obtained at 3 V within 103−100 ms. Also, coatings made of butadiene−styrene rubber containing $H_4SiMo_{12}O_{40}$ have been reported.[71] Composite films of poly(vinyl alcohol) and POM acids ($H_4SiW_{12}O_{40}$) are described by Lazareva et al.[72−74] Results are presented on composite films of poly(vinyl alcohol)−POMs with hydroxypropyl cellulose and Me cellulose.

According to Heller et al., the common metallization processes for microelectronic integrated-circuit devices, which are chemical vapor deposition and sputtering, do not provide adequate coverage to vertical or near vertical walls.[75] A need exists for optimizing the metallization process.

Polyoxometalates such as $H_3PW_{12}O_{40}$ were used as nucleating agents for the deposition of metals in microelectronic devices during the process of forming interconnections.[75] Solutions of POM and water soluble polymers such as poly(vinyl alcohol) were spin coated on oxidized clean silicon wafers. The coated wafers were optionally patterned by lithography, oxidized in an air furnace (400 °C) to remove the organic coating, and then reduced in a hydrogen furnace to form a tungsten metallic layer.

POMs were also found in engineering thermosets such as epoxy resin and melamine resins, functioning as conductive fillers[76] and hardneres.[77] $M_{3/2}PW_{12}O_{40}$ salts (M = Ni, Co, Cu, Zn) were claimed as hardeners in epoxy resins when used at 0.5−5% levels. Takenaka described epoxy resins and melamine resin films doped with peroxy heteropolyacids. The films were prepared by mixing the peroxy acid solutions with resin prepolymers followed by cure at 150 °C for 20 min.[78] The cost associated with the use of POMs over other common inexpensive fillers was not addressed in these patents.

Several examples exist where POMs have been trapped in polymers after functioning as polymerization catalysts of the corresponding monomers.[79−82]

V. Dyes/Pigments/Inks

The ability of POMs to form stable precipitates with cationic dyes has resulted in considerable patent activity from industries related to pigments, dyes, and inks.[83−95] There continues to be a need for better control of particle size, particle size distribution, surface activity, surface area, porosity, and color quality. The technology literature in this field focuses on a qualitative description of insoluble POM complexes with various dyes. Limited information is given with respect to the stoichiometry and the characteristics of these materials.

Hair et al.[83] described dye−poly(ethylene glycol)−heteropolyanion compositions suitable for use in ink jet printer applications. Poly(ethylene glycol)−dye (azo, xanthene, methine, polymethine compounds, or anthraquinone) derivatives were precipitated from aqueous solutions by the addition of heteropolyacids [preferentially $H_nP(Si)M(\equiv Mo,W)_{12}O_{40}$] to produce colored submicron particles. Aqueous dispersions of these particles together with the appropriate additives (i.e., biocides, antioxidants, viscosity controlling agents, and surface tension controlling agents) were found to possess excellent ink characteristics (waterfastness, dot and edge definition, and ink spreading).

The color brightness of heteropolyacid precipitated cationic dyes was substantially improved with the use of selected amines, color-enhancing agents, according to a patent assigned to Mobay Chemical Corp.[84] Pigments with sufficient color values were obtained, suitable for formulating high-quality lithographic inks. Silicomolybdic acid was the most preferred complex heteropolyacid for preparing pigments for printing inks, particularly for quick set off-set printing. Silicometalates displayed better brilliance but adversely affected the shade of some pigments such as Rhodamine B (Color Index Basic Violet 10). Tungsten-based pigments tended to fade lighter, while molybdenum pigments tended to fade darker. Color Index Basic Red 12 with silicomolybdic acid was commercially used in the United States in a very minor amount as a shading component; its color was too poor to be used as a substantial pigment component. In fact, although the Pigment and Dyestuff Manual of Bayer A.G., a producer of Color Index Basic Red 12, suggested that a precipitate of this dye (called Astra Phloxine G) would find utility in a flexographic printing ink, it has not been commercialized as of yet.

Clarke[85] patented the compositions of complexes of the Keggin type acids with a very large number of basic dyes and described their use in colorant formulations for acidic fibers such as polyesters and polyacrylonitriles. The dyes were precipitated from aqueous solutions by adding a heteropolyacid, and the insoluble powders were incorporated into viscous solutions or thickeners used for textile printing. Similarly Lacatell et al.[86] claimed the use of xanthene−$H_3PM(\equiv Mo,W)_{12}O_{40}$ complexes for quenching fluorescence. Complexes of polyoxometalates with tri- or tetracationic polymethinine dyes ($\lambda_{max} > 780$ nm) were claimed as useful colorants for pigmenting paints, printing inks, and plastics.[87] Ludwig described the preparation of insoluble salts of heteropolyacids (illustratively $H_3PM(\equiv Mo,W)_{12}O_{40}$, with aryl pararosaniline dyes at high yields from highly acidic aqueous solutions. The compounds had excellent utility as pigments, primarily in textiles (i.e. denims) and inks (replacement for indigo dyes).[88]

Kasahara et al.[89,90] described a method to produce pigment formulations of heteropolyacid/cationic dye salts from aprotic solvents such as DMSO in the presence of nonionic surfactants. The pigments showed excellent dispersability in amino alkyl coatings. A USSR patent[91] claimed specific pigments of Rhodamine Zh− and Rhodamine 4G−$H_4SiMo_{12}O_{40}$ in the presence of a surfactant to form a rose lake. (Lake ≡ a pigment consisting of an organic soluble coloring agent precipitated by a metallic salt.)

Even aqueous solutions of heteropolyacids have been claimed for their coloring/staining properties. For example a 10 wt % solution $H_3PW_{12}O_{40}$ in H_2O was patented as water-erasable ink for fabrics.[93] A dilute (1%) aqueous solution of $H_3PMo_{12}O_{40}$ was used as after-treatment for improving the light-fastness of dyed, bleached, or fluorescent dye-whitened fiber products.[94]

Ishii et al.[95] described the chemical treatment of the surface of hot-dip zinc/aluminum alloy-plated steel sheets with molybdate and phosphomolybdate solutions (pH 3.5−6.0) to form bright blue surfaces. Fluoride ions, present in the solutions served as etching agents.

VI. Recording Materials

The photosensitivity of the POM acids of Mo and W formed the science base for potential photographic processes claimed in two patents by Lyman in the early 1960s.[96,97] He showed that a photographic process could be built on photosensitive systems composed of POM acids and organic reducing agents. A variety of compounds were proposed as reducing agents. The more common ones were polyhydric alcohols such as ethylene glycol, propylene glycol, and glycerin. Other classes of organics such as polyethers, exemplified by ethylene glycol diethyl ether and diethylene glycol diethyl ether, were also used. The claims in the first patent related to a “printing out” process in which a visible image was formed by exposure alone. Heteropolyacids were sensitized to longer wavelengths extending through the visible spectrum by derivitizing with xanthene dyes. Without optical sensitizers the materials had their maximum sensitivity at wavelengths below 450 nm. The process yielded images with very fine grain and was suitable for high-resolution work. It was also useful for routine reproduction of drawings and documents. The second patent related to a process intended to replace silver as the photosensitive material by compounds of tungsten and molybdenum. The driving force for the invention was cost reduction and extended shelf-life of the POM sensitizers. The process claimed the formation of latent images on the heteropoly-sensitized materials and their subsequent development. Salts of Ag, Hg, Pd, and Au were employed as physical developers. Materials sensitized with heteropolytungstic acids needed to be developed within a few days after exposure because the latent images retrogressed. Materials sensitized with heteropolymolybdic acids could be stored for some time because on storage there was little retrogression of the latent image.

A number of more recent patents also claimed cationic dye−POM complexes as useful materials for recording purposes. Salts of laking cationic dyes with heteropolyacids of W and Mo that contained P, Si, V, Co, Al, Mn, or Cr were used to produce pigments with $\lambda_{max} > 700$ nm that were markable by semiconductor lasers.[98] A patent by Bast[99] claimed pigment formulations stable in nitrocellulose which were based on salts of heteropolyacids with lakes of bis(aminophenyl)(aminonaphthyl)methane. Jesse[100] described a formula based on basic dye−heteropolyacid salts which had good dispersability in nitrocellulose lacquer and produced inks with high gloss and color on Al and acetate films. Similarly, Ozawa[101] described a cyanine dye/HPA composition as a recording/reproduction medium responding to a laser beam.

Yabuta[102] described formulations that were based on heat-sensitive organic base color developer, comprising of insoluble diazonium salts of heteropolyacids. The formulations were used as paper coatings to produce recording materials. Similarly a Japanese patent assigned to Dainippon Printing Co.[103] described a receptor sheet for heat-transfer recording that had a developer layer consisting of heteropolyacids pretreated with ammonium or aminium compounds and a sulfonic acid resin as a binder. A Japanese patent on thermal color-forming materials described the use of $H_4SiW_{12}O_{40}$ as improving the color-forming sensitivity and lowering the color-forming temperature of formulated films of vinyl acetate−vinyl chloride polymers.[104]

Ishijima[105] showed that 10 parts of vinyl acetate polymer in 90 parts of MeOH and 3 parts $H_3PMo_{12}O_{40}$ when coated on a polyester film, dried, and exposed to electronic flash-discharge lamp through an offset-printed original gave a bluish black image. When the copy was used on an overhead projector, an image with good contrast was obtained. The copy also served as a superior master for diazo copying. A patent assigned to Toppan Printing Co., Ltd.[106] described imaging materials and processes that were based on ill-defined molybdate precipitates of acylated leucomethylene blue. The images were recorded by the following methods: (a) thermal recording; (b) thermal recording to form latent images which were developed by light whose wavelength was longer than that of UV region; (c) imagewise exposure to UV light and development by light whose wavelength was longer than that of UV region.

VII. Electrophotography. Toners

A good number of POM patents were found in the area of electrophotography (copiers). The POMs and their salts, primarily with organic cations, have been claimed to function either as the active ingredients in photochromic coatings or as charge control agents in toners.

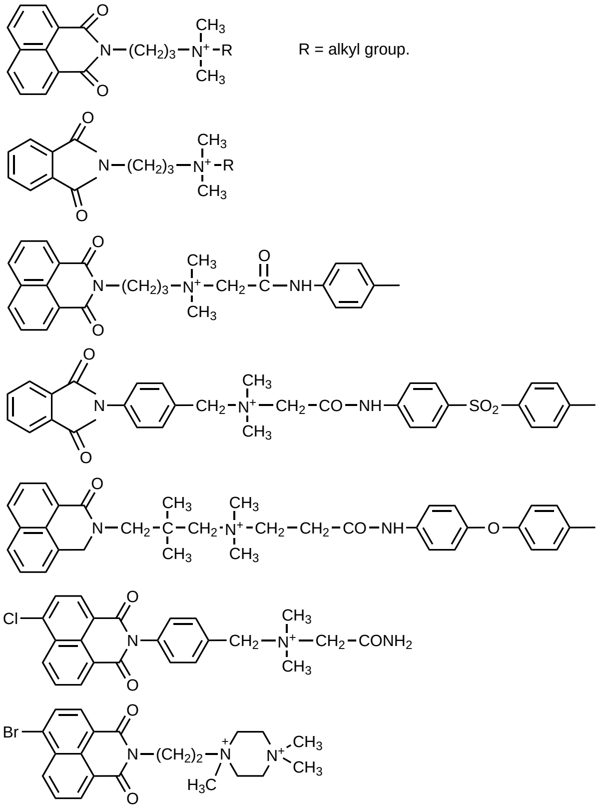
Averbach[107,108] claimed the Keggin type POMs together with a reducing agent such as phenylglycolic acid, and a binder such as poly(vinyl alcohol) as the active ingredients in photochromic coatings related to the production of images. Copies were produced by the imagewise exposure (UV light) of the photochromic layer and were stabilized by wetting the exposed layer with an aqueous alkaline solution (e.g. 8−10 wt % Na_2CO_3 or K_2CO_3). Sato et al.[109] described an electrophotographic photoreceptor that included $H_3PMo_{12}O_{40}$ or Na^+ or NH_4^+ salts as part of the photosensitive layer. Morishima et al.[110] patented an aqueous solution comprising a POM, an iron−cyano complex, and a phosphate salt as a treating solution for planographic printing plates for the purpose of making the nonimage areas of the plates hydrophilic.

Polyoxometalate salts of the 3,6-bis(amino)-9-(2′-carboxyphenyl)xanthenium class of dyes were utilized in a patent by Labana related to a electrophoretic imaging process.[111] The materials were produced by precipitation of the dyes with $Na_3PW_{12}O_{40}$/$H_3PMo_{12}O_{40}$. They were imbedded into a nonconductive liquid carrier and used as the electrically conductive particles in an electrophotographic imaging system.

Diallylammonium salts of heteropolyanions were among a long list of anions that were found to be good charge control agents for toners.[112] Charge control agents are used to provide the sign and level of toner charging in electrophotographic equipment, to counteract the drift in charging of the toner binder, and to ensure that the charging of the toner remains constant. Other important attributes of the charge control agents is their good dispersability and their high heat stability (>250 °C for >30 min). The diallylammonium salt of $PMo_{12}O_{40}^{3-}$ exhibited heat stability greater than 300 °C. The same compounds were also claimed as charge-improving agents for powders and paints for surface coatings in particular in triboelectrically or electrokinetically sprayed powder coatings. According to Suzuki et al.,[113] complexes of polyoxometalates with quaternary ammonium cations offer excellent performance as charge-controlling agents due to their very good stability with respect to humidity, heat, light, mechanical shock, and age. Examples included a toner formula that contained $[(C_4H_9)_4N]_3[PW_{12}O_{40}]$. When the toner was used in a commercial photocopying machine, it produced good-quality images even after 10 000 copies. Comparative examples using tetraalkylammonium salts of organic ions under high humidity and repetitive copies (10 000) produced copies with low density and “fogging” characteristics.

Harnisch et al.[114] claimed a series of colorless insoluble organic salts of heteropolyacids as charge control agents in toners. Examples of the cations are shown in Table 5. The preferred heteropolyanions were referred to as phosphotungstomolybdate and silicomolybdate with unspecified formulas. Polyoxometalates were claimed among others as the anions of quaternary ammonium salts in resin matrixes used for coatings of carrier core particles for electrophotography.[115] Similarly a patent assigned to Ricoh[116] claimed POM acids, their hydrates and their quaternary ammonium salts as charge control agents in toners that consist of a binder (i.e. epoxy resin, polyester resin, or polyol) and a coloring agent.

Table 5. Examples of Cations Used To Precipitate Heteropolyacids and Produce Charge-Control Agents for Toners[114]



VIII. Precursors of Oxide Films (Optoelectronics; Optical Components)

Discreet POM clusters are poor film formers. They require a carrier matrix (usually an organic polymer or resin) to provide the film-forming properties and processability. On the other hand, isopolytungstates, -molybdates, and -vanadates can form infinite network structures, which can be processed to form films and coatings. These isopolyoxometalate-derived network films are of great interest in optoelectronic industry primarily because of the ease of processing, their long-term and thermal stability, and their high refractive index. The films are commonly formed from aqueous solutions of peroxide groups containing polymetallic acids. The latter ones are produced from the oxidation of the metals and/or metal carbides by aqueous H_2O_2.

In a series of patents and publications, Okamoto et al. from the Hitachi Central Laboratories described the class of so-called “polytungstic acids having peroxo groups” as suitable optical materials for microoptical components, such as thin film waveguides, microlenses, or microprisms.[117−123] The compounds were prepared by the direct reaction of tungsten or tungsten carbide with a 15% aqueous solution of H_2O_2 and isolated as pale yellow solids upon evaporation of the solvent. Based on elemental, redox titration and thermogravimetric analyses the two types of materials were represented by the general formulas $WO_3{\cdot}xH_2O_2{\cdot}yH_2O$ (wherein $0.4 \leq x \leq 0.7$ and $2 \leq y \leq 3$) and $WO_3{\cdot}xCO_2{\cdot}yH_2O_2{\cdot}zH_2O$

(wherein $0.08 \leq x \leq 0.25$, $0.05 \leq y \leq 1.0$, and $2 \leq z \leq 3$). Although supporting evidence was not provided, the authors described as an example of these types of materials a dodecatungstate anion having peroxide groups and the following formula: $H_{10}[H_2W_{12}O_{37}(O_2)_3(OOH)_4]\cdot nH_2O$.

IR monitoring during UV irradiation of the films as well as gas analysis suggested that curing of the films occurred through the formation of edge-shared WO_6 bridges [increase of the relative intensity and broadening of the stretch at 660 cm^{-1} assigned to the $W-O_c-W$ vibrations (O_c) = edge-shared oxygen]. The driving force for the process was the decomposition of H_2O_2 to oxygen and H_2O. Both gases were detected to evolve during curing.[122]

The materials had good properties that rendered them suitable for use in optical applications. These properties were as follows: (A) Good water solubility and film formation. Thin films with excellent mechanical strengths were formed through spin-coating applications. (B) Photosensitivity upon exposure to UV light, electron beam, or X-rays that converted the films to insoluble materials. (C) High refractive index values (e.g. $n_{6328Å} \geq 2$). (D) Transparency to light with $\lambda > \lambda_{vis}$, and strong UV absorbance. (E) Stability of optical properties better than those of organic polymer materials.

The sensitivity of the films was shown to improve upon doping with Nb or Ta or Mo (achieved by doping the starting material with NbC or TaC or MoC). Ta-doped polytungstic acid showed high e-beam sensitivity (almost the same value with the organic resists that are used in practice). The films showed strong oxygen plasma durability, which made it possible to create 0.2 μm line and space patterns through submicron lithography (using the two-layer resist process).

Homogeneous metallic tungsten films were formed by Okamoto and Ishikawa on a silicon substrate by reducing spin-coated tungsten oxide films under H_2 gas at ~400 °C.[123] In a similar experiment, Ge et al.[124] doped trace amounts of $H_4SiW_{12}O_{40}$ into tungsten blue oxide powders prior to their reduction to tungsten powders. Thus SiO_2 nanoparticles were deposited on the reduced powder surface.

Kamimori et al.[125] used aqueous metatungstic acid solutions prepared from H_2WO_4 and Na_2WO_4 to coat glass substrates which upon heat treatment at 200 °C formed tungsten oxide films with electrochromic properties.

Kubo et al.[126, 127] patented the mixed metal polytungstate/Nb or Ta or Ti oxides as radiation-sensitive materials on silicon wafers. Uniform thin coatings were formed by the spin-coating method. They exhibited high durability to oxygen plasma, and they were superior to the films comprising only tungsten in sensitivity to UV light, electron beams, and X-rays due to the addition of niobium, titanium, and/or tantalum. Patterns were formed by a bilayer resist method where a bottom organic layer was etched using oxygen plasma while the upper polyacid layer acted as an etching mask.

Related to the polytungstate work, Hinokuma et al.[128] also from the Hitachi Central Laboratories prepared films of peroxomolybdic acid by spin-coating techniques on indium tin oxide (ITO) conducting electrodes and investigated their electrochromic properties. The peroxomolybdic acid solutions were prepared similarly to those of peroxopolytungstic acid. Metallic molybdenum powder was dissolved in aqueous H_2O_2 to yield an orange acidic solution. Excess H_2O_2 was removed catalytically, and after drying, a dried powder was obtained with the following empirical formula $MoO_3\cdot pH_2O_2\cdot qH_2O$. Uniform, crack-free films (up to 0.4 μm) were spin coated from dilute aqueous solutions of the material onto ITO substrates and annealed at 80−150 °C for 1 h.

The electrochromism of the films was investigated in 1 M $LiClO_4$/propylene carbonate solution with a Pt counter and a Ag reference electrode. The coloration−bleaching process can be represented by the expression:

$$\underset{\text{transparent}}{MoO_3\cdot nH_2O + xLi^+ + xe^-} \leftrightarrow \underset{\text{colored}}{Li_xMoO_3\cdot nH_2O} \quad (1)$$

where n is a variable that depends on the heat treatment temperature. A simplified model was proposed for the activity of the film, similar to that proposed for the $WO_3\cdot nH_2O$ films. In this model, a columnar cluster-like structure of $MoO_{3+z}{}^{2z-}$ assemblies is thought to form ranging from the electrolyte interface to the ITO electronic conductor. This creates interstice spaces that serve as Li^+-conducting channels, and hence intercalation (coloration) takes place both at the film/electrolyte solution interface and inside the film.

Comparison in heat sensitivity found the $MoO_3\cdot nH_2O$ films more heat sensitive. The current intensity of their cyclic voltammogram decreased rapidly as treatment temperature was elevated. In contrast, $WO_3\cdot nH_2O$ films showed almost the same cyclic voltammogram if they were heated between 100 and 160 °C. These observations were suggestive of structural differences between the two kinds of amorphous films.

Kubo et al.[129] described thin films made of 1:1 mixtures of molybdenum and tungsten oxides that were prepared from H_2O_2 reactions with the metals. The color of these films was completely bleached with the application of 1 V to the reference electrode. Films made solely with molybdenum oxide were not completely bleached under the same conditions.

Polycrystalline VO_2 thermochromic films were prepared on silicon substrates from polyvanadate solutions using spin-coating techniques.[130] The polyvanadates were prepared by the oxidation of metallic vanadium powders with 30% H_2O_2 solution followed by condensation to form lamellae clusters structurally analogous to 2D V_2O_5. A VO_2 film after annealing in an inert atmosphere showed a sharp resistivity change at 67 °C amounting to 3 orders of magnitude. Concomitant optical switching was observed for the same sample in the wavelength region 340−2500 nm.

Tungsten- or molybdenum-doped films, $V_{1-x}M_xO_2$ (M = W, Mo) were obtained in a similar manner. The switching temperature (T_c) for these films depended upon the content and the type of the heteroelement (W or Mo). A linear relationship was reported between T_c and the coefficient x for tungsten-doped films. A film doped with 1.5% tungsten exhibited a T_c as low as 36 °C, which is a convenient temperature for applications. The materials have potential to be used in large-area thermochromic smart windows.

Lampert et al.[131] patented an electrochromic device that was based on the electrochromism of a WO_3 film on a F- or Sb-doped SnO_2 oxide and a counter electrode coated with a polymer electrolyte and an organothiol material such as RSH or RSM (M = monovalent cation). The organothiol served as an ion storage medium during the electrochromic cycle of the device. In its colored form it forms disulfide bonds which break during the bleaching process to combine with the cations (e.g. Li^+; see equations below).

$$WO_3 + xM^+ + xe^- \leftrightarrow M_xWO_3 \qquad (2)$$

$$2xRSM \leftrightarrow xRSSR + 2xM^+ + 2xe^- \qquad (3)$$

Savadogo et al.[132−134] reported a considerable overall improvement in the properties of Au/n-Sb_2S_3 Schottky barrier solar cells when highly photoconductive and polycrystalline n-Sb_2S_3 films were deposited with 10^{-5} M $H_4SiW_{12}O_{40}$ in a chemical bath. The improvement in solar cell properties was attributed to the presence of WO_3 that enhanced the absorption coefficient in the films. The results are thought to be of technological significance in Sb_2S_3 semiconductor devices.

Pan et al.[135] reported on the codeposition of WO_3 and $H_3PMo_{12}O_{40}$ on an ITO substrate by controlled potential coulometry. Phosphotungstic acid cannot be deposited as a thin film by itself, as WO_3 is well-known to do, but can be incorporated into the latter to enhance its coloration. The disadvantages of the composite film were a residual color upon oxidation (bleached sample), the slow rate of bleaching, and the slow rate of diffusion of Li^+ in the WO_3 film leading to a slower response (blue color generation).

Yao et al. treated electrochemically the front surface (n-type) of a polysilicon photovoltaic cell with a solution of $K_4SiW_{12}O_{40}$ in H_2SO_4 (0.5 M) and reported improvements on its performance.[136] The reduction on reflectivity of the cell by the formation of a tungsten oxide coating was offered as explanation for the improved performance. Characterization of the coating is needed to verify the role of the POM.

Shrinivas et al.[137] used poly(vinyl alcohol) phosphotungstic acid solutions as precursors for thin (20−30 nm) tungsten films on Si/SiO_2. The tungsten films were obtained from the POM resist by 400 °C air oxidation followed by ≥450 °C hydrogen reduction.

Lanthanide-containing POM complexes exhibit electroluminescence properties that make them attractive candidates for optoelectronic applications.[138] This class of POMs is reviewed extensively elsewhere in this issue. Yamase,[139] in a broad patent application, patented a series of heteropolyanions $(L_xXM_mO_n)^{p-}$, where L = Y, La, Ce, Pr, Nd, Sm, Eu, Ho, Er, and/or Yb; X = Sb, As, and /or P; M = W or Mo; x, m, n, and p are positive integers, as luminescent agents. In a later specific application he claimed the preparation of an electroluminescent layer on a glass support by precipitation of $[Eu(W_5O_{18})_2]_2^{9-}$ anion from its aqueous solution as a Ba salt.[140] Similarly Kawabata[141] described an electroluminescent element comprised of an active layer of $Ba_9[Eu(W_5O_{18})_2]$, an unidentified phosphorescent compound, and a dielectric filler $BaTiO_3$, $SrTiO_3$ in cyanoethyl poly(vinyl alcohol), and cyanoethyl cellulose matrix. Despite these claims, the commercial utility of devices such as ITO cells (SnO_2:In_2O_3 electroluminescence cells) was questioned even by Yamase[142] himself because of the small number of internal carriers that produce quite low electroluminescence intensity.

A Japanese patent by Sasaki described an application of peroxopolytungstic acid and/or peroxoheteropolytungstic acid as oxidation protection coatings for Os/W cathode emitters. The patent claimed protection from unwanted oxidation during the manufacturing process.[143]

IX. Membranes. Sensors

A large number of application patents and publications deal with the building of membrane-based devices and sensors that exploit the high ionic conductivity of POMs, their capability to form a plethora of salts with virtually any cation, and their ability to undergo redox processes under many mild conditions. The most common uses of these membranes are in selective electrodes, in gas detection apparatuses, in solid-state electrochromic devices, and in liquid and solid electrolytic cells.

A. Selective Electrodes

Sheu et al.[144] developed organic ammonium ion selective PVC membrane electrodes based on crown ether−phosphotungstic acid precipitates. Electrodes based on 18-crown-6/POM gave the best performance and exhibited good linear responses with near-Nernstian slopes for organic ammonium ions such as $BuNH_3^+$, $C_6H_5CH_2NH_3^+$, $Et_2NH_2^+$ and Et_3NH^+ within the concentration range 10^{-1}−10^{-5} M. Good selectivity over NH_4^+, alkaline, and alkaline earth cations and some transition metals was observed. The optimum pH working range for the electrodes was about 2−6. A Japanese patent claimed PVC polymer/plasticizer membranes doped with tetraalkylammonium salts of $PMo_{12}O_{40}^{3-}$ or $SiW_{12}O_{40}^{4-}$ as ion-selective electrodes for the high-precision determination of cationic surfactant concentrations.[145] Similarly, an ion-selective electrode membrane for determination of tetrabutylammonium that was composed of PVC dibutyl phthalate as plasticizer and tetrabutylammonium molybdotungstophosphate of unspecified W:Mo ratio was claimed in a Soviet Union patent.[146] Loading of POM was 1−5 wt %.

Volkov et al.[147] in another Soviet Union patent claimed an ion-selective electrode membrane for determination of Al^{3+} and Ga^{3+} ions that was composed of PVC matrix and polyvanadomolybdates salts of Al or Ga of unspecified formula. Loading of POM varied between 52 and 83 wt %. An analogous Pb^{2+}-specific, PVC-based electrode impregnated with monobenzo-15-crown-5 ether and $H_3PMo_{12}O_{40}$ or H_3-

$PW_{12}O_{40}$ was described by Sheen et al.[148] The electrode had a detection limit of 1×10^{-6} M and fairly small selectivity coefficients for foreign ions. Srivastava et al.[149] fabricated a solid membrane sensor using a structurally unidentified polytungstoantimonate embedded in polystyrene as an electroactive phase. Preliminary studies showed some promising selectivity for mercury in the concentration range 5×10^{-5} to 10^{-1} M at pH 4–6. Interference occurred from monovalent ions but not from divalent and polyvalent ones.

Many of the selective electrodes described in the literature were constructed for use in clinical chemistry. An electrode specific for the determination of Metformin hydrochloride (MfCl), a hypoglycemic agent, was described by Rizk et al.[150–152] The electrode was based on the incorporation of $[Mf]_2HPM(\equiv Mo,W)_{12}O_{40}$ salts into a PVC membrane, which was plasticized with dioctyl phthalate. It was used for the potentiometric determination of MfCl in solution and in its pharmaceutical preparations. Linear responses with good Nernstian slope over a relatively wide concentration range were observed. The selectivity of the electrode was very good for Mf with respect to a large number of inorganic and organic cations.

Campiglio described an ion selective electrode for the potentiometric microtitration of vitamin B_1.[153] The electrode was based on a PVC matrix impregnated with a benzyldimethyltetradecylammoniumphosphotungstate ion association complex as the electroactive material and dioctyl phthalate as plasticizer. A graphite electrode was coated with the membrane and used in conjunction with a Ag–AgCl double junction reference electrode to detect the end point of the titration. The method gave satisfactory results in the range of 1–4 mg of vitamin B_1 (recoveries, 100.00 ± 0.25%; mean relative standard deviation, 0.22%), and it was successfully applied to the analysis of pharmaceutical preparations. Other examples of PVC/POM-based electrodes for clinical analysis include an ion-selective electrode for dimedrol ions[154] and an electrode for the quantitative analysis of Zoplicone (1-piperazinecarboxylic acid, 4-methyl-, 6-(5-chloro-2-pyridinyl)-6,7-dihydro-7-oxo-5*H*-pyrrolo-[3,4-*b*]pyrazin-5-yl ester; a hypnotic agent) in tablets.[155]

Eppelsheim and Hampp[156] described a biosensor for the determination of the neurotransmitter acetylcholine. The sensor was based on a two-layer selective poly(vinyl chloride)-poly(vinyl acetate) membrane consisting of a choline phosphotungstate as the electroactive compound. The linear response region extended from 2×10^{-5} to 0.01 mol/L and the lower detection limit was 5×10^{-6} mol/L at a response time of 4 min. Ito et al. claimed a biosensor that was based on isopolytungstic acid or heteropolytungstic acid and was useful for the determination of albumin in a sample.[157]

B. Gas Sensors

In a series of patents, Polak et al.[158–162] and Petty-Weeks[163] described the preparation and properties of organic-inorganic polymer membranes made of water soluble organic polymers [i.e., poly(vinyl alcohol), poly(ethylene oxide), poly(ethylene glycol), cellulose acetate, etc.] and heteropolyacids or their salts. The membranes were used in gas sensors for the detection of hydrogen and gaseous compounds capable of dissociating into or combining with hydrogen ions. The membrane preparation consisted of dissolving a certain ratio of the POM (primarily of the Keggin type) and the organic polymer in water, mixing for a period of time at room or elevated temperature and evaporating the solvent to form a transparent membrane, usually a few microns thin. The membranes exhibited a single glass transition temperature (T_g), had no phase separation visible by optical or SEM microscopy, and had improved yield strengths and Young's modulii over those of each of the components. A second phase appeared when POM levels exceeded 70 wt % in the membrane.

The heteropolyacids (/anions) interacted effectively with the polar groups of the organic polymers primarily through hydrogen bonding and were immobilized as a single phase within the polymer networks. A large range of ratios of POMs/polymer were claimed to form effective membranes. It is safe to assume that water molecules also assisted in the formation of the polymer network. Infrared spectroscopy of a membrane formed from poly(vinyl alcohol) and $H_3PW_{12}O_{40}$ showed strong bands at 820, 885, 972, and 1075 cm^{-1} that were attributed to intermolecular interactions between the organic polymer and the heteropolyacid.

The membranes were sputtered onto Pt or Pd disks (catalysts for H_2 oxidation), mounted on double gas chamber cells (reference and sample), and were shown to accurately determine the hydrogen concentration in the sample cell by measuring the EMF potential difference across the membrane.

The infamous formation of blue color in heteropolycomplexes upon reduction of Mo^{6+} and/ or W^{6+} was exploited by Goswami et al. to fabricate a reversible solid-state optical sensor for CO.[164] The basic materials of the sensor were (a) a Pd(II) or Ru(VIII) or Os(VIII) compound that functioned as a catalyst for oxidation of CO to CO_2, (b) a heteropolymolybdate, -tungstate, or even -vanadate that was reduced by the reduced form of the catalyst, and (c) a so-called reversing agent such as a Fe(III) or Cr(VI) or Ce(IV) complex that served as reoxidant of the heteropolycomplex. The inorganic complexes were embedded in an organic polymer film such as poly(vinyl chloride), polystyrene, cellulose derivatives, siloxanes, etc. Lipophilic ions and surfactants were used to compatibilize the inorganic salts with the polymer membrane. The polymer was deposited on an optical fiber, and the performance of the device was assessed by measuring the attenuation of transmitted light at the time of exposure with CO. Total internal reflection or absorption measurements were correlated with the concentration of CO. It took several hours to reverse the color (ca. 16 h). Shortening the time of color reversal would increase the probability for commercialization. Another variation of a gas detector was claimed in a patent by Shuler et al.[165] According to the invention, a silica gel impregnated with Pd^{2+} and Cu^{2+} and silicomolybdic acid or ammonium paramolybdate and some acid were used as CO detectors and in general purifiers of reducing gases such as H_2S or acetylenic compounds. Upon exposure to the reducing gas Pd^{2+} and Cu^{2+} were reduced to Pd^0 and Cu^+, and in turn Pd^0 reduced the POM to a blue state. On exposure to air the monovalent copper catalyzed the oxidation of palladium and the molybdate blue to reinstate the starting conditions. The silica gel substrate (a moisture absorbent) provided the necessary water to ionize the reagent salts so that the redox cycle could occur.

A German patent claimed the use of $H_3PW_{12}O_{40}$ in an electrochemical cell, comprised of H_2SO_4 as an electrolyte and $Fe_2(SO_4)_3$ as additional catalyst, to detect oxidizable gases found in polluted air from semiconductor manufacturing plants.[166] Such gases were NO_2, SO_2, or hydrides B_2H_6 SiH_4, PH_3, or AsH_3. Another German patent claimed a solid electrolyte detector that contained a diffusion barrier of porous material for the detection of waste gases such as NO_x.[167] Among the claimed electrolytes were $H_3PM(Mo,W)_{12}O_{40}$. The detector was claimed to operate from −50 to 500 °C. The patent did not provided experimental results to support the claim.

Improvements of the functional life of such sensors have been achieved with the use of various porous solid-state encapsulants that encapsulate at least one component of the chemical sensor.[168−170]

Kawakami prepared a disk of a dried (80 °C and <20% humidity) $H_3PMo_{12}O_{40}$ by molding it at a 5 t/cm^2 pressure to be used as a hydrometer element.[171,172] Lead wires were attached to it, and upon application of an ac voltage (at 1 kHz frequency) the electrical resistance across the pellet was measured. It was found to be 2400 Ω at 50% relative humidity and 13 Ω at 90% relative humidity. The reversibility of the device and its response as a function of humidity levels need to be demonstrated before pursuing commercialization.

C. Solid-State Electrochromic Devices

Babinec described the fabrication of a solid-state electrochromic device that was based on $H_3PW_{12}O_{40}$ or an alleged nonisolated $H_2W_{12}O_{40}{}^{6-}$ anion prepared in situ by the acidification of Na_2WO_4 solution with HCl.[173] The performance of the device relied on the reversible color change of POM anions embedded into a quaternized 4-vinylpyridine−styrene copolymer film. The film was applied through spin-coating techniques on the surface of a ITO glass electrode, the other side of which was coated with silver paint to facilitate electrical connections. A second ITO electrode coated with an ion conductor such as Fe^{2+} perfluorinated sulfonated polymer (e.g. Nafion) on one side and silver paint on the other was used as a counter electrode. The two electrodes were clamped together so that they sandwiched the POM-containing film. Application of 1.5−2.5 V across the silver-painted portions of the slides caused the formation of color. The device was cycled from its color to the clear state ca. 4000 times without any significant loss in performance.

In another paper Babinec gave more details on the POM/poly(4-vinylpyridine)−10% polystyrene modified electrodes.[174] Using spectroelectrochemistry, regimes of stable performance for the ITO electrodes were established. The electrodes had excellent optical uniformity, a color similar to that of WO_3, optical densities >1.0 A at 640 nm and were stable to color/bleach cycling for about 20 000 cycles in aqueous acid. Its coloration efficiency [defined as a change of optical densities of colored and bleached states, $\Delta OD/\Delta Q = \log(T_{colored}/T_{bleached})/\Delta Q$] at −0.5 V was ∼55 cm^2/C sufficient to achieve optical density of 1.0 A (at 640 nm) and yielding an electrochemical efficiency of 18. The kinetics of color development, on the other hand, were significantly slower than that of the solid-state vacuum-deposited WO_3. It took about 35 s at −1.10 V and 300 s at −0.5 V to reach optical density of 1.0 A at 640 nm. XPS analysis of cycled electrodes showed a reduction of W/N ratios (by 20% after 20 000 cycles) suggestive of leaching of the POM (conditions: pH 2; 0.1 M NaCl).

A set of Japanese patents by Nakamura et al.[175,176] described an electrochromic display device that was based on $H_4SiW_{12}O_{40}$ compacted to a disk (10 mm diameter, 0.5 mm thick) and sandwiched between a graphite electrode and a SnO_2 glass plate covered with a 1 mm thick WO_3 layer. The disk was formed by applying a pressure of 1 t/cm^2. When a 1.5 V square wave was applied to make the SnO_2 negative and reversed for 1 s each, the coloring current was 18 mA and the decoloring current 24 mA vs 10 and 19 mA, respectively, for 7 N H_2SO_4. The response time was also shorter. The device was still operative at 200 °C. A separate device was prepared different from the one above only in the fact that $H_4SiW_{12}O_{40}$ was in the form of an organic solution (e.g. in γ-butyrolactone).[176]

D. Electrochemical (Fuel) Cells

This section and the one that follows on electrode modification deal with electrochemistry and electrocatalysis applications, two fields that are being reviewed separately in this issue. Therefore this coverage will be limited in examples from the patent literature and relevant publications from applied research. Emphasis will be given on device/material description.

The solid-state ionic conductivity of polyoxometalates was exploited in electrochemical cells designed by Nakamura et al.[177,178] Polyoxometalate acids or their salts when compression molded under pressures exceeding 100 kg/cm^2 to a desired shape or used as single crystals were found to exhibit outstanding ionic conductivity even at temperatures of ca. 200 °C. Their performance was comparable to those of conventional liquid electrolytes but without the disadvantages of leakage and inconvenience in handling of the latter ones. The high pressures were needed to eliminate any microfine porosity from the pellets. Table 6 combines the room-temperature specific resistance for a number of polyoxometalates. Plates with dimensions 15 mm × 15 mm × 2 mm were prepared by compression molding at pressure of 1000 kg/cm^2. Specific resistance was measured by the AC bridge at a fixed frequency of 1 kHz.

Table 6. Specific Resistance of Polyoxometalate Plates (Selective Data from Ref 178)

compound	specific resistance (Ω·cm)	compound	specific resistance (Ω·cm)
$H_3PMo_{12}O_{40}\cdot 30H_2O$	11	$K_6P_2W_{18}O_{62}\cdot 14H_2O$	123
$H_3PMo_{12}O_{40}\cdot 30H_2O$ single crystal	5	$K_{10}P_2W_{17}O_{61}\cdot 22H_2O$	131
$H_3PW_{12}O_{40}\cdot 30H_2O$	12	$(NH_4)_6TeMo_6O_{24}\cdot 7H_2O$	326
$H_3PW_{12}O_{40}\cdot 30H_2O$ single crystal	7	$(NH_4)_8CeMo_{12}O_{42}\cdot 8H_2O$	281
$(NH_4)_3PMo_{12}O_{40}\cdot 3H_2O$	21	$(NH_4)_6MnMo_9O_{32}\cdot 8H_2O$	235
$K_3PMo_{12}O_{40}\cdot 6H_2O$	22	$Na_5W_6O_{24}\cdot 8H_2O$	235
$Na_3PMo_{12}O_{40}\cdot 21H_2O$	17	$(CN_3H_6)_6TeW_6O_{24}\cdot 7H_2O$	520
$(NH_4)_3PW_{12}O_{40}\cdot 3H_2O$	20	$(NH_4)_3H_4AsW_{12}O_{42}\cdot 4H_2O$	311
$K_3PMo_{12}O_{40}\cdot 6H_2O$	20	$H_4GeW_{12}O_{40}\cdot 30H_2O$	73
$Na_3PW_{12}O_{40}\cdot 21H_2O$	19	$K_2SeMo_6O_{21}\cdot 6H_2O$	217
$H_4SiMo_{12}O_{40}\cdot 26H_2O$	12	$Na_3AlMo_6O_{21}\cdot 11H_2O$	195
$Na_4SiMo_{12}O_{40}\cdot 22H_2O$	24	$K_4ZrMo_{12}O_{40}\cdot 18H_2O$	188
$H_4SiW_{12}O_{40}\cdot 30H_2O$	13	ZrO_2-CaO (solid solution)	10000 (600 °C); 40 (1000 °C)
$Na_4SiW_{12}O_{40}\cdot 22H_2O$	22	β-Al_2O_3	700 (RT); 14(300 °C)
$H_5BW_{12}O_{40}\cdot 30H_2O$	13		

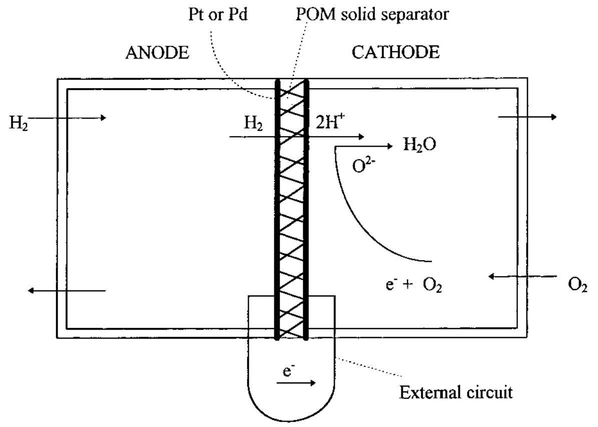


Figure 4. Schematic of an electrochemical cell utilizing a polycrystalline POM acid as a H^+ conductive solid separator. Based on ref 177.

The table shows that the polyoxometalate plates exhibit extremely low degrees of specific resistance as compared with the conventional solid electrolytes. In general the acid forms are more conductive than the salts.

The compression molded POM plates were demonstrated to function effectively as partition walls between the anode and cathode chambers of H_2 (catalyst Pt or Pd) /O_2 fuel cells. They allowed the selective permeation of protons alone from the anode to the cathode chamber presumably through hydrogen-bonded networks facilitated by solvent molecules. The electrons generated by the oxidation were fed into the anode by an external circuit, reduced O_2 to O^{2-} which combined with the arriving protons to form H_2O (Figure 4). Upon constant partial pressures of oxygen and steam, the electromotive force generated by the cell is proportional to the logarithm of the partial pressure of hydrogen in the anode chamber [see Nernst equation: $E = E_0 + RT/nF \ln(c^{p2}H_2O/a^{p2}H_2c^{p2}O_2)$ wherein $a^{p}H_2$ denotes the partial pressure of hydrogen in the anode chamber and $c^{p}H_2O$, $c^{p}O_2$ denote the partial pressures of water and oxygen in the cathode]. Thus the device could be used for the determination of partial pressure of H_2. Likewise the concentration of O_2 could be determined when the partial pressures of hydrogen and steam are kept constant. The electrolytic generation of H_2 from steam using a sheet of polycrystalline $H_3PMo_{12}O_{40}\cdot 30H_2O$ as a H^+ conductive solid separator was described in another Japanese patent by Nakamura.[179] According to the patent both sides of the separator were coated with a Pt black catalyst. The POM separator divided a plastic vessel into an anode and a cathode compartment. A gastight lid was placed over the plastic vessel to prevent gas flow between the two compartments. The air in the cathode compartment was displaced with H_2 at a pressure of 0.1 atm. A voltage impressed between the electrode and steam under pressure was forced into the anode chamber whereupon the reaction $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$ occurred, the H^+ diffused through the separator and yielded H_2 (100%) at the cathode. The cell was operated at room temperature by using an electrode surface area of 0.385 cm^2 and a voltage of 2 V.

Limitations of the above cells were the strong influence of humidity on their protonic conductivity, diffusional problems, and the high ionic resistance associated with excessive electrolyte thickness.

Many other liquid and solid fuel cells that are based on POM acids are described in the current literature.[180-187] Giordano et al.[180,181] developed a low-temperature fuel cell based on a liquid phosphotungstic acid that was intended to overcome the limitations of Nakamura's solid fuel cells. The cell design was characterized by a continuous feed of electrolyte to the matrix (a glass microfiber felt, with 80% porosity) that was sandwiched between two water-proofed gas diffusion electrodes. The electrodes consisted of two layers. A carbon paper, waterproofed with polyfluoroethylene–propylene and a catalyst layer of Pt/C (20% Pt) mixed with poly(tetrafluoroethylene). The cell had low internal resistance and was able to produce an output power density of about 700 mW/cm^2 at 1.5 A/cm^2. Lifetime tests showed that the cell performance remained stable for prolong periods of time of operation.

Another prototype of a proton exchange membrane fuel cell was fabricated recently by Park et al.[182] by doping sulfonate polysulfone polymer with $H_3PW_{12}O_{40}$ from common (DMF) solvent. The solution mixture was spin coated on a glass substrate and dried at 80 °C under vacuum for 24 h. A thin film 30–200 μm was formed. It was then sandwiched at a pressure of 120 kg/cm^2 between a pair of commercial electrodes, coated with Nafion. The POM-doped membrane showed high current density that was a function of the POM content. A membrane doped with 30% POM had a current density of 55 mA/cm^2. The current density of the membrane alone was 14 mA/cm^2. The promotion on the cell performance was attributed to the high proton conductivity of the POM. Comparison with commercial Nafion showed lower performance.

Kummer et al.[185] described in detail a redox fuel cell which consisted of anode and cathode compartments separated by a cation exchange membrane (Nafion 415). An electrolyte solution which consisted of $VOSO_4/H_5PMo_{10}V_2O_{40}$ or $H_3PMo_{12}O_{40}$ was circulated in the cathode compartment. The POM acted as a catalyst during the oxidation of $VOSO_4$ to $[VO_2]_2SO_4$. An electrolyte solution which consisted of $H_3PW_{12}O_{40}$ or $H_3PMo_{12}O_{40}$ was circulated in the anode compartment in the presence of a reducing catalyst (Pt, Pd, Rh, Ru, etc.). The reservoirs of the electrolytes contained inlets for O_2 (cathode) and H_2 gas (anode). During the cell operation upon circulation in the cathode compartment $VOSO_4$ was oxidized by O_2 and in the anode compartment $H_3PW_{12}O_{40}$ or $H_3PMo_{12}O_{40}$ was reduced by H_2 in the presence of a noble catalyst for a period of time. The open circuit voltage of the fuel cell was found to be 0.9 V.

Akimoto patented a cell that consisted of $H_nX(Si,P)W_{12}O_{40}$ solution compartment and a H_2 gas compartment separated by a proton permeable gas−liquid separation membrane.[186] The membrane and the compartment containing the POM were connected to a potential source that allowed the flow of H^+ through the membrane.

According to Kim et al.[187] $H_nX(Si,P)M(Mo,W)_{12}O_{40}$ acids immobilized in polysulfone membranes were claimed to function as vapor-phase dehydration, dehydrogenation, and oxidation catalysts.

X. Electrode Modification by POMs

Of great technological importance of our times is the storage of energy in a compact form that can be easily charged and discharged as lightweight batteries and/or capacitors. Optimization of the components of these various systems is an ongoing activity. Polyoxometalates have been utilized in modifying activating carbon electrodes to improve their storage charge capacity and subsequently fabricate electric double-layer capacitors with optimized energy storage properties. The polyoxometalates that are capable of reversible redox reactions provide a secondary charge storage mechanism without decreasing the charge storage ability of the activated carbon.

According to two patents by Cuellar et al.,[188,189] the POMs were absorbed into the activated carbon using vacuum/impregnation and soaking procedures. Loading of POMs up to 40 wt % was feasible. In an example, high surface area (BET surface area ca. 500−2000 m^2/g) activated carbon was impregnated with an acid electrolyte such as H_2SO_4 and a polyoxometalate such as $H_4PMo_{11}VO_{40}$ to form a slurry. The modified carbon was isolated by decantation, dried, grated, pressed into an electrode, and assembled into a capacitor cell. Comparison of performance characteristics at charge voltages between 0.5 and 1.3 V with capacitors made with unmodified carbon electrodes found significant enhancements (up to 65%) in the specific energy stored by the POM-modified electrodes.

A modification of the capacitors described above was offered in a patent by Li et al.[190] assigned to Motorola, where a protonated ion conductive polymer [poly(4-vinylpyridine)] doped with the polyoxometalate (isopolymolybdate) was incorporated into the activated carbon electrode of a double-layer capacitor. On the basis of its cyclic voltammogram (charging/discharging over a limited voltage range), the capacitor was shown to function well in acidic, neutral, and basic environments.

Dilute solutions of heteropolyacids were used to activate vitreous carbon or graphite electrodes resulting in potential gains up to 1 V vs the unmodified versions for the reaction of H_2 evolution from H_2O.[191,192] The electrodes were treated by keeping them at −1.2 V vs SCE for several minutes in heteropolyacid solutions of the Keggin or Dawson type. ESCA analysis of the electrode surface after treatment showed the presence of POM elements (i.e. silicon and tungsten). The intended use of the modified electrodes was for an electrocatalytic cell for hydrogen production.

During the past few years, significant developments on electrode modification by POMs have taken place aiming to improve the reaction rates of fuel cells and produce economically sufficient currents for practical uses.[193−197] Electrocatalysts that are incorporated into the fuel cell electrodes are required to have high activity for the electrochemical reduction of oxygen, as well as being able to withstand a working environment of relatively high temperatures and strong acid levels. Recent work by Savadogo et al. has shown that POMs exhibit these attributes. In two recent patents he described the fabrication and performance of polycomponent electrodes for electrochemical and fuel cells.[193,194] The electrodes were made on a chemically treated graphite support, via treatment with chloroplatinic acid or chloropalladic acid, followed by treatment with a POM solution at various concentrations. A binder waterproofing agent such as poly(tetrafluoroethylene) (Teflon) was also used as additional catalyst support. Examples of POMs used in this application were $(NH_4)_6H_2Mo_{12}O_{40}$ and $(NH_4)_6H_2W_{12}O_{40}$. The fabrication process required a heat treatment step of the graphite/Pt (or Pd)/POM electrode to 345 °C which could have been sufficient to decompose the Keggin structure. Thus, it is doubtful that the Keggin structure is part of the finished multicomponent electrode. The performance of the electrodes was found to be superior to that of electrodes made in the absence of POMs. A graphite/Pd/“$H_2Mo_{12}O_{40}$” electrocatalyst demonstrated an increase in the catalytic activity exchange current density for the electrochemical oxidation of hydrogen in potassium hydroxide, at 80 °C, when compared to an analogous graphite/Pt (or Pd) electrode. Also, a graphite/Pd/“$H_2W_{12}O_{40}$” electrocatalyst demonstrated an increase in the catalytic activity for electrochemical reduction

Table 7. POMs as Dopants of Electrically Conductive Polymers

polyoxometalate	polymer	function/application	reference
$H_2W_{12}O_{40}^{6-}$	polypyrrole	proton permeability	232
$PMo_{12}O_{40}^{3-}$	polypyrrole	electrocatalytic reduction of O_2 and ClO_3^-	227
	poly(5-amino-1-naphthol)	detection of catecholamines	234
		chemical polymerization	229
		electrocatalysis of ClO_3^-	231
$H_3PM_{12}O_{40}$, M = Mo, W	polyaniline (PANI)	from crystalline to amorphous polymer	228, 230
$H_4SiW_{12}O_{40}$		electrocatalytic reduction of ClO_3^-, BrO_3^-	233
$P_2W_{18}O_{62}^{6-}$	polypyrrole	catalysis of O_2 reduction	235
$Dy(SiMo_{11}O_{39})_2^{13-}$	polypyrrole	electrocatalytic reduction of ClO_3^-, BrO_3^-	232

of oxygen, at 180 °C, when compared to an analogous graphite/Pt (or Pd) electrode. Optimum results were obtained with electrodes that contained 1−2 wt % Pt or Pd and approximately 50 wt % POM. Considering the high cost and low availability of noble metals, these electrodes could offer an attractive alternative to the current Pt(Pd)/graphite electrodes.

In a series of recent publications, Savadogo and coworkers extended the POM-based electrode modification to other metal electrodes such as nickel, cobalt, and copper.[198−214] The POM-modified electrodes exhibited increases in the exchange current density and decreases in overpotential for the electrocatalysis of the hydrogen evolution reaction.

Some details on the adsorption of POMs on electrode surfaces are provided by Anson. In a paper with Kuhn he studied the irreversible adsorption of $P_2W_{18}O_{62}^{6-}$ on various electrode surfaces to form monolayer type films.[215] A chemisorption process in which charge transfer from the electrode surface to the anion occurred was suggested to explain the unusually strong adsorption phenomenon. The process was exploited to form multilayers on electrode surfaces in which the first layer of adsorbed POM served to anchor the subsequent layers. Layers of large cations such as $Os(bpy)_3^{2+}$ were deposited in an alternate fashion with POMs. The stoichiometry of the salt film was maintained with the incorporation of small cations. Applications in electrocatalysis, electrochemical devices and sensors can be envisioned. Similarly, other POMs were found to adsorb strongly onto a variety of electrode surfaces.[216] Two electrocatalytic studies were demonstrated with $PW_{11}O_{39}Fe(OH_2)^{4-/5-}$ and $SiW_{11}O_{39}Fe(OH_2)^{5-/6-}$ adsorbed on a hanging mercury drop electrode. One was the reduction of H_2O_2 and the other the reduction of NO_2^-. The voltammograms for the later electrocatalysis showed that the process proceeded through an Fe^{II}−nitrosyl complex at −0.1 V which was reduced to NH_3 at −0.6 V.

XI. Capacitors

Heteropolyacids and their salts have been claimed as electrolytes for capacitors (solids and solutions).[217−222] One such capacitor that contained $H_4SiW_{12}O_{40}$ (ca. 2 wt %) was claimed by Morimoto.[217] The capacitor consisted of a polar organic solvent such as γ-butyrolactone. Amines, organic acids, or organic acid amine salts functioned as electrolytes. The capacitor had resistivity of 160 Ω·cm and a sparking (≡breakdown) voltage 135 V.

Alwitt demonstrated that electrolytic capacitors which consisted essentially of salts of $H_4SiM(=Mo,W)_{12}O_{40}$ in a polar organic solvent such as DMF had lower dissipation factors at low temperatures than conventional electrolyte solutes such as salts of organic acids, borates, or borate complexes.[218] The capacitors also maintained good reliability at high-temperature operation up to 150 °C. Aging studies at 125 °C for 310 h showed constant resistivity. The capacitors employed an aluminum foil anode and an aluminum foil cathode separated by a paper spacer. After being wound into a cylindrical shape, the foils and separator together with the electrolyte were sealed in a suitable container. An earlier patent by Hand described a similar capacitor electrolyte which was based on ammonium or amine salts of $H_3PM(=Mo,W)_{12}O_{40}$ in anhydrous DMF.[222]

XII. POMs as Dopants in Electrically Conductive Polymers

A lot of interest has been generated in the area of electrically conductive polymers with regards to the incorporation of POMs (primarily of the Keggin type) into the polymer matrix.[223−232] A rich literature exists on the immobilization of POMs by polymers such as polypyrrole, polythiophene, polyaniline, poly(1-naphthol), or poly(*p*-phenylene). Utilities of these doped materials have been proposed in the area of catalysis, due to the ease of separation of the POM catalyst from the reaction mixture when it is embedded in a polymer matrix. The incorporation process involves the chemical or electrochemical oxidation of a polymerizable monomer to form a polymer in the presence of POM solution. The more commonly used electrochemical oxidation of the monomer takes advantage of the heteropolyacid as the electrolyte. Upon the application of the suitable oxidation potential, the conductive polymer is deposited on the working electrodes (usually carbon or graphite) doped with the anions of the heteropolyacid. The POM-doped membrane modified electrodes are sought as electrochemical catalysts. A comprehensive list of POM dopants in conductive polymers and their intended applications/functions is shown in Table 7.

Polypyrrole doped with POMs (ie., $SiW_{12}O_{40}^{4-}$ and $P_2W_{18}O_{62}^{6-}$) via electrochemical polymerization exhibited redox properties inherent to the POMs and to the polypyrrole moiety.[223−257] The anions were retained in the polymer matrix without being ion-exchanged after repeated potential cycles in electrolyte solutions containing no POMs. Charge compensation on reduction was accomplished by cation insertion instead of anion release. The spin density of the polymer with $P_2W_{18}O_{62}^{6-}$ was small, indicating bipolaron formation accelerated by POMs.

Freund et al. described a process to produce polypyrrole$-PMo_{12}O_{40}^{3-}$ thin (40$-$100 nm) films by inducing polymerization from a stable pyrrole-oxidant solution via solvent evaporation.[226,227] The conductivity of the films was in the range of 15$-$30 S/cm. Films with similar conductivity were reported by Ritter via spin coating polypyrrole/$H_3PMo_{12}O_{40}$ on glass substrates.[228]

Ding et al. reported polypyrrole films doped with $Co(W_2O_7)_6^{10-}$ and $CuW_{12}O_{40}^{6-}$ anions that exhibited an ESR signal attributable to a polymer$-$POM adduct.[229,230] Films of polypyrrole doped with molybdates were reported by Vernitskaya et al.[231] A composite film composed of $H_2W_{12}O_{40}^{6-}$ anions and polypyrrole was prepared from the electrochemical polymerization of pyrrole in polytungstic acid solution. The composite film revealed proton permeability.[232] Its absorption spectrum varied with the applied potential. A large absorption change occurred at 800 nm for potentials lower than -0.2 V that corresponds to the reduction of W(VI) to W(V).[233] Electrodes modified with a $PW_{11}O_{39}Fe^{III}(OH_2)^{4-}$/poly(*N*-methylpyrrole) polymer or $PW_{11}O_{39}Fe^{III}(OH_2)^{4-}$/polyaniline were recently claimed as amperometric sensors of NO and NO_2^-.[234,235] When a carbon electrode modified with $PW_{11}O_{39}Fe^{III}(OH_2)^{4-}$/poly(*N*-methylpyrrole) polymer was used as the working electrode in a conventional three-electrode electrochemical apparatus, its reduction current varied linearly with the concentration of NO_2^- ions (range of 10^{-5} to 10^{-1} M). The two-electron reduction waves of the WO_6 centers of the $PW_{11}O_{39}Fe^{II}(OH_2)^{5-}$ anion were significantly enhanced by the addition of nitrite. This behavior suggests that during the electrocatalysis the reduced form of the POM embedded into the polymer film reacts with the added substrate. The formation of an iron$-$nitrosyl complex $PW_{11}O_{39}Fe^{II}(NO)^{5-}$ was suggested. Supported evidence for the formation of the complex (POMFe$^{II}-$NO) were provided by the in situ absorption spectrum ($\lambda_{max} = 463 \pm 3$ nm) of a $PW_{11}O_{39}Fe^{III}(OH_2)^{4-}$/poly(*N*-methylpyrrole) deposited on a transparent $In_2O_3-SnO_2$ and after use as the working electrode for the electrocatalysis of $NaNO_2$. On adjusting the potential of the electrode to more negative values (e.g. -1.2 V), the complex was reduced and NH_4^+ cations were generated. The electrochemical and catalytic responses of the sensor were maintained when kept in an acetate buffer solution.

On the basis of these technologies, an electrode was fabricated for the in vivo determination of small amounts of NO, that was based on Fe$^{III}-$POM (preferably $PW_{11}O_{39}Fe^{III}(OH_2)^{4-}$) embedded into an electrically conductive polymer (preferably, poly(*N*-methylpyrrole)) which was coated with an anionic polymer selected among sulfonated polyimide, sulfonated polystyrene, or perfluorinated polysulfonate.[236]

Zinc electrodes that were first electrolytically treated with POMs were used to electropolymerize pyrrole monomers from propylene carbonate solutions in the presence of *p*-toluenesulfonate ions. The adhesion of the polypyrrole films to the substrate increased after heat treatment at 180 °C for several hours.[237]

A glassy carbon electrode modified with a conducting polypyrrole film doped with $PMo_{12}O_{40}^{3-}$ anion was employed with a dual-electrode arrangement (generating and collecting detectors) in liquid chromatography for the determination of catecholamines.[238] Linear responses ranged over 3 orders of magnitude with a low detection limit of 5.0×10^{-9} mol/L for norepinephrine.

Polyaniline films doped with $H_3PMo_{12}O_{40}$, $H_4PMo_{11}Fe^{II}O_{39}$, and $H_4PMo_{11}Mn^{II}O_{39}$ were described by Lapkowski et al.,[239] as well as Keita et al.[240] Wang described polyaniline films doped with $PV_2Mo_{10}O_{40}^{5-}$ formed on carbon fiber microelectrodes. They were utilized for the electrocatalytic reduction of ClO_3^- and BrO_3^- ions.[241] Analogous reactions were described by Keita et al. in poly(4-vinylpyridine) films formed on glassy carbon electrodes.[242]

Very stable homogeneous films in acid and in organic solvents were prepared by the electropolymerization of 1-naphthol in an acetonitrile solution of $H_6P_2W_{18}O_{62}$.[243]

XIII. Wood Pulp Bleaching (Oxidative Delignification)

The goal of bleaching of wood pulp is to remove the residual lignin and to brighten the pulp by degradation or removal of any chromophores that may still be present. The common process uses chlorine which reacts with the chromophores and residual lignin to form chlorinated aromatics and dioxins which pose a serious threat to the environment. Polyoxometalates, used as reversible oxidants, offer a safe alternative to elemental chlorine. Weinstock et al.[258] reported the use of $H_5PMo_{10}V_2O_{40}$ for the bleaching of pulp. $H_5PMo_{10}V_2O_{40}$ was mixed with water and pulp in a sealed vessel and was heated at a 100 °C for 4 h. Some of the V^{5+} ions were reduced to V^{4+} by the functional groups of the residual lignin. The pulp was washed with water, NaOH solution, and H_2O_2. Prior to reuse the reduced POM was reoxidized by exposure to air, dioxygen, peroxides, or ozone. In a series of publications and patents derived from a collaborative multidisciplinary effort between academia and government the feasibility of wood pulp bleaching by POMs was demonstrated convincingly.[259−264] Weinstock, Hill, et al. reported on the utilization of O_2 in combination with POMs for the oxidative delignification of wood pulp. The process consisted of the anaerobic bleaching of lignin by an aqueous POM_1 solution at high pH. The redox potential of POM_1 should be between the potential of cellulose and lignin. $K_5SiW_{11}VO_{40}$ fulfills the conditions of high pH and appropriate redox potential.[259,261,264] The oxidized lignin fragments and reduced POM were separated from the pulp and were thoroughly washed. Provisions were taken for the concentration/recycling of the wash water. Oxidation of soluble organic compounds to CO_2 and H_2O were catalyzed by a second polyoxometalate, POM_2 [e.g. α-$Na_xH_{5-x}(PMo_{10}V_2O_{40})$]. In an optimized process a unique POM would catalyze both the oxidation of the pulp and of the resulting soluble organic compounds.

A schematic representation of the (idealized) process reactions is shown in the scheme below.

$$\text{pulp} + \text{POM}_{\text{ox}} \rightarrow \text{bleached pulp} + 2\text{H}^+ + \text{POM}_{\text{red}} \quad (4)$$

$$\text{Org}_{(s)} + \text{POM}_{\text{red}} + {}^1/_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{POM}_{\text{ox}} + \text{CO}_2 + \text{H}_2\text{O} \quad (5)$$

Successful implementation (commercialization) of such a process offers important environmental benefits.

Paren et al. claimed a process for the delignification of pulp based on peroxide and/or peracids in the presence of water soluble salts of elements in groups 4, 5, and 6 and at least one heteroatom such as Si, P, or B capable of forming heteropolyacids. The description of the patent alluded to the in situ formation of Keggin type anions preferentially molybdates as activators of bleaching process.[265,266] A patent by Kaneda claimed the use of thiourea with peroxides for the bleaching of paper pulp in the presence of $K_2HPW_{12}O_{40}$.[267] Also a mention of the synergistic use of POMs for the delignification of pulp appeared in a current Russian publication.[268]

XIV. Analysis

Under the heading of analysis one can accumulate an enormous number of publications and to lesser degree patents that relate to the chemistry of POMs. The ability of Mo and W to form POMs with almost all elements of the periodic table, many of which exhibit distinct spectroscopic features, offers the opportunity to the analytical chemist to develop methodology for the determination of such heteroelements as well as for discreet compounds. And these activities do not seem to diminish with the progress of time.[269−374]

Table 8 lists a number of elemental analysis methods generated by the POM chemistry and properties. Recent Chinese and Soviet (Russian) literature dominates this table. The spectroscopic determination of the elements in most of the cases relies on the formation of complexes of mostly unidentified heteropolyacids with cationic dyes and on the application of Beer's law at a $\lambda_{\max}$ specific for these complexes.

A few examples will be presented herein for illustrative purposes. Wang et al.[269,270] claimed a quick and sensitive method for the determination of Si by measuring the luminescence of luminol upon its oxidation by a heteropolymolybdate or -vanadate formed after reaction with the silicate-containing samples. Enhancing agents such as rhodamine, coumarin, fluorescein, and their derivatives were used. The method is quick and has high sensitivity (SiO_2 content 0.5 mg/L can be detected). It was used to detect SiO_2 content in steam, water, and metals.

A glassy carbon electrode was coated with a film of $SiMo_{12}O_{40}^{4-}$ and used for voltammetric determination of Si in black liquor of paper factory.[271] The linear determination range was $8.3 \times 10^{-7}-1.7 \times 10^{-3}$ mol/L using 4.0×10^{-3} mol/L $(NH_4)_2Mo_9O_{24}$/6.8×10^{-2} mol/L sodium citrate/0.48 mol/L HNO_3 system. The detection limit was 8.0×10^{-7} mol/L; the recovery was 97.3−104.4%; the relative standard deviation was 0.85% ($n = 9$).

In another example Osakai described a voltammetric sensor for phosphate analysis.[272] The sensor relied on the electrochemical formation of $PW_{12}O_{40}^{3-}$ at the interface between an aqueous sample solution (containing the phosphate ions) and a nitrobenzene solution containing hexamolybdate anion $Mo_6O_{19}^{2-}$. The detection at the voltammetric current due to interfacial transfer of the heteropoly anion formed was proportional to the phosphate concentration in the range from 0.02 to 0.5 mM. As expected, SiO_3^{2-} interfered with the detection of PO_4^{3-} but AsO_4^{2-} and GeO_4^{2-} did not cause significant interference.

Two U.S. patents by Stone claimed test swabs filled with phosphomolybdic acids that were used for the qualitative determination of lead, mercury, arsenic, and bismuth.[273]

Table 9 shows a few examples of cation separations that are based on the chemistry of POMs.

According to a Soviet Union patent, Yttrium was recovered from aqueous solutions by coprecipitation with $H_3PM(\equiv Mo,W)_{12}O_{40}$ and a cationic dye.[274] Separation of Re from acidic solutions by adding large amounts of Mo and W to form unidentified POM complexes was described in an East German patent.[275] Trace amounts of Am and Eu were recovered from acid solutions by extraction with a solution of $H_3PMo_{12}O_{40}$ and dibutyl (diethylcarbamoyl)phosphonate in nitrobenzene according to a Chech patent.[276]

Crown ethers such as 18-crown-6 in conjunction with $H_3PW_{12}O_{40}$ were used to separate via precipitation Pb^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} from acidic solutions.[277] The same crown ethers with $H_3PMo_{12}O_{40}$ were also used for the successful extraction of rare earth ions. Pr^{3+} exhibited the highest selectivity.[278]

Soviet patents claimed the recovery of heavy nonferrous metals from aqueous solutions by precipitation reactions with POMs in the presence of $R_4N^+Cl^-$.[279,280]

A method was patented for the removal of silica from water by the addition of an isopolymolybdate or -tungstate under acidic conditions to produce a HPA. The HPA was reprecipitated by the addition of a cationic surfactant, organic amine base, etc.[281]

Table 10 lists methodologies for analysis of distinct compounds based again on the properties and chemistry of POMs.

Qualitative and quantitative determination of analytes (substances in body fluids) was carried out by heteropolyacids in the presence of aromatic amine reducing and complexing agents ($E_{\text{red}} \leq 0.45$ V vs NHE) that form insoluble blue precipitates.[282] The intensity of the blue color was quantified either by reflection photometry or by separation of the precipitate, dissolution in a suitable solvent such as DMSO, and absorption spectra measurements. Examples of analytes that were determined were glucose, cholesterol, lactate, NADH, and ethanol.

Patrick et al. described aqueous solutions of α-$Li_xNa_{4-x}SiW_{12}O_{40}$ of very high concentrations (e.g. 2400

Table 8. Elemental Analysis Aided by Polyoxometalate Chemistry and Properties

element	method	limit of detection/comments	reference
Si	extraction, voltammetry as $SiMo_{12}O_{40}^{4-}$	4×10^{-8} mol/L	284
	as $H_4SiM(\equiv Mo,W)_{12}O_{40}$ oxidizer of luminol, measure intensity of luminescence	0.5 mg/L SiO_2	285
	polarography, in Sb(III)−Mo(VI)−ethanol−HCl	used to determine silicon in ores	286
	polarography, as $H_4SiMo_{12}O_{40}$	determination of Si in natural waters [limit, 0.008 μg/mL]	287
	as $H_4SiMo_{12}O_{40}$ extracted in butanol or isobutanol, reduced by a laser at $\lambda = 337-515$ and measure the thermolens signal of the laser beam		288
	photometry, as heteropoly blue ($SiMo_{12}$)	used to determine SiO_2 in solids	289, 290
	spectrophotometry, as molybdotungstosilicates reduced by ascorbic acid	determination of SiO_2 in refractory materials	291
	voltammetry, with $H_4SiMo_{12}O_{40}$ modified glassy carbon electrode	8.0×10^{-7} mol/L	292
Si trace	in graphite; decompose graphite, convert Si to SiF_4 first, then to $H_4SiMo_{12}O_{40}$, reduce with ascorbic acid, measure absorbance at 810 nm	0.05 ppm/g of graphite; recovery, 101%.	293
P	decompose with HNO_3, convert to $H_3PMo_{12}O_{40}$ dissolve in excess base and titrate the excess of the latter with an acid solution.		295
	spectrophotometry, as PMo_{12} blue in Ni−P alloys	error ca. 1%	296
	ICP−AES (from steel)	1 μg/g	297
	photometry, as an association complex of molybdotungstophosphoric acid and crystal violet		298
	photometrically as an association complex of molybdovanadophosphate−triphenylmethane in an oxygen-containing organic solvent		299, 300
P	spectrophotometry, as $H_3PMo_{12}O_{40}$ reduced by ascorbic acid	precision 0.002%, P in waste waters, PO_4^{3-} in vegetables, 0.2−2.0 μg of PO_4^{3-}/mL	301−304
	spectrophotometry ($\lambda_{max} = 680$ nm), P−Sb−Mo HPA−crystal violet PVA system	detn of P in superalloys; limits, 0.002−0.02 mg/50 mL	305
	spectrophotometry, ($\lambda_{max} = 584$ nm, $\epsilon = 1.3 \times 10^6$ L/mol·cm), ethylrhodamine B−$H_3PMo_{12}O_{40}$−PVA system	detn of trace P in steel; limits, 0−0.25 μg/25 mL	306
	spectrophotometry ($\lambda_{max} = 644$ nm, $\epsilon = 8.5 \times 10^4$ L/mol·cm), malachite green−$H_3PMo_{12}O_{40}$−PVA system	limits, 0−3.5 μg/25 mL	307
	polarography ($E_{red} = -0.52$ V vs SCE), P−Sb−W−HPA in H_2SO_4/acetone solution	limit, 2.0×10^{-7} mol/L	308
	polarography, of a P−Sb−W−HPA system	range $2 \times 10^{-8}-10^{-6}$ g/mL; limit, 8×10^{-9} g/mL	309
	polarography ($E_{red} = -1.12$ V vs SCE), in 0.1 mol/L soln containing ascorbic acid and molybdate; 100-fold silicate does not interfere	linear range 5×10^{-8} to 4×10^{-5} mol/L; detection limit, 2×10^{-5} mol/L	310
	polarography ($E_{red} = -0.42$ V vs SCE), in HCl−Sb(III)−$(NH_4)_2MoO_4$, acetone/butanone on a dropping mercury electrode	limit, 6×10^{-8} mol/L	311
	spectrophotometry ($\lambda_{max} = 390$ nm) after extraction as vanadomolybdophosphoric acid with MIBK		312
	spectrophotometry ($\lambda_{max} = 610$ nm, $\epsilon = 1.47 \times 10^5$ L/mol·cm), malachite green−phosphoantimonomolybdate	0−8 μg/25 mL; detection in copper and ores	313
	photometry		314, 315
P, As	kinetic wavelength-pair method	0.5−6 μg/mL	294
P, As	spectrophotometry ($\lambda_{max} = 620$ nm, $\epsilon_P = 2.95 \times 10^5$ L/mol·cm, $\epsilon_{As} = 1.8 \times 10^5$ L/mol·cm), malachite green − $H_3PMo_{12}O_{40}/H_3AsMo_{12}O_{40}$−MeOH system	limits, 0−8 μg/25 mL of P, 0−6 μg/25 mL	316
P, As	spectrophotometry of association heteropoly molybdate complexes with dyes (e.g. malachite green)	detection of phosphate in seawater and iron and steel samples	317
			316
P, As	spectrophotometry of the ion-association complexes of HPA Mo acids with ethylrhodamine B in PVA ($\lambda_{max} = 584$ nm, $\epsilon_P = 2.2 \times 10^5$ L/mol·cm; $\epsilon_{As} = 2.4 \times 10^5$ L/mol·cm)	linear range, 0−2.5 μg/25 mL	318
P, Si, As	spectrophotometry		319
P, Si, As	fluorimetry of HPA−rhodamine 6G in PVA	linear range, 0−0.5 μg of P, Si/25 mL; 0−2.0 μg of As/25 of mL; detection in copper alloys	320
As	spectrophotometry ($\lambda_{max} = 840$, 720 nm), of reduced Mo−Sb−As complex		321
As	polarography ($E_{red} = -0.37$ V vs SCE), in HCl−Sb(III)−$(NH_4)_2MoO_4$, acetone/butanone on a dropping mercury electrode	detection in lead−zinc ores	322, 323
Ge	spectrophotometry, as ion-association complex of $GeMo_{12}$ with malachite green		324

Table 8 (Continued)

element	method	limit of detection/comments	reference
Ge	spectrophotometry, as $GeMo_{12}$ blue ($\lambda_{max} = 680$ nm); oxalic acid was used to eliminate interferences with P, As, and V; Si interference was eliminated as SiF_4		325
Ge	spectrophotometry, as ion-association complex of $GeMo_{12}$ with butylrhodamine B ($\lambda_{max} = 595$ nm, $\epsilon = 2.72 \times 10^5$ L/mol·cm)	detection of trace Ge in ginseng and metallurgical sludge	326
Sn	indirect spectrophotometry from the reduction of $SiMo_{12}$ by Sn(II) ($\lambda_{max} = 750$ nm, $\epsilon = 4.25 \times 10^4$ L/mol·cm)		327
Al	spectrophotometry, as an ion-association complex of molybdoaluminum HPA with crystal violet ($\lambda_{max} = 595$ nm)		328
Ti	spectrophotometry as ion-association complex of molybdotitanophosphoric acid with Nile Blue ($\lambda_{max} = 590$ nm, $\epsilon = 1.94 \times 10^5$ L/mol·cm)	linear range, 0−4.8 μg/25 mL detected in steel and aluminum alloys	329
V	spectrophotometry, as $PW_{11}V^{IV}O_{40}{}^{5-}$	3 μg/mL; detn of V in steel	330
	photometry, as vanadomolybdophosphate		331
Cu	spectrophotometry, based on Cu(II) catalytic effect on $H_3PMo_{12}O_{40}$/I redox reaction; interference from Sn^{2+}, Fe^{2+}, V^{5+}	used to determine Cu in La_2O_3 and aluminum alloys	332, 333
Mo	spectrophotometry, as phosphotungstomolybdate blue ($\lambda_{max} = 500$ nm, $\epsilon = 1.3 \times 10^3$ L/mol·cm)	linear range, 0−0.2 g/L Mo; determination in high-speed steel	334, 335
W	spectrophotometry, as phosphotungstomolybdovanadate ($\lambda_{max} = 740$ nm, $\epsilon = 3.2 \times 10^3$ L/mol·cm)	linear range, 0−3.0 mg/25 mL; detn of W in high-speed steel	336
Nb	spectrophotometry of ion-associated complex of molybdoniobate with crystal violet in PVA and arabic gum ($\lambda_{max} = 640$ nm, $\epsilon = 8.52 \times 10^5$ L/mol·cm)	linear range, 0−0.4 μg/mL; detn of Nb in alloys and rocks	337, 338, 339
Nb	polarography, as niobium molybdenum blue HPA reduced with ascorbic acid ($E_{red} = -1.10$ V vs SCE)	linear range, 0.005−0.4 mg/L; limit, 0.002 mg/L; detn of Nb in alloy steel refractories	340
Hf	spectrophotometry, of ion-associated complex of molybdolanthanohafnic acid with Nile Blue in PVA ($\lambda_{max} = 590$ nm, $\epsilon = 1.5 \times 10^7$ L/mol·cm)	linear range, 0−250 ng/25 mL Hf(IV)	341
Zr	spectrophotometry of an ion-associated complex of zircomolybdic acid with Nile Blue (1:4) in PVA ($\lambda_{max} = 615$ nm, $\epsilon = 3.7 \times 10^5$ L/mol·cm)	linear range, 0−5 μg of Zr/25 mL; detn of Zr in ores	342
Sc	spectrophotometry of an ion-associated complex of molybdoscandic acid with Nile Blue (1:3) in PVA ($\lambda_{max} = 585$ nm, $\epsilon = 3.59 \times 10^5$ L/mol·cm)	linear range, 0−2.0 μg/25 mL; detn of Sc in ores	343
Th	spectrophotometry, of an ion-associated complex of molybdothoric acid with Nile Blue (1:3) in PVA ($\lambda_{max} = 590$ nm, $\epsilon = 4.45 \times 10^6$ L/mol·cm)	linear range, 0−28 μg/L Th; limit, 3.4 μg/L; no interference from 100-fold Ce(III), 50-fold U(IV), and 20-fold P(V); detn of Th in geological samples	344
Y	spectrophotometry, by using Nile blue, $MoO_4{}^{2-}$, and PVA ($\epsilon = 4.45 \times 10^6$ L/mol·cm)	linear range, 0−140 μg/L; detn of Y in magnesium alloys	345
Te	spectrophotometry, of an ion-associated complex of molybdotelluric acid with butylrhodamine B in PVA ($\lambda_{max} = 570$ nm, $\epsilon = 3.2 \times 10^5$ L/mol·cm)	linear range, 0−6 μg/25 mL of Te; detn of Te in flue dust	346
Ta	by spectrophotometry of an ion-associated complex of molybdotantalate acid with Nile Blue (1:3) in PVA ($\lambda_{max} = 625$ nm, $\epsilon = 2.26 \times 10^6$ L/mol·cm)	linear range, 0−2.6 μg/mL Ta(IV); detn of trace Ta(IV) in steels and some ores	347
Hg	colorimetrically with dithizone in the presence of $H_3PW_{12}O_{40}$	stable Hg^{2+}−dithizone complex	348
Bi	spectrophotometry, as molybdobismuthophosphoric acid, reduction with ascorbic acid	0.4−3.2 μg/mL	349
Au	kinetic spectrometric method using the reduction of $H_3PMo_{12}O_{40}$ by formic acid as an indicator reaction	detn of trace Au in natural water	350
Tl	precipitation with $H_3PW_{12}O_{40}$ and TBABr, redissolution of ppt in alkaline solution and determination of Tl by spectrophotometry		351
Sb	spectrophotometry, as ternary HPA Sb−As−Mo-ascorbic acid	detn of Sb in pure Ni	352
S	spectrophotometry after conversion to sulfide form; an HPA is used as reagent		353

g/450 mL of H_2O) that form a heavy liquid (specific gravity ≥ 2.85) useful in mineral separations (heavy components from light components such as silica).[283] Current use of bromoform ($d = 2.87$ g/mL) or 1,1,2,2-tetrabromoethane ($d = 2.95$ g/mL) needs to be phased out due to environmental hazards. Solutions of sodium metatungstate ($Na_6H_2W_{12}O_{40}$) have been proposed as safe replacements ($d = 2.8$ g/mL), but their high viscosity and their instability at temperatures higher than 60 °C have inhibited their use. Heavy liquids of α-$Li_xNa_{4-x}SiW_{12}O_{40}$ were used to separate heavy minerals such as zircon, rutile, ilmenite, monazite, xenotime, hematite, magnetite, diamonds, and garnets from minerals such as quartz, feldspars, gypsum, vermiculite, clay, and serpantine minerals.

Table 9. Separations Based on the Chemistry of Polyoxometalates

element	method	limit of detection, sensitivity	reference
Sr^{2+}/Ca^{2+}	crown ethers/$H_4SiW_{12}O_{40}$, radiometric titration	traces to 6 × 10^{-3} mol of Sr^{2+} in the presence of 0.2 mol/L Ca^{2+}	370
U	$H_3Mo_{12}O_{40}$/kinetic spectrophotometry	0.02 μg/L; good tolerance for Th and Sc	371
U(IV)	$P_2W_{17}O_{61}^{10-}$/1:2 spectrophotometry	$\epsilon_{510\ nm}$ = 1010 L/mol·cm, separation from Pu	372
$^{89,90}Sr^{2+}/^{137}Cs^{+}$	crown ethers/$H_3PMo_{12}O_{40}$ radiometric titration	separation coefficient > 10^3 at yields 99% for Cs and 95% for Sr; concentration, 10^{-3} g/L	373
^{237}Np and ^{239}Pu	anion exchange catalysis	$PV_2Mo_{10}O_{40}^{5-}$, $PMo_{12}O_{40}^{3-}$, $CeMo_{12}O_{40}^{4-}$, $PV_6Mo_6O_{40}^{9-}$	374

Table 10. Analysis of Compounds Aided by Polyoxometalate Chemistry and Properties

compound	method/comments	reference
adenyl groups	by chemiluminescence through a glyoxal derivative in the presence of HPA or POM	354
isothiozolones	by spectrophotometry of adduct formed with phosphomolybdotungstic acid	355
terpenes	by spectrophotometry of unidentified stable colored complex formed with $H_3PMo_{12}O_{40}$	356
hydroquinone	by spectrophotometry upon adduct formation with tungstovanadophosphoric acid	357
retinol	by spectrophotometry after reaction with $H_3PMo_{12}O_{40}$	358
sodium carboxymethyl cellulose	by precipitation with $H_3PMo_{12}O_{40}$ in the presence of $BaCl_2$ followed by titration of the unreacted reagent with diantipyrylmethane solution	359
ascorbic acid	indicator paper impregnated with $(NH_4)_3PMo_{12}O_{40}$ and tartaric acid or malonic acid	360
polyacrylamide	by colorimetry with POM or HPA as the color reagent	361
surfactants	unidentified surfactants by precipitation with Keggin acids and amperometric titration	362
dimethyl acetamide	after precipitation with HPA, titrate the unreacted HPA with dimethylacetamide using an electrochemical endpoint indicator	363, 364, 365
sulfate ions	by voltammetry after formation of an unidentified reduced heteropolymolybdate complex	366
sulfate ions	by spectrophotometry of an unidentified heteropolymolybdate blue complex reduced by $SnCl_2$ (λ_{max} = 575 nm), detection limit, 1.5 × 10^{-6}M SO_4^{2-}; detn of SO_4^{2-} in natural water samples	367
bromate, iodate	by electrochemical reduction on a glassy carbon electrode modified with $H_3PMo_{12}O_{40}$; linear range, 8 × 10^{-10}–1 × 10^{-7} mol/L for iodate and 1.6 × 10^{-9}–3 × 10^{-7} mol/L for bromate; low limit, 4 × 10^{-10} mol/L for iodate and 1 × 10^{-9} for bromate	368
NO	by spectrophotometry after complexation with $XW_{11}O_{39}Fe(OH_2)^{n-}$, X = P, Si	369

XV. Protein Precipitation Agents

A well-known application of POMs is their ability to precipitate proteins. Earlier examples were compiled by Pope.[375] Some of the most recent examples are summarized herein.[376–386] Of the POMs, most often $H_3PW_{12}O_{40}$ is the agent of choice. In a method described by Yeang et al.[377] the POM–protein precipitate was redissolved in NaOH, and a Lowry colorimetric microassay was used to quantify the proteins. A simpler quantitative method was based on UV absorbance at 280 nm.

One of the two common methods for the detection of HDL cholesterol in human serum is precipitation with phosphotungstate/$MgCl_2$.[378] (The other one is by precipitation with dextran/$MgCl_2$.) Methods were patented for the colorimetric determination of HDL cholesterol by magnesium phosphotungstate[379] and by using a solid-state precipitation device.[380]

Use of phosphomolybdic acid to precipitate proteins found in wines was reported as a method for removal of unstable proteins from the wines. Upon exposure to elevated temperatures, these proteins can denature, agglomerate, and form/haze and/or precipitate.[381] This can pose a problem to the wineries when it occurs after bottling.

Phosphotungstic acid was also used to precipitate water soluble amino acids from casein in cheddar-type cheese.[382]

In a French patent by Kelner, $H_4SiW_{12}O_{40}\cdot nH_2O$ was used at 1–5% levels together with tungstic acid in Kaolin/cellulose-based cigarette filters to remove 83–89% of nicotine and its homologues from smoke.[383]

XVI. Staining Agents

The staining ability of POMs is also well recognized and exploited.[387–393] Barnakov described the use of 1% $H_3PW_{12}O_{40}$ on SEM samples of lipid membranes and proteins that improve the adhesion of the materials on the hydrophobic grids.[388] Yamashita et al.[389] described the use of $H_3PW_{12}O_{40}$ as a staining agent of formalin-fixed paraffin-embedded clinical samples for enhancement of immunoreactivity with the microwave method.

XVII. Processing of Radioactive Wastes

A good number of applied analytical publications deal with the usage of POMs as process aids for the processing of radioactive nuclei.[394–403] Blasius et al.[394] patented a process that utilizes heteropolyacids and macrocyclic crown ethers to extract cesium ions from aqueous solutions. Cs^{134} and Cs^{137} are usually present in small quantities in medium active aqueous wastes (MAW). Their presence renders the processing and solidification (vitrification) of these wastes more difficult because they evaporate to a noticeable degree and leach out of the vitrified products that are intended for permanent storage such as glass blocks, cement blocks, and bitumen blocks. Furthermore, if Sr^{90} were simultaneously extracted from MAW, low active aqueous wastes (LAW) would be obtained since, after a relatively short decay period, practically the entire activity of MAW originates from the relatively long-lived radionucleotides Cs^{137} ($t_{1/2}$ = 30 years) and Sr^{90} ($t_{1/2}$ = 26 years).

Solid adducts of $H_nX(\equiv Si, P)M(\equiv Mo,W)_{12}O_{40}$ with crown ethers were prepared by mixing various ratios of the two components in common solvents (e.g. acetone). The more preferred mole ratio of crown ether to POM acid was within the limits: $0.5{:}1 \leq$ crown ether:POM $\leq 2{:}1$. Preferred crown ethers were benzo-15-crown-5, dibenzo-21-crown-7, and dibenzo-30-crown-10. Ion exchangers were prepared when the solid adduct was formed in the presence of alumina or silica gel. Experiments were described where it was demonstrated that these ion exchangers removed Cs^+ from MAW solutions. In a separate patent the same authors claimed a process where the crown ether/POM adducts (ratios crown ether: POM equal to or greater than stoichiometry) were used to extract Cs^+ from aqueous solution into nitrobenzene or nitromethane.[395] Limitation of these approach is the fact that $H_3PMo_{12}O_{40}$ is also soluble in the aqueous phase and causes interference with the subsequent process of MAW such as vitrification. In addition, small anions associated with Cs^+ such as Cl^- and NO_3^- are difficult to extract. Thus specific reagents that contain voluminous polarizable anions (e.g. picric acid) are used in conjunction with crown ethers. Conversely, in a series of simulated tests, Lin et al. demonstrated extraction percentages as high as 99.1% in nitrobenzene.[396]

In a German patent, Deicke claimed a method of separation of Cs^+ from radioactive waste by precipitation with $H_3PM(\equiv Mo,W)_{12}O_{40}$ followed by NH_4OH treatment to dissolve the precipitate and subjecting it to an electric field. The cathode solution contained practically all the Cs^+ as CsCl with less than 1% of P or Mo.[397]

Pfrepper described the recovery of Cs as Cs molybdate from Cs−POM salts after heat treatment with $SrCO_3$ at 750 °C for 30 min.[398] In a subsequent patent he described the recovery of Cs from cesium polyoxometalate salts by dissolving the salt into NH_4OH and reprecipitating by reaction with a basic oxide such as CaO. The Cs was isolated as $Cs_2\ CO_3$ after the addition of $(NH_4)_2CO_3$.[399]

In a patent by Kamoshita et al., POMs were used as pH-controlling agents during reprocessing of Am.[400]

XVIII. Sorbents of Gases

The solid forms of POMs have been claimed as sorbents of gases in numerous patents. These applications fall in the field of solid-state catalysis, the science of which is reviewed elsewhere in this issue. A few examples are described herein.

Yang et al. claimed the use of Keggin type POMs and their salts for the adsorption of flue gases (NO_x, SO_2, and CO_2) followed by the decomposition of the NO_x gases to N at $T = 250-550$ °C.[404] Von Wedel et al. described a complex solid catalyst system that included among others $H_3PM(\equiv Mo,W)_{12}O_{40}$. The catalyst was used for the decomposition of highly toxic organic compounds in gases from incineration of municipal refuse.[405] Fukuda et al. claimed the use of a fixed bed of $H_3PMo_6W_6O_{40}$ on a porous support for the purification of vent air from odorous components especially amines and mercaptants.[406] Bao et al. described the use of Keggin type acids as absorbents for H_2S. TGA and DSC confirmed that the products were solid sulfur, HPA blue, and water. The reduced HPA could be reoxidized with the use of oxidants such as NO_2, Fe^{3+}, Cl_2, etc.[407] A Czechoslovakian patent claimed the use of insoluble POM salts and poly(alkylene glycols) as Sorbents for the selective sorption of Ra gas.[408] A Russian patent claimed the effective removal of N_2O from a gas mixture by using an unidentified sodium ferrate(II)−heteropolytungstate absorbent containing P or Si as the heteroatom.[409] A Japanese patent described a catalytic converter for the reduction of NO_2 to give NO in polluted air or gases and which converter included $H_3PMo_{12}O_{40}$.[410] Ryazantsev et al. described a treatment for waste gases from the pulping industry that included radiation treatment at a dose of 0.1 Mrad in conjunction with catalytic oxidation through a zeolite which was modified with Co, Fe, and polyphosphotungstic acid. The method achieved the effective removal of H_2S, Me_2S, and α-pipene.[411]

A patent with very broad claims was recently issued on mesoporous molecular sieve compositions of heteropoly- and isopolyanions with anionic surfactants. Uses were proposed in catalysis, sorbents, pigments, electronics, optics, membranes, etc.[412]

A patent by Degussa described a hydrothermal process for making microporous POM catalysts. The preparation method consists of a hydrothermal reaction of the metal, its corresponding oxide, a diamine, phosphoric acid, and water.[413]

XIX. Miscellaneous Applications

A patent by David utilized POMs in the etching process of polymer matrix composites (PMC).[414] Conventional etching of molybdenum is typically done in basic solutions using ferricyanide according to the equation

$$6Fe(CN)_6{}^{3-} + Mo + 8OH^- \rightarrow 6Fe(CN)_6{}^{4-} + MoO_4{}^{2-} + 4H_2O \quad (6)$$

The etching process cannot be used when the molybdenum is incorporated in a PMC that is made of a low dielectric organic resin such as polyimide, because under the strong basic conditions the organic polymer is decomposed. Lowering the pH to below 11 causes the formation of undesirable molybdate polymer residues that stop the etching process. David claimed the formation of aqueous etching solutions of nearly neutral pH by adding to the ferricyanide solution soluble molybdates or tungstates and suitable heteroelements that could form in situ heteropolycomplexes (e.g. H_3PO_4). Unspecified soluble heteropolycomplexes (most likely, of the lacunary or substituted lacunary type) allowed the etching process to continue without impacting the stability of the PMC.

Jackson disclosed the use of $H_3PW_{12}O_{40}$ aqueous solutions for treatment of polyamide fibers to increase their fire resistance as measured by limited oxygen index (LOI).[415] This test determines the minimum percentage of oxygen in the atmosphere to sustain burning of the material. Specific examples of the specification showed that aqueous treatments with POMs had LOI values as high as 45%.

Hill et al. demonstrated the use of $H_5PV_2Mo_{10}O_{40}$ as a supported catalyst for the decontamination of mustard (HD) analogues.[416] The POM was immobilized effectively on carbon fibers such as PPAN (pyrolyzed polyacrylonitrile) and Ambersorb 527 (Rohm & Haas) and showed very low desorption even under catalytic conditions. The supported POMs were shown to be effective catalysts for the oxidation of thioether HD analogues by *tert*-butyl hydroperoxide. Applications of this type of research are envisioned in the fabrication of clothing for protection from chemical warfare agents.

A recent German patent claimed the use of POMs as additives to binder suspensions such as fresh concrete, ready-mix for reducing cracking during hardening. Similarly, they were claimed as a secondary treatment of concrete that has been hardened (claimed as tougheners).[417]

Wall in a German patent claimed ceramic formulations composed of metal and nonmetal oxides (i.e., Al_2O_3, B_2O_5, P_2O_5, SiO_2, etc.) including POM salts of the Keggin structure in which oxygen had been replaced by fluoride. The formulations are suitable for dental applications.[418]

XX. Conclusions

The patent and referee literature survey indicates that the utilization of Keggin type POMs continues to grow in many areas in addition to the traditional area of catalysis. As their fundamental chemistry has matured, these POMs are being embraced by material scientists and technologists and are tested with regard to numerous applications. They are usually integrated in multicomponent assemblies to take advantage of their unique value-adding properties in a synergistic way with the properties of the other components of the composites. Properties such as ion conductivity, electrochromicity, redox activity, good thermal stability, and complex formation with a multitude of cations are exploited in applications that include coatings, membranes, films, electrochemical devices, pigments, analytical reagents, etc. Among these properties, the good thermal stability of POMs has frequently been cited as the advantage in applications over other comparable materials. The author feels that interesting areas for further development are in toner technology, in isopolyoxometalate film formation technology, in electrode modification technology, and in sol−gel/POM composites. With a few exceptions, the patent literature, because of its nature, offers very little proof for compositional as well as utility claims. Comparative studies with existing commercial systems are also very few. Therefore the need exists for better characterization of the systems used in POM-based applications that will include comparison with current commercial products. As the utilization of POMs increases, it is important to continue to couple the fundamental research with the technological developments in order to seriously expand the opportunities for these materials. The multidisciplinary approach to science offers great optimizm that the applications of the Keggin type POMs will grow, but also that the field will broaden to include applications that are based on many of the other known POM structures.

XXI. Acknowledgments

I am grateful to Jim Malek of the Dow Corning Information Center for his help with the literature searches.

XXII. References

(1) Lomakina, S. V.; Shatova, T. S.; Kazansky, L. P. *Corros. Sci.* **1994,** *36,* 1645.
(2) Wu, N.; Wang, S.; Wang, Z.; Xu, H.; Fang, J. *Yingyong Huaxue* **1993,** *10,* 5; *Chem. Abstr.* **1993,** *119,* 186166n.
(3) Buettner, U.; Jostan, J. L. German Patent DE 3407095 A1, 1985; *Chem. Abstr.* **1985,** *103,* 219247.
(4) Asahi Chemical Industry Co., Ltd. Japanese Patent JP 59200769 A2, 1984; *Chem. Abstr.* **1984,** *102,* 82691.
(5) Otsuka Chemical Co., Ltd. Japanese Patent JP 58164792 A2, 1983; *Chem. Abstr.* **1983,** *101,* 11337.
(6) Pikel'nyi, A. Ya.; Reznikova, G. G.; Brynza, A. P.; Khmelovskaya, S. A.; Pikel'naya, O. A. *Russ. J. Electrochem. (Transl. Elektrokhimiya)* **1995,** *31,* 484.
(7) Pikel'nyi, A. Ya.; Reznikova, G. G.; Brynza, A. P.; Khmelovskaya, S. A. *Zashch. Met.* **1994,** *30,* 443.
(8) Bech-Nielsen, G.; Tang, P. T. World Patent 9310278 A1, 1993; *Chem. Abstr.* **1993,** *119,* 101536.
(9) Nippon Muki Kagaku Kogyo K. K. Japanese Patent JP 57065763 A2, 1982; *Chem. Abstr.* **1982,** *97,* 94098.
(10) Harada, S.; Oota, Y.; Yota, T.; Tanabe, S. Japanese Patent JP 06100803 A2, 1994; *Chem. Abstr.* **1994,** *121,* 111631.
(11) Roberts, G. L., Jr.; Fessler, R. G. U.S. Patent 3346604, 1967; *Chem. Abstr.* **1967,** *68,* 3981.
(12) Roberts, G. L., Jr.; Fessler, R. G. U.S. Patent 3365313, 1968; *Chem. Abstr.* **1968,** *68,* 70265.
(13) Besecker, C. J.; Marritt, W. A. U.S. Patent 4900853 A, 1990; *Chem. Abstr.* **1990,** *113,* 134256.
(14) Shindo, Y.; Kabeya, M.; Tanimura, K.; Yamazaki, F. Japanese Patent JP 05311457 A2, 1993; *Chem. Abstr.* **1993,** *120,* 223581n.
(15) Shindo, Y.; Kabeya, M.; Tanimura, K.; Yamazaki, F. Japanese Patent JP 05140760 A2, 1993; *Chem. Abstr.* **1993,** *119,* 122200m.
(16) Shindo, Y.; Kabeya, M.; Yamazaki, F. Japanese Patent JP 05070968 A2, 1993; *Chem. Abstr.* **1993,** *120,* 35686b.
(17) Shindo, Y.; Kabeya, M.; Tanimura, K.; Yamazaki, F. Japanese Patent JP 05195242 A2, 1993; *Chem. Abstr.* **1993,** *119,* 276194z.
(18) Shindo, Y.; Kabeya, M.; Yamazaki, F. Japanese Patent JP 04311578 A2, 1992; *Chem. Abstr.* **1992,** *118,*129410t.
(19) Shindo, Y.; Kabeya, M.; Yamazaki, F. Japanese Patent JP 05132788 A2, 1993; *Chem. Abstr.* **1993,** *119,* 143989r.
(20) Shindo, Y.; Kabeya, M.; Tanimura, K.; Yamazaki, F. Japanese Patent JP 05156465 A2, 1993; *Chem. Abstr.* **1993,** *119,* 185866d.
(21) Shindo, Y.; Kabeya, M.; Tanimura, K.; Yamazaki, F. Japanese Patent JP 05156464 A2, 1993; *Chem. Abstr.* **1993,** *119,* 185865c.
(22) Shindo, Y.; Kabeya, M.; Yamazaki, F. Japanese Patent JP 04311577 A2, 1992; *Chem. Abstr.* **1992,** *118,* 129411.
(23) Jenkins, W. G.; Keemer, C.; Lamborn, H. T.; Curcio, M. U.S. Patent 5356469, 1994; *Chem. Abstr.* **1994,** *122,* 268214.
(24) Jenkins, W. G.; Keemer, C.; Lamborn, H. T.; Curcio, M. U.S. Patent 5296032 A 1994; *Chem. Abstr.* **1994,** *121,* 59782.
(25) Fang, J.; Wang, J.; Liu, T.; Liu, Q.; Song, W. *Yingyong Huaxue* **1993,** *10,* 53; *Chem. Abstr.* **1993,** *120,* 112576v.
(26) Ido, H.; Wada, Y.; Nakayama, T.; Nishimoto, H. Japanese Patent JP 06280082 A2, 1994; *Chem. Abstr.* **1994,** *122,* 18946.
(27) Nakazato, M.; Konishi, Y. Japanese Patent JP 06280041 A2, 1994; *Chem. Abstr.* **1994,** *122,* 61727.
(28) Fan, L. *Shuichuli Jishu* **1994,** *20,* 150; *Chem. Abstr.* **1994,** *122,* 88978.
(29) Konishi, Y. Japanese Patent JP 06306631 A2, 1994; *Chem. Abstr.* **1994,** *122,* 111714.
(30) Yokochi, C.; Isayama, K.; Shibata, A.; Tomoshige, K. Japanese Patent JP 06248473 A2, 1994; *Chem. Abstr.* **1994,** *122,* 139336.
(31) Kharina, G. V.; Kochergin, V. P. *Zh. Prikl. Khim. (S.-Peterburg)* **1996,** *69,* 1755; *Chem. Abstr.* **1996,** *126,* 136853.
(32) Simpson, C. *CHEMTECH* **1997,** *27,* 40.
(33) Han, K.; Fang, J. *J. Electron Spectrosc. Relat. Phenom.* **1997,** *83,* 93.
(34) Judeinstein, P.; Schmidt, H. *J. Sol−gel Sci. Technol.* **1994,** *3,* 189.
(35) Minami, N.; Hiraoka, M.; Izumi, K.; Uchida, Y. Japanese Patent JP 08113732 A2, 1996; *Chem. Abstr.* **1996,** *125,* 117543.
(36) Minami, N.; Hiraoka, M.; Izumi, K.; Uchida, Y. Japanese Patent JP 08113731 A2, 1996; *Chem. Abstr.* **1996,** *125,* 117542.
(37) Minami, N.; Hiraoka, M.; Izumi, K.; Uchida, Y. Japanese Patent JP 08141493 A2, 1996; *Chem. Abstr.* **1996,** *125,* 171066.

(38) Katsoulis, D. E.; Keryk, J. R. Abstract ACS National Meeting, Inorganic Chemistry Section, Aug 20−24, **1995,** Chicago.
(39) Tasumisago, M.; Honjo, H.; Sakai, Y.; Minami, T. *Solid State Ionics* **1993,** *59,* 171.
(40) Tasumisago, M.; Honjo, H.; Sakai, Y.; Minami, T. *Solid State Ionics* **1994,** *74,* 105.
(41) Asuka, M.; Myazaki, M.; Nakatani, Y.; Myamoto, K. Japanese Patent JP 07333401 A2, 1995; *Chem. Abstr.* **1996,** *124,* 215718.
(42) Asuka, M.; Myazaki, M.; Nakatani, Y.; Myamoto, K. Japanese Patent JP 07305000 A2, 1995; *Chem. Abstr.* **1995,** *124,* 148915.
(43) Asuka, M.; Myazaki, M.; Nakatani, Y.; Myamoto, K. Japanese Patent JP 07247379 A2, 1995; *Chem. Abstr.* **1995,** *124,* 119510.
(44) Asuka, M.; Nakatani, Y.; Myamoto, K. Japanese Patent JP 06306308 A2, 1994; *Chem. Abstr.* **1994,** *122,* 242452.
(45) Asuka, M.; Myazaki, M.; Nakatani, Y.; Myamoto, K. Japanese Patent JP 06200185 A2, 1994; *Chem. Abstr.* **1994,** *124,* 58348.
(46) Asuka, M.; Myazaki, M.; Nakatani, Y.; Myamoto, K. Japanese Patent JP 07333401 A2, 1994; *Chem. Abstr.* **1994,** *124,* 215718.
(47) Matsuda, S.; Chigusa, T.; Tatsumisuna, M.; Minami, T. Japanese Patent JP 06005232 A2, 1994; *Chem. Abstr.* **1994,** *121,* 145569.
(48) Asuka, M.; Myazaki, M.; Nakatani, Y.; Myamoto, K. Japanese Patent JP 08005803 A2, 1996; *Chem. Abstr.* **1996,** *124,* 292493.
(49) Tsuchida, I.; Saito, T. Japanese Patent JP 63254112 A2, 1988; *Chem. Abstr.* **1988,** *110,* 213627.
(50) Killian, G.; Jacobi, R. German Patent DE 1289652, 1969; *Chem. Abstr.* **1969,** *70,* 97729.
(51) Nakajima, M.; Okanoe, E.; Mogami, T. Japanese Patent JP 61272282 A2, 1988; *Chem. Abstr.* **1986,** *107,* 87264.
(52) Orel, B,; Lavrencic-Stangar, U.; Hutchins, M. G.; Kalcher, K. *J. Non-Cryst. Solids* **1994,** *175,* 251.
(53) Stangar, U. L.; Orel. B.; Hutchins, M. G. *Proc. SPIE—Int. Soc. Opt. Eng.* **1994,** *2255* (Optical Materials Technology for Energy Efficiency and Solar Energy Conversion XIII), 261; *Chem. Abstr.* **1994,** *122,* 117628.
(54) Stangar, U. L.; Orel. B. *Kovine, Zlitine, Technol.* **1994,** *28,* 445; *Chem. Abstr.* **1994,** *122,* 277520.
(55) Tanahashi, I.; Mitsuyu, T.; Tatsumisuna, M.; Minami, T. Japanese Patent JP 07283084 A2, 1995; *Chem. Abstr.* **1995,** *124,* 191617.
(56) Satake, T.; Yoneda, T. Japanese Patent JP 01192742 A2, 1989; *Chem. Abstr.* **1989,** *112,* 163860.
(57) Ayusawa, S.; Kondo, S. Japanese Patent JP 60220503 A2, 1985; *Chem. Abstr.* **1985,** *104,* 132910.
(58) Nakajima, M.; Okanoe, E.; Mogami, T. Japanese Patent JP 62061048 A2, 1987; *Chem. Abstr.* **1987,** *107,* 124676.
(59) Tell, B.; Wagner, S. *Appl. Phys. Lett.* **1978,** *33,* 837.
(60) Tell, B.; Wudl, F. *J. Appl. Phys.* **1979,** *50,* 5944.
(61) Mohapatra, S. K.; Boyd, G. D.; Storz, F. G.; Wagner, S.; Wudl, F. *J. Electrochem. Soc.* **1979,** *126,* 805.
(62) Tatsumisago, M.; Minami, T. *J. Am. Ceram. Soc.* **1989,** *72,* 484.
(63) Orel, B.; Stangar, U. L.; Opara, U.; Gaberscek, M.; Kalcher, K. *J. Mater. Chem.* **1995,** *5,* 617.
(64) Knoth, W. H. *J. Am. Chem. Soc.* **1979,** *101,* 759.
(65) Katsoulis, D. E.; Keryk, J. R. *Mater. Res. Soc. Symp. Proc.* **1996,** *435* (Better Ceramics through Chemistry VII: Organic Inorganic Hybrid Materials), 589.
(66) Katsoulis, D. E.; Keryk, J. R. European Patent Appl. EP723970 A2, 1996; *Chem. Abstr.* **1996,** *125,* 211234.
(67) Katsoulis, D. E.; Keryk, J. R. U.S. Patent 5391638 1995; *Chem. Abstr.* **1995,** *123,* 56947.
(68) Yoneda, T.; Satake, N.; Nishida, M.; Nakahara, S. Japanese Patent JP 02138373 A2, 1990; *Chem. Abstr.* **1990,** *113,* 193585.
(69) Yoneda, T.; Satake, N.; Nishida, M.; Nakahara, S. Japanese Patent JP 02049075 A2, 1990; *Chem. Abstr.* **1990,** *113,* 134283.
(70) Suzuki, T.; Ozaki, Y. Japanese Patent JP 63104027 A2, 188; *Chem. Abstr.* **1988,** *109,* 119759.
(71) Ul'berg, Z. R.; Ivzhenko, N. N.; Dvornichenko, G. L.; Buadze, R. O.; Koniashvili, S. A. *Ukr. Khim. Zh. (Russ. Ed.)* **1992,** *58,* 390; *Chem. Abstr.* **1992,** *117,* 152819w.
(72) Lazareva, T. G.; Il'yushenko, I. A.; Alimov, I. F. *Vysokomol. Soedin., Ser. A Ser. B* **1994,** *36,* 1481; *Chem. Abstr.* **1994,** *123,* 114436.
(73) Lazareva, T. G.; Vashuk, E. V.; Alimov, I. F.; Ie′yushchenko, I. A.; Makhover, A. Z. *Proc. SPIE—Int. Soc. Opt. Eng.* **1996,** *2716* (Smart Materials Technologies and Biomimetics), 267.
(74) Lazareva, T. G.; Sviridova, R. N.; Il'yuschchenko, I. A.; Ermolenko, I. N. *Zh. Anal. Khim.* **1993,** *48,* 111; *Chem. Abstr.* **1993,** *120,* 181756r.
(75) Heller, A.; Argitis, P.; Carls, J. C. U.S. Patent 5292558, 1994.
(76) Nishida, M.; Kuramoto, S.; Yoneda, T. Japanese Patent JP 02312106 A2, 1990; *Chem. Abstr.* **1990,** *115,* 62572.
(77) Chuvaev, V. F.; Barash, A. B.; Yaroslavtseva, E. M. Soviet Patent SU 1397458 A1, 1988; *Chem. Abstr.* **1988,** *109,* 171645.
(78) Takenaka, Y. Japanese Patent JP 03258874 A2, 1991; *Chem. Abstr.* **1991,** *116,* 131337.
(79) Ansonii, E. M. Japanese Patent JP 08176281 A2, 1996; *Chem. Abstr.* **1996,** *125,* 222771.
(80) Kostas, J. N. U.S. Patent 5491249 A, 1996; *Chem. Abstr.* **1996,** *124,* 233507.
(81) Katsoulis, D. E.; Keryk, J. R. U.S. Patent 5608096, 1997; *Chem. Abstr.* **1997,** *126,* 251572.
(82) Mazany, A. M. European Patent EP 755938 A1, 1997; *Chem. Abstr.* **1997,** *126,* 200209.
(83) Hair, M. L.; Lok, K. P.; Winnik, F. M. U.S. Patent 4705567 A, 1987; *Chem. Abstr.* **1987,** *108,* 77366.
(84) Oliver, V. S.; Tames, W.; Proshaska, H. H.; Wieser, K. H. U.S. Patent 4576649 A, 1986; *Chem. Abstr.* **1986,** *104,* 226423.
(85) Clarke, R. A. U.S. Patent 3387916, 1968; *Chem. Abstr.* **1968,** *69,* 37050.
(86) Locatell, L.; Norland, K.; Roberts, F. D.; Zepp, C. World Patent WO 9113122 A1, 1991; *Chem. Abstr.* **1991,** *117,* 160309v.
(87) Closs, F.; Albert, B.; Wienand, H. European Patent EP 619346 A1, 1994; *Chem. Abstr.* **1994,** *122,* 268151.
(88) Ludwig, T. E. U.S. Patent 4444592 A, 1984; *Chem. Abstr.* **1984,** *101,* 112429.
(89) Kasahara, Y.; Arai, F. Japanese Patent JP 62013464 A2, 1987; *Chem. Abstr.* **1987,** *106,* 215581.
(90) Kasahara, Y.; Arai, F.; Nakazawa, H. Japanese Patent JP 61185568 A2, 1986; *Chem. Abstr.* **1986,** *106,* 20066.
(91) Nazvantseva, G. A.; Glazyrin, I. M.; Kozadaeva, V. F. USSR Patent SU 834046, 1981; *Chem. Abstr.* **1981,** *95,* 117150.
(92) Mokovskaya, A. Kh.; Khvorostova, A. P. USSR Patent SU 190510, 1966; *Chem. Abstr.* **1966,** *68,* 3976.
(93) Konuki, I. Japanese Patent JP 05179188 A2, 1993; *Chem. Abstr.* **1993,** *119,* 205640.
(94) Kakinuma, K.; Nose, K.; Goto, Y. Japanese Patent JP 75136488, 1975; *Chem. Abstr.* **1975,** *84,* 61072.
(95) Ishii, H.; Ogino, T. World Patent WO 9425640 A1, 1994; *Chem. Abstr.* **1994,** *122,* 220400.
(96) Lyman, C. U.S. Patent 2895892, 1959.
(97) Lyman, C. U.S. Patent 2981622, 1961.
(98) Flohr, H.; Jesse, J.; Albert, B. German Patent DE 3520109 A1, 1986; *Chem. Abstr.* **1986,** *107,* 60742.
(99) Bast, K.; Plankenhorn, E. German Patent DE 2707972 A1, 1978; *Chem. Abstr.* **1978,** *90,* 105796.
(100) Jesse, J. German Patent DE 3435433 A1, 1986; *Chem. Abstr.* **1986,** *105,* 25887.
(101) Ozawa, T.; Maeda, S.; Kurose, Y. Japanese Patent JP 62124986 A2, 1987; *Chem. Abstr.* **1987,** *108,* 46893.
(102) Yabuta, K. Japanese Patent JP 63193883 A2, 1988; *Chem. Abstr.* **1988,** *110,* 85591.
(103) Dainippon Printing Co. Japanese Patent JP 60054888 A2, 1985; *Chem. Abstr.* **1985,** *103,* 79573.
(104) Oji Paper Co., Ltd. Japanese Patent JP 58166095 A2, 1983; *Chem. Abstr.* **1983,** *101,* 141139.
(105) Ishijima, K. Japanese Patent JP 7704848 A2, 1977; *Chem. Abstr.* **1977,** *86,* 148825.
(106) Toppan Priniting Co., Ltd. Japanese Patent JP 57103895 A2, 1982; *Chem. Abstr.* **1982,** *98,* 207579.
(107) Averbach, A. U.S. Patent 3623866, 1971; *Chem. Abstr.* **1971,** *76,* 66324.
(108) Averbach, A. U.S. Patent 3687672, 1972; *Chem. Abstr.* **1972,** *77,* 171261.
(109) Sato, T.; Inoue, H. Japanese Patent JP 63008460 B4, 1988; *Chem. Abstr.* **1988,** *109,* 64278.
(110) Morishima, T.; Shimizu, R. U.S. Patent 3769043, 1973; *Chem. Abstr.* **1973,** *80,* 102339.
(111) Labana, S. S. U.S. Patent 3432415, 1969; *Chem. Abstr.* **1973,** *70,* 110516.
(112) Baur, R. Dr,; Macholdt, H. T. German Patent DE 4142541 A1, 1993; *Chem. Abstr.* **1993,** *120,* 334828.
(113) Suzuki, N.; Okamura, K.; Sugiyama, G.; Suzuka, S. European Patent EP 203532 A2, 1986; *Chem. Abstr.* **1986,** *107,* 68031.
(114) Harnisch, H.; Raue, R. German Patent DE 3738948 A1, 1993; *Chem. Abstr.* **1989,** *111,* 144073.
(115) Ikeda, T.; Sato, Y. European Patent EP 426124 A2, 1991; *Chem. Abstr.* **1991,** *115,* 243953.
(116) Ricoh Kk. Japanese Patent JP 08006299 A2, 1996; *Chem. Abstr.* **1996,** *124,* 274447.
(117) Ishikawa, A.; Ito, Y.; Okamoto, H.; Kudo, T.; Miyauchi, K. U.S. Patent 5035478 A, 1991; *Chem. Abstr.* **1991,** *116,* 224352.
(118) Okamoto, H.; Ishikawa, A.; Kudo, T.; Myauchi, K. Japanese Patent JP 63113452 A2, 1988; *Chem. Abstr.* **1988,** *109,* 119719.
(119) Okamoto, H.; Iwayagi, T.; Kudo, T. Nonogaki, S. Japanese Patent JP 61272930 A2, 1986; *Chem. Abstr.* **1988,** *107,* 68340.
(120) Okamoto, H.; Ishikawa, A.; Kudo, T. *Bull. Chem. Soc. Jpn.* **1989,** *62,* 2, 2723.
(121) Okamoto, H.; Ishikawa, A.; Kudo, T. *J. Electrochem. Soc.* **1989,** *136,* 2646.
(122) Okamoto, H.; Ishikawa, A.; Kudo, T. *J. Photochem. Photobiol., A* **1989,** *49,* 377.
(123) Okamoto, H.; Ishikawa, A. *Appl. Phys. Lett.* **1989,** *55,* 1923.
(124) Ge, R.; Wang, P.; Lai, H. *Xiyou Jinshu Cailiao Yu Gongcheng* **1993,** *22,* 28; *Chem. Abstr.* **1993,** *120,* 250440x.
(125) Kamimori, T.; Nagai, J.; Mizuhashi, M. Japanese Patent JP 61123690 A2, 1986; *Chem. Abstr.* **1986,** *106,* 166277.
(126) Kudo, T.; Ishikawa, A.; Okamoto, H.; Miyauchi, K. Japanese Patent JP 63216042 A2, 1988; *Chem. Abstr.* **1988,** *110,* 85547.

(127) Okamoto, H.; Ishikawa, A.; Kudo, T. *Thin Solid Films* **1989,** *172,* L97.
(128) Hinokuma, K.; Kishimoto, A.; Kudo, T. *J. Electrochem. Soc.* **1994,** *141* 876.
(129) Kudo, T.; Kishimoto, A.; Hinokuma, K. *Kenkyu Hokoku*—*Asahi Garasu Zaidan* **1992,** *60,* 119; *Chem. Abstr.* **1992,** *118,* 244442s.
(130) Takahashi, I.; Hibino, M.; Kudo, T. *Jpn. J. Appl. Phys., Part 2* **1996,** *35,* L438.
(131) Lampert, C. M.; Ma, Y. P.; Doeff, M. M.; Visco, S. World Patent WO 9322707 A1, 1993; *Chem. Abstr.* **1993,** *121,* 121414.
(132) Savadogo, O.; Mandal, K. C. *Electron. Lett.* **1992,** *28,* 1682.
(133) Savadogo, O.; Mandal, K. C. *J. Electrochem. Soc.* **1994,** *141,* 2871.
(134) Savadogo, O.; Mandal, K. C. *J. Appl. Phys.* **1994,** *27,* 1070.
(135) Pan, B. H.; Lee, J. Y. *J. Electrochem. Soc.* **1996,** *143,* 2784.
(136) Yao, N. A.; Ahavi, A. K.; N'Guessan, K.; Kouadja, K. *Renewable Energy* **1995,** Volume Date 1995, *6,* 829; *Chem. Abstr.* **1995,** *124,* 61492.
(137) Srinivas, R. A.; Rosen, A.; Heller, A. *Proc. Electrochem. Soc.* **1993,** *93*—*25* (Interconnects, Contact Metallization, and Multilevel Metallization/Reliability for Semiconductor Devices, Interconnects, and Thin Insulator Materials), 190; *Chem. Abstr.* **1993,** *121,* 23727.
(138) Lis, S. *Acta Phys. Pol., A* **1996,** *90* (2, Proceedings of the 2nd Winter Workshop on Spectroscopy and Structure of Rare Earth Systems, 1996, Part 2), 275.
(139) Yamase, T. Japanese Patent JP 62230620 A2, 1987; *Chem. Abstr.* **1987,** *108,* 173535.
(140) Yamase, T. Japanese Patent JP 04189892 A2, 1992; *Chem. Abstr.* **1992,** *118,* 29617x.
(141) Kawabata, K. Japanese Patent JP 06251872 A2, 1994; *Chem. Abstr.* **1994,** *122,* 277534.
(142) Yamase, T.; Uheda, K. *J. Electrochem. Soc.* **1993,** *140,* 2378.
(143) Sasaki, S.; Aida, T.; Watabe, I.; Yaguchi, T.; Tanuma, H.; Ishikawa, A. Japanese Patent JP 04106831 A2, 1992; *Chem. Abstr.* **1992,** *117,* 203581.
(144) Sheu, H.-C.; Shih, J.-S. *Anal. Chim. Acta* **1996,** *324,* 125.
(145) Kasai, Y.; Yamanaka, S. Japanese Patent JP 05273174 A2, 1993; *Chem. Abstr.* **1993,** *121,* 37207.
(146) Tsyganok, L. P.; Omel'chenko, V. A.; Sobol, L. V.; Netesina, I. P.; Glazkova, R. E. Soviet Patent SU 1712857 A1, 1992; *Chem. Abstr.* **1988,** *118,* 160135.
(147) Volkov, V. L.; Zakharova, G. S.; Manakova, L. I. Soviet Patent SU 1567958 A1, 1990; *Chem. Abstr.* **1987,** *113,* 144488.
(148) Sheen, S. R.; Shih, J. S. *Analyst (Cambridge, U.K.)* **1992,** *117,* 1691.
(149) Srivastava, S. K.; Sahgal, V.; Vardhan, H. *Sens. Actuators, B* **1993,** *13,* 391.
(150) Shoukry, A. F.; Rizk, M. S.; Abdel-Fattah, H. M.; Issa, Y. M.; Atia, E. M. *J. Chem. Technol. Biotechnol.* **1994,** *60,* 217.
(151) Rizk, M. S. *J. Chem. Technol. Biotechnol.* **1994,** *61,* 67.
(152) Rizk, M. S. *Egypt. J. Anal. Chem.* **1994,** *3,* 243; *Chem. Abstr.* **1994,** *122,* 248483.
(153) Campiglio, A. *Analyst (Cambridge, U.K.)* **1994,** *119,* 2209.
(154) Gorelov, I. P.; Toloknova, T. V. *J. Anal. Chem. (Transl. Zh. Anal. Khim.)* **1995,** *50,* 271.
(155) Bouklouze, A. A.; Vire, J.-C.; Quarin, G. C.; Kauffmann, J.-M. *Electroanalysis (N.Y.)* **1994,** *6,* 1045.
(156) Eppelsheim, C.; Hampp, N. *Analyst (Cambridge, U.K.)* **1994,** *119,* 2167.
(157) Ito, K.; Ito, K.; Wakita, S.; Okamoto, T. Japanese Patent JP 04152249 A2, 1992; *Chem. Abstr.* **1992,** *117,* 167152.
(158) Polak, A.; Beuhler, A. J. U.S. Patent 4500667, 1985; *Chem. Abstr.* **1985,** *102,* 186315. U.S. Patent 4560444, 1985; *Chem. Abstr.* **1985,** *104,* 199127.
(159) Polak, A.; Beuhler, A. J. U.S. Patent 4594297, 1986; *Chem. Abstr.* **1986,** *105,* 46391.
(160) Polak, A.; Beuhler, A. J.; Cramm, J. A. European Patent EP191209, 1986; *Chem. Abstr.* **1986,** *106,* 112796.
(161) Polak, A.; Beuhler, A. J. U.S. Patents 4689122, 1987; *Chem. Abstr.* **1987,** *107,* 249191. U.S. Patent 4710278, 1987; *Chem. Abstr.* **1987,** *108,* 194806. U.S. Patent 4636314, 1987; *Chem. Abstr.* **1987,** *106,* 103490.
(162) Polak, A.; Young, P. U.S. Patent 4714482, 1987; *Chem. Abstr.* **1988,** *108,* 95874
(163) Petty-Weeks, S. U.S. Patent 4661211, 1987; *Chem. Abstr.* **1987,** *107,* 69923.
(164) Goswami, K.; Saini, D. P. S.; Klainer, S. M.; Ejiofor, C. H. U.S. Patent 5405583, 1995; *Chem. Abstr.* **1995,** *123,* 24878.
(165) Shuler, K. E.; Schrauzer, G. E. German Patent DE 2528618, 1976; *Chem. Abstr.* **1976,** *85,* 24980.
(166) Kiesele, H. German Patent DE 3941554, 1991; *Chem. Abstr.* **1991,** *115,* 165605.
(167) Schmidtpott, H.; Wagner, I. German Patent DE 3513761 A1, 1986; *Chem. Abstr.* **1987,** *106,* 55168.
(168) Golstein, M. K. U.S. Patent 5063164, 1991; *Chem. Abstr.* **1991,** *116,* 78389.
(169) Goldstein, M. K.; Oum, M. S.; Kerns, K. L. World Patent WO 9607091, 1996; *Chem. Abstr.* **1996,** *124,* 351228.
(170) Koseki, K.; Sakurada, S.; Mukoda, K. Japanese Patent JP 04283652 A2, 1992; *Chem. Abstr.* **1993,** *118,* 83437b.
(171) Kawakami, A. Japanese Patent JP 62007682 B4, 1987; *Chem. Abstr.* **1987,** *107,* 42217.
(172) Kawakami, A. Japanese Patent JP 62007681 B4, 1987; *Chem. Abstr.* **1987,** *106,* 158476.
(173) Babinec, S. J. U.S. Patent 5377039, 1994; *Chem. Abstr.* **1994,** *122,* 146739.
(174) Babinec, S. J. *Proc. Electrochem. Soc.* **1994,** *94,* 30.
(175) Nakamura, K.; Iijima, T. Japanese Patent JP 53048985, 1978; *Chem. Abstr.* **1978,** *89,* 224004.
(176) Nakamura, K.; Iijima, T. Japanese Patent JP 53048986, 1978; *Chem. Abstr.* **1978,** *89,* 207318.
(177) Nakamura, O.; Kodama, T.; Ogino, I.; Miyake, Y. Japanese Patent JP 51106694, 1976; *Chem. Abstr.* **1976,** *86,* 19085.
(178) Nakamura, O.; Kodama, T.; Ogino, I.; Miyake, Y. U.S. Patent 4024036, 1977.
(179) Nakamura, O.; Kodama, T.; Ogino, I.; Miyake, Y. Japanese Patent JP 76106683, 1976; *Chem. Abstr.* **1976,** *86,* 35749.
(180) Giordano, N.; Staiti, P.; Hocevar, S.; Arico, A. S. *Electrochim. Acta* **1996,** *41,* 397.
(181) Hocevar, S.; Passalacqua, E.; Vivaldi, M.; Patti, A.; Giordano, N. *Electrochim. Acta* **1996,** *41,* 2817.
(182) Park, M. W.; Yang, J. C.; Han, H. S.; Shul, Y. G.; Lee, T. H.; Cho, Y. I. *Denki Kagaku, oyobi, Kogyo, Butsuri Kagaku* **1996,** *64,* 743; *Chem. Abstr.* **1996,** *125,* 15161.
(183) Koseki, K.; Iwasaki, H.; Izumi, J.; Oodo, N.; Sakurada, S. Japanese Patent JP 07065624 A2, 1995; *Chem. Abstr.* **1995,** *122,* 304328.
(184) Przyluski, J.; Wieczorek, W.; Giordano, N.; Poltrarzewski, Z.; Staiti, P.; Polish Patent PL 165820 B1, 1995; *Chem. Abstr.* **1995,** *126,* 20931.
(185) Kummar, J. T.; Oei, D.-G. U.S. Patent 4396687, 1983; *Chem. Abstr.* **1983,** *99,* 161528. U.S. Patent 4407902, 1983; *Chem. Abstr.* **1983,** *100,* 10061.
(186) Akimoto, M.; Niiyama, H. Japanese Patent JP 62196388 A2, 1987; *Chem. Abstr.* **1987,** *108,* 13085.
(187) Kim, J. J.; Lee, W. Y.; Song, I. K. U.S. Patent 5227141 A, 1993; *Chem. Abstr.* **1993,** *120,* 33373.
(188) Calahan, J. L.; Cueller, E. A.; Desmond, M. J.; Currie, J. C. U.S. Patent 4633372 A, 1986; *Chem. Abstr.* **1986,** *106,* 187578.
(189) Cuellar, E. A.; Desmond, M. J. U.S. Patent 4630176 A, 1986; *Chem. Abstr.* **1986,** *106,* 167396.
(190) Li, C.; Bai, L.; Ke, L. K. U.S. Patent 5501922, 1996; *Chem. Abstr.* **1996,** *124,* 294598.
(191) Nadjo, L.; Keita, B. French Patent FR 2573779 A1, 1986; *Chem. Abstr.* **1986,** *106,* 75016 (Equivalent, Canadian Patent CA1275385).
(192) Nadjo, L.; Keita, B. World Patent WO 8901058 A1, 1989; *Chem. Abstr.* **1989,** *110,* 201589.
(193) Savadogo, O., Dzebet, E. N. Canadian Patent 2092587, 1994; *Chem. Abstr.* **1994,** *122,* 110696.
(194) Savadogo, O., Essalik, A. U.S. Patent 5298343, 1994; *Chem. Abstr.* **1994,** *121,* 39190.
(195) Savadogo, O., Essalik, A. *Proceedings of the First International Symposium on New Materials for Fuel Cell Systems;* Savadogo, O., Roberge, P., Veziroglu, T. N., Eds.; Montreal, July 9—13, 1995; Editions de l'Ecole Polytechnique de Montreal: Montreal, p 688.
(196) Ndzebet, E.; Savadogo, O. *Int. J. Hydrogen Energy* **1995,** *20,* 635.
(197) Savadogo, O.; Amuzgar, K.; Piron, D. L. *Int. J. Hydrogen Energy* **1990,** *15,* 783.
(198) Savadogo, O.; *J. Electrochem. Soc.* **1992,** *139,* 1082.
(199) Savadogo, O.; Piron, D. L. *Int. J. Hydrogen Energy* **1990,** *15,* 715.
(200) Savadogo, O.; Thibault, S. *Int. J. Hydrogen Energy* **1989,** *14,* 865.
(201) Savadogo, O.; Allard, C. *Can. Metal. Quar.,* **1990,** *29,* 285.
(202) Savadogo, O.; Allard, C. *J. Appl. Electrochem.,* **1991,** *29,* 73.
(203) Savadogo, O. *Mater. Chem. Phys.,* **1993,** *35,* 145.
(204) Amuzgar, K.; Savadogo, O. *J. Appl. Electrochem.,* **1992,** *22,* 166.
(205) Savadogo, O.; Carrier, F. *J. Appl. Electrochem.,* **1992,** *22,* 437.
(206) Savadogo, O.; Ndzebet, E. *J. Appl. Electrochem.,* **1993,** *23,* 915.
(207) Savadogo, O.; Levesque, Ndzebet, E., Martel, A., Lessard, J. *Int. J. Hydrogen Energy* **1992,** *17,* 101.
(208) Savadogo, O.; Barolacci, G. *Int. J. Hydrogen Energy* **1992,** *17,* 109.
(209) Savadogo, O.; Forget, E. *Int. J. Hydrogen Energy* **1991,** *16,* 665.
(210) Ndzebet, E.; Savadogo, O. *Int. J. Hydrogen Energy* **1992,** *17,* 751.
(211) Savadogo, O.; Lavoie, H. *Int. J. Hydrogen Energy* **1992,** *17,* 473.
(212) Savadogo, O.; Carrier, F., Forget, E. *Int. J. Hydrogen Energy* **1994,** *19,* 429.
(213) Savadogo, O. *Electrochim. Acta* **1992,** *37,* 1457.
(214) Savadogo, O.; Levesque, S. *J. Appl. Electrochem.* **1991,** *21,* 457.
(215) Kuhn, A.; Anson, F. C. *Langmuir* **1996,** *12,* 5481.
(216) Rong, C.; Anson, F. C. *Inorg. Chim. Acta* **1996,** *242,* 11.
(217) Morimoto, T.; Matsubara, T.; Hamaya, Y.; Iwano, N. Japanese Patent JP 62114207 A2, 1987; *Chem. Abstr.* **1987,** *108,* 14972.

(218) Alwitt, R. S. German Patent DE 2618616, 1976; *Chem. Abstr.* **1976,** *86,* 25094 (English equivalent, U.S. Patent 4031436).
(219) Tomizawa, T.; Tamaru, A.; Aoki, A. Japanese Patent JP 04340211 A2, 1992; *Chem. Abstr.* **1992,** *118,* 224065.
(220) Fukuda, M.; Yamamoto, H.; Isa, I. Japanese Patent JP 04216607 A2, 1992; *Chem. Abstr.* **1992,** *117,* 263043.
(221) Guentner, A.; Baur, O. German Patent DE 3930310 C1, 1991; *Chem. Abstr.* **1991,** *114,* 198055.
(222) Hand, J. E. U.S. Patent 3502947, 1970; *Chem. Abstr.* **1970,** *72,* 116052
(223) Sung, H.; So, H.; Paik, W. K. *Electrochim. Acta* **1994,** *39,* 645.
(224) Cho, K.; Chung, S. D.; Ryu, K.; Kim, Y.; Choy, J.-H.; Kim, H. *Synth. Met.* **1995,** *69,* 481.
(225) Sung, H.; Lee, T.; Paik, W. *Synth. Met.* **1995,** *69,* 485.
(226) Freund, M. S.; Karp, C.; Lewis, N. S. *Curr. Sep.* **1994,** *13,* 66.
(227) Freund, M. S.; Karp, C.; Lewis, N. S. *Inorg. Chim. Acta* **1995,** *240,* 447.
(228) Ritter, S. K. *Chemtracts: Inorg. Chem.* **1995,** *7,* 163; *Chem. Abstr.* **1995,** *125,* 145194.
(229) Ding, J.; Dong, S.-J. *Huaxue Xuebao* **1996,** *54,* 193; *Chem. Abstr.* **1996,** *124,* 233838.
(230) Ding, J.; Dong, S.-J. *Gaodeng Xuexiao Huaxue Xuebao* **1996,** *17,* 1191; *Chem. Abstr.* **1996,** *125,* 169507.
(231) Vernitskaya, T. V.; Efimov, O. N.; Gavrilov, A. B. *Electrokhimiya* **1994,** *30,* 1123; *Chem. Abstr.* **1994,** *121,* 302131.
(232) Ohtsuka, T.; Wakabayashi, T.; Einaga, H. *J. Electroanal. Chem.* **1994,** *377,* 107.
(233) Ohtsuka, T.; Wakabayashi, T.; Einaga, H. *Synth. Met.* **1996,** *79,* 235.
(234) Bidan, G.; Fabre, B.; Lapkowski, M. World Patent WO 9423291 A1, 1994; *Chem. Abstr.* **1994,** *122,* 122121.
(235) Fabre, B.; Bidan, G.; Lapkowski, M. *J. Chem. Soc., Chem. Commun.* **1994,** 1509.
(236) Fabre, B.; Bidan, G.; Cespuglio, R.; Burlet, S. World Patent WO 9606347 A1, 1996; *Chem. Abstr.* **1996,** *125,* 50091.
(237) Zaid, B.; Aeiyach, S.; Lacaze, P. C. *Synth. Met.* **1994,** *65,* 27.
(238) Liu, A.; Wang, E. *Anal. Chim. Acta* **1994,** *296,* 171.
(239) Lapkowski, M.; Turek, W.; Barth, M.; Lefrant, S. *Synth. Met.* **1995,** *69,* 127.
(240) Keita, B., Bouaziz, D., Nadjo, L. *J. Electroanal. Chem. Interfacial Electrochem.* **1988,** *255,* 303.
(241) Wang, B.; Dong, S. *Fenxi Huaxue* **1996,** *24,* 382; *Chem. Abstr.* **1996,** *124,* 354896.
(242) Keita, B., Nadjo, L. *J. Electroanal. Chem. Interfacial Electrochem.* **1988,** *243,* 481.
(243) Pham, M. C.; Mostefai, M.; Lacaze, P. C. *Synth. Met.* **1992,** *52,* 305.
(244) Bidan, G.; Genies, E.; Lapkowski, M. European Patent EP 323351 A1, 1989; *Chem. Abstr.* **1989,** *111,* 207397 (English equivalent, Canadian Patent CA1332643).
(245) Hasik, M.; Turek, W.; Stochmal, E.; Lapkowski, M.; Pron, A. *J. Catal.* **1994,** *147,* 554.
(246) Koziel, K.; Lapkowski, M. *Mater. Sci. Forum* **1993,** *122* (Conducting Polymers: Transport Phenomena), 167.
(247) Wang, P.; Li, Y. *J. Electroanal. Chem.* **1996,** *408,* 77.
(248) Luzny, W.; Hasik, M. *Solid State Commun.* **1996,** *99,* 685.
(249) Freund, M. S.; Karp, C.; Lewis, N. S. *Inorg. Chim. Acta* **1995,** *240,* 447.
(250) Jones, V. W.; Kalaji, M.; Walker, G. *J. Chem. Soc., Faraday Trans.* **1994,** *90,* 2061.
(251) Pham, M.-C.; Bouallala, S.; Le, L. A.; Dang, V. M.; Lacaze, P.-C. *AIP Conf. Proc.* **1996,** *354,* 82.
(252) Liu, M.; Dong, S. *Electrochim. Acta* **1995,** *40,* 197.
(253) Zheng, J.; Liu, Y.; Zhang, H. *Chin. Chem. Lett.* **1992**, *3*, 215; *Chem. Abstr.* **1992,** *121,* 20810.
(254) Liu, A.; Wang, E. *Anal. Chim. Acta* **1994,** *296,* 171.
(255) Dong, S.; Liu, M. *Electrochim. Acta* **1994,** *39,* 947.
(256) Pham, M.-C.; Bouallala, S.; Le, L. A.; Dang, V. M.; Lacaze, P.-C. *Electrochim. Acta* **1996,** *42,* 439.
(257) Gomez-Romero, P.; Lira-Cantu, M. *Adv. Mater. (Weinheim Ger.)* **1997,** *9,* 144.
(258) Weinstock, I. A.; Atalla, R. H.; Agarwal, U. P.; Minor, J. L.; Petty, C. *Spectrochim. Acta, Part A* **1993,** *49A,* 819.
(259) Weinstock, I. A.; Atalla, R. H.; Reiner, R. S.; Moen, M. A.; Hammel, K. E.; Houtman, C. J.; Hill, C. L. *New J. Chem.* **1996,** *20,* 269.
(260) Weinstock, I. A.; Atalla, R. H.; Hill, C. L. World Patent WO 9526438 A1, 1995. *Chem. Abstr.* **1995,** *124,* 59630.
(261) Atalla, R. H.; Weinstock, I. A.; Hill, C. L.; Reiner, R. S. U.S. Patent 5549789, 1996; *Chem. Abstr.* **1996,** *125,* 250734.
(262) Weinstock, I. A.; Hill, C. L.; Atalla, R. H. U.S. Patent 5552019, 1996; *Chem. Abstr.* **1996,** *125,* 250735.
(263) Weinstock, I. A.; Minor, J. L.; Atalla, R. H. *Act. Dioxygen Homogeneous Catal. Oxid., [Proc. Int. Symp.], 5th* **1993,** 487.
(264) Weinstock, I. R.; Hill, C. L. World Patent WO 9405849 A1, 1994; *Chem. Abstr.* **1994,** *121,* 233328.
(265) Paren, A.; Jaekaerae, J.; Patola, J. World Patent WO 9535407 A1, 1995; *Chem. Abstr.* **1996,** *124,* 179286.
(266) Paren, A.; Jaekaerae, J.; Patola, J. World Patent WO 9535408 A1, 1995; *Chem. Abstr.* **1996,** *124,* 179285.
(267) Kaneda, T.; Jinnai, K.; Koshizuka, T.; Kimura, A. Japanese Patent JP 07082243 A2, 1995; *Chem. Abstr.* **1995,** *123,* 82854.
(268) Suvorova, S. I.; Leonova, M. O.; Shapiro, I. L.; Pen, P. Z. *Izv. Vyssh. Uchebn. Zaved., Lesn. Zh.* **1996,** (1−2), 22; *Chem. Abstr.* **1997,** *126,* 33300.
(269) Wang, S.; Chen, Y. Chinese Patent CN 1091828 A, 1994; *Chem. Abstr.* **1994,** *124,* 44331.
(270) Wang, S.; Chen, Y. Chinese Patent CN 1090045 A, 1994; *Chem. Abstr.* **1994,** *123,* 245660.
(271) Chen, Li.; Zhao, G.; Li, S. *Fenxi Shiyanshi* **1995,** *14,* 21; *Chem. Abstr.* **1995,** *124,* 32304.
(272) Osakai, T.; Himeno, S.; Saito, A.; Katano, H. *Electroanalysis (N.Y.)* **1993,** *5,* 275.
(273) Stone, M. J. U.S. Patent 5330917, 1994; *Chem. Abstr.* **1994,** *121,* 169250. U.S. Patent 5364792, 1994; *Chem. Abstr.* **1994,** *122,* 122123.
(274) Nikiforov, A. F.; Poteryaeva, V. V.; Nichkova, I. I.; Lobukhina, T. V. Soviet Patent SU 1564116 A1, 1990; *Chem. Abstr.* **1990,** *113,* 117950.
(275) Pfrepper, G.; Kreklow, B. East German Patent DD 268166 A1, 1989; *Chem. Abstr.* **1989,** *111,* 156984.
(276) Rais, J.; Petrzilkova, H. Chech Patent 215493 B, 1985; *Chem. Abstr.* **1985,** *102,* 169194.
(277) Svec, V.; Mikulaj, V.; Hanzel, R. *J. Radioanal. Nucl. Chem.* **1996,** *208,* 487.
(278) Nazarenko, A. Y.; Zaitsev, S. A.; Sukhan, V. V. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1993,** *36,* 38; *Chem. Abstr.* **1993,** *120,* 152372g.
(279) Nikiforov, A. F.; Rogacheva, L. N.; Nichkova, I. I.; Pushkarev, V. V. Soviet Patent SU 1036775 A1, 1983; *Chem. Abstr.* **1983,** *99,* 162057.
(280) Barkovskii, V. F.; Velikanova, T. V.; Neudachina, L. K.; Yudina, L. N. Soviet Patent SU 416315, 1974; *Chem. Abstr.* **1974,** *81,* 108019.
(281) Heckmann, K.; Jonke, M. German Patent DE 3602183 C1, 1987; *Chem. Abstr.* **1987,** *107,* 161307.
(282) Hoenes, J.; Wielinger, H.; Unkrig, V. German Patent DE 3940010 A1, 1991 (English equivalent, U.S. 5382523); *Chem. Abstr.* **1991,** *116,* 37504.
(283) Patrick, J. M.; Patrick, V. A. World Patent WO 9319849, 1993; *Chem. Abstr.* **1993,** *120,* 221752.
(284) Moller, A.; Helms, I.; Henze, G.; Scholz, F. *Fresenius' J. Anal. Chem.* **1993,** *345,* 567.
(285) Wang, S.; Chen, Y. Chinese Patent CN 1091828, 1994; *Chem. Abstr.* **1994,** *124,* 44331.
(286) Yin, H.; Huang, C. *Lihua Jianyan, Huaxue Fence* **1993,** *29,* 106; *Chem. Abstr.* **1993,** *120,* 234950h.
(287) Li, J.; Lai, H. *Guilin, Gongxueyuan Xuebao* **1995,** *15,* 279; *Chem. Abstr.* **1995,** *124,* 184921.
(288) Grishko, V. P.; Grishko, V. I. Soviet Patent SU 1582123 A1, 1990; *Chem. Abstr.* **1990,** *114,* 16842.
(289) Babkina, T. A.; Shamsutdinova, Y. N.; Simonova, A. F. Soviet Patent SU 1065770 A1, 1984; *Chem. Abstr.* **1984,** *100,* 131801.
(290) Chen, G.; Xu, G.; Hao, J.; Li, F.; Liu, C.; Chen, R. *Yejin Fenxi* **1995,** *15,* 13; *Chem. Abstr.* **1995,** *124,* 305794.
(291) Sorokina, L. V.; Osipenko, V. V.; Sorokin, A. V. *Ogneupory* **1993,** *8,* 15; *Chem. Abstr.* **1993,** *120,* 198602k.
(292) Chen, L.; Zhao, G.; Li, S. *Fenxi, Shiyanshi* **1995,** *14,* 21; *Chem. Abstr.* **1995,** *124,* 32304.
(293) Yamaguchi, H.; Yamada, K.; Okochi, H.; Hasegawa, R. *Bunseki Kagaku* **1993**, *42,* 141; *Chem. Abstr.* **1993,** *118,* 224542w.
(294) Lopez, C. M.; Sicilia, D.; Rubio, S.; Perez-Bendito, D. *Anal. Chim. Acta* **1993,** *283,* 481.
(295) Dolgorev, A. V.; Mineeva, V. F. Soviet Patent SU 1437350 A1, 1988; *Chem. Abstr.* **1988,** *110,* 146855.
(296) Mullen, J. L. *Plat. Surf. Finish.* **1993,** *80,* 59; *Chem. Abstr.* **1993,** *118,* 224550x.
(297) Chen, M. *At. Spectrosc.* **1992,** *13,* 190.
(298) Ganago, L. I.; Ishchenko, N. N.; Starobinets, L. G. Soviet Patent SU 1140035 A1, 1985; *Chem. Abstr.* **1985,** *102,* 214362.
(299) Ganago, L. I.; Iscchenko, N. N. Soviet Patent SU 810608, 1981; *Chem. Abstr.* **1981,** *94,* 202195.
(300) Suvorova, S. N.; Stegendo, Z. K. Soviet Patent SU 481832, 1975; *Chem. Abstr.* **1975,** *84,* 98904.
(301) Szocs, E.; Szocs, S. Romanian Patent RO 66827, 1978; *Chem. Abstr.* **1978,** *93,* 106462.
(302) Nazarova, V. I.; Labinskaya, N. I. Soviet Patent SU 373600, 1973; *Chem. Abstr.* **1973,** *79,* 45488.
(303) Nakazato, M.; Saito, K.; Ishikawa, F.; Fujinuma, K.; Moriyasu, T.; Nishima, T.; Tamura, Y. *Kenkyu Nenpo—Tokyo-toritsu Eisei Kenkyyusho* **1993,** *44,* 138; *Chem. Abstr.* **1993,** *121,* 33409.
(304) Hang, T.; Cheng, G.; Zhang, Z.; Han, D.; Ji, W. *Zhongguo Yaoke Daxue Xuebao* **1993,** *24,* 380; *Chem. Abstr.* **1993,** *120,* 157866f.
(305) Wu, L. *Guangpu Shiyanshi* **1996,** *13,* 27; *Chem. Abstr.* **1996,** *126,* 98544.
(306) He, X.; Liu, X.; Liu, S.; Xu, S. *Fenxi Shiyanshi* **1996,** *15,* 63; *Chem. Abstr.* **1996,** *125,* 346340.

(307) Wang, Y.; Liu, Z. *Huanjing, Wuran Yu Fangzhi* **1995,** *17,* 42; *Chem. Abstr.* **1995,** *124,* 96879.
(308) Liu, J. *Yankuang Ceshi* **1994,** *13,* 195; *Chem. Abstr.* **1994,** *122,* 229523.
(309) Lu, G.; Liang, H.; Yao, L. *Fenxi Huaxue* **1993,** *21,* 1043; *Chem. Abstr.* **1993,** *119,* 261689r.
(310) Wang, C.; Lou, T. *Fenxi Huaxue* **1993,** *21,* 644; *Chem. Abstr.* **1993,** *119,* 138331r.
(311) Chen, L. *Talanta* **1992,** *39,* 765; *Chem. Abstr.* **1992,** *118,* 115844a.
(312) Bajger, Z. *Hutn. Listy* **1993,** *48,* 41; *Chem. Abstr.* **1993,** *120,* 152474s.
(313) Duan, Q.; Liang, K. *Yejin Fenxi* **1992,** *12,* 23; *Chem. Abstr.* **1992,** *118(20),* 204276j.
(314) Zhang, S.; Li, H.; Yiu, J.; Zhou, L. **1995,** *36,* 602; *Chem. Abstr.* **1995,** *124,* 305750.
(315) Ptushkina, M. N.; Rozhkova, N. A. *Zavod. Lab.* **1992,** *58,* 1; *Chem. Abstr.* **1992,** *118,* 72631j.
(316) Wang, M. *Fenxi Shiyanshi* **1993,** *12,* 33; *Chem. Abstr.* **1993,** *120,* 260066u.
(317) Goto, N.; Oshima, M.; Motomizu, S. *Bunseki Kagaku* **1993**, *42,* 151; *Chem. Abstr.* **1993,** *118,* 265604m.
(318) Xu, S.; Zhang, Y. *Fenxi Huaxue* **1993,** *21,* 685; *Chem. Abstr.* **1993,** *119,* 151278y.
(319) Huang, X.; Ji, M.; Wang, W.; Zhou, N. *Fenxi Huaxue* **1995,** *23,* 1277; *Chem. Abstr.* **1995,** *124,* 104954.
(320) Song, G. *Fenxi Shiyanshi* **1992,** *11,* 36; *Chem. Abstr.* **1992,** *119,* 108062m.
(321) Su, F. *Lihua Jianyan, Huaxue Fence* **1994,** *30,* 40; *Chem. Abstr.* **1994,** *122,* 229531.
(322) Chen, J.; Huang, X. *Fenxi Shiyanshi* **1993,** *12,* 56; *Chem. Abstr.* **1993,** *120,* 288870a.
(323) Jiang, F. *Lihua Jianyan, Huaxue Fence* **1992,** *28,* 240; *Chem. Abstr.* **1992,** *118,* 182294j.
(324) Mirzoyan, F. V.; Tarayan, V. M.; Airyan, E. Kh. Soviet Patent SU 971799 A1, 1982; *Chem. Abstr.* **1982,** *98,* 46186.
(325) Liang, P. *Lihua Jianyan, Huaxue Fence* **1992,** *28,* 160; *Chem. Abstr.* **1992,** *118,* 93402a.
(326) Deng, G.; Guan, L.; Li, Q.; Wang, Y. *Lihua Jianyan, Huaxue Fence* **1992,** *28,* 148; *Chem. Abstr.* **1992,** *118,* 93399e.
(327) Huang, C.; Yin, H. *Lihua Jianyan, Huaxue Fence* **1996,** *32,* 171; *Chem. Abstr.* **1996,** *126,* 103216.
(328) Mirzoyan, F. V.; Vartapetyan, S. M. Soviet Patent SU 1343308 A1, 1987; *Chem. Abstr.* **1987,** *108,* 15523.
(329) Li, Z.; Wang, J. *Fenxi Huaxue* **1994,** *22,* 150; *Chem. Abstr.* **1994,** *120,* 288947f.
(330) Muralikrishna, U.; Murty, J. A. *Chem. Anal. (Warsaw)* **1993,** *38,* 379; *Chem. Abstr.* **1993,** *119,* 285339c.
(331) Luo, S. *Lihua Jianyan, Huaxue Fence* **1995,** *31,* 361, 364; *Chem. Abstr.* **1995,** *124,* 277163.
(332) Wang, J.; Ruan, W.; He, R. *Youkuangye* **1993,** *12,* 51; *Chem. Abstr.* **1993,** *120,* 235008u.
(333) Wang, J.; He, R.; Wang, J. *Lihua Jianyan, Huaxue Fence* **1992,** *28,* 277, 279; *Chem. Abstr.* **1992,** *119,* 61845b.
(334) Luo, S. *Chongging Daxue Xuebao* **1992,** *15,* 54; *Chem. Abstr.* **1992,** *120,* 234937j.
(335) Luo, S. *Fenxi Shyanshi* **1993,** *12,* 97; *Chem. Abstr.* **1993,** *120,* 94246f.
(336) Luo, S. *Lihua Jianyan, Huaxue Fence* **1996,** *32,* 168; *Chem. Abstr.* **1996,** *126,* 139221.
(337) Tao, H. *Yankuang Ceshi* **1995,** *14,* 298; *Chem. Abstr.* **1995,** *124,* 248993.
(338) Li, Z.; Wang, J. *Fenxi Shiyanshi* **1992,** *11,* 6; *Chem. Abstr.* **1992,** *118,* 160057g.
(339) Li, Z.; Xu, Q. *Yejin Fenxi* **1992,** *12,* 9; *Chem. Abstr.* **1992,** *118,* 20429p.
(340) Li, J.; Jiang, X. *Fenxi Huaxue* **1996,** *24,* 1065; *Chem. Abstr.* **1996,** *125,* 315573.
(341) Li, Z.; Xu, Q. *Fenxi Huaxue* **1993,** *21,* 1254; *Chem. Abstr.* **1993,** *120,* 181831m.
(342) Li, Z.; Wang, J.; Xu, Q. *Fenxi Huaxue* **1993,** *21,* 639; *Chem. Abstr.* **1993,** *119,* 151273t.
(343) Wang, J.; Li, Z.; Xu, Q.; Liu, M. *Yejin Fenxi* **1996,** *16,* 14; *Chem. Abstr.* **1996,** *125,* 184280.
(344) Li, Z.; Wang, J.; Xu, Q. *Fenxi Huaxue* **1996,** *24,* 927; *Chem. Abstr.* **1996** *125,* 264489.
(345) Li, Z.; Wang, J.; Cheng, G.; Xu, Q. *Fenxi Huaxue* **1996,** *24,* 1240; *Chem. Abstr.* **1996,** *125,* 54155.
(346) Li, Z.; Xu, Q. *Fenxi Huaxue* **1993,** *21,* 272; *Chem. Abstr.* **1993,** *119,* 14447p.
(347) Li, Z.; Xu, Q. *Fenxi Shiyanshi* **1992,** *11,* 1; *Chem. Abstr.* **1992,** *118,* 93380s.
(348) Garcia, R. J.; Pozo, M. F.; Torrades, C. F. *Quim. Ind. (Madrid)* **1994,** *41,* 19; *Chem. Abstr.* **1994** *122,* 305413.
(349) Abdallah, A. M.; El-Shahawi, M.; El-Defrawy, M. M.; Askar, E. E. *Chem. Anal. (Warsaw)* **1992,** *37,* 589; *Chem. Abstr.* **1992,** *119,* 108078w.
(350) Wenying, C.; Jianyuan, Y.; Luo, L.; Wang, D. *Fenxi Huaxue* **1995,** *23,* 1355; *Chem. Abstr.* **1995** *124,* 37129.
(351) Trokhimenko, O. M.; Falendysh, N. F.; Trachevskii, V. V.; Pilipenko, A. T. Soviet Patent SU 1709196 A1, 1992; *Chem. Abstr.* **1992,** *117,* 183969z.
(352) Liu, X.; *Shanghai Youse Jinshu* **1995,** *16,* 93; *Chem. Abstr.* **1995,** *124,* 248946.
(353) Grishko, V. P.; Grishko, V. I.; Yudelevich, I. G. Soviet Patent SU 1298663 A1, 1987; *Chem. Abstr.* **1987,** *107,* 16939.
(354) Sato, N.; Shirakawa, K. European Patent EU 675360 A2, 1995; *Chem. Abstr.* **1995,** *123,* 334325.
(355) Hill, M. W.; Sharman, D. F. World Patent WO 9203727 A1, 1992; *Chem. Abstr.* **1992,** *116,* 247666.
(356) Korytseva, V. F.; Zhetukhhima, E. V. *Gidroliz. Lesokhim. Promst.*, **1991,** *(7),* 19; *Chem. Abstr.* **1991** *118,* 214065d.
(357) Murty, J. A.; Muralikrishna, U. *Orient. J. Chem.* **1992,** *8,* 348; *Chem. Abstr.* **1982** *118,* 182458r.
(358) Selles, E.; Fresno, M. J.; Reillo, A. *Acta Technol. Legis Med.* **1995**, *6* (3, Suppl., XXI Congresso Internazionale della Societa Fermaceutica del Mediterraneo Latino, 1994), 598.
(359) Kostareva, L. A.; Gruzdova, N. S.; Balueva, L. V. Soviet Patent SU 1503003 A1, 1989; *Chem. Abstr.* **1989,** *112,* 8896.
(360) Savchenko, L. A.; Semenov, G. V.; Makarov, N. V.; Domnina, E. N. Soviet Patent SU 1746304 A1, 1992; *Chem. Abstr.* **1992,** *119,* 48060x.
(361) Aoki, M.; Igarashi, K. Japanese Patent JP 08101127 A2, 1996; *Chem. Abstr.* **1996,** *125,* 75014.
(362) Bogoslovskij, V. V.; Ryabukhima, I. V. Soviet Patent SU 1583822 A1, 1990; *Chem. Abstr.* **1990,** *114,* 124945.
(363) Bogoslovskij, V. V.; Yakushina, E. V.; Mol'skaya, O. L.; Andreev, S. A. Soviet Patent SU 1800357 A1, 1993; *Chem. Abstr.* **1993,** *120,* 314955.
(364) Bogoslovskij, V. V.; Ryabukhina, I. V.; Yakushina, E. V.; Mol'skaya, O. L. Soviet Patent SU 1704067 A1, 1992; *Chem. Abstr.* **1992,** *117,* 62000.
(365) Bogoslovskij, V. V.; Yakushina, E. V.; Zhironkina, I. A. *Khim. Volokna* **1992,** No. 4, 58; *Chem. Abstr.* **1992,** *119,* 119361j.
(366) Miki, K. Japanese Patent JP 04274752 A2, 1992; *Chem. Abstr.* **1992,** *120,* 68361.
(367) Niazi, S. B.; Ansari, T. M.; Zaki, S. M. *J. Res. (Sci.), Volume Date 1990−1991,* **1991,** *3,* 47; *Chem. Abstr.* **1991,** *118,* 204233t.
(368) Jin, L.; Liu, T.; Sun, X.; Fang, Y. *Fenxi Huaxue* **1993,** *21,* 1117; *Chem. Abstr.* **1993,** *120,* 68164h.
(369) Kuznetsova, L. I.; Detusheva, L. G.; Yurchenko, E. N.; Likholobov, V. A. Soviet Patent 1174250 A1, 1992; *Chem. Abstr.* **1992,** *119,* 61983.
(370) Mikulaj, V.; Svec, V. *J. Radioanal. Nucl. Chem.* **1994,** *183,* 127;
(371) Jianhua, W.; Ronghuan, H.; Jianguo, W. *J. Radioanal. Nucl. Chem.* **1992,** *162,* 57.
(372) Bion, L.; Moisy, Ph.; Madic, C. *Radiochim. Acta* **1995,** *69,* 251.
(373) Yaksin, V. V.; Vilkova, O. M.; Laskorin, B. N. *Dokl. Akad. Nauk* **1992,** *325,* 967; *Chem. Abstr.* **1992,** *118,* 72610b.
(374) Fedoseev, A. M.; Tananaeuv, I. G. *Radiokhimiya* **1994,** *36,* 422; *Chem. Abstr.* **1994,** *122,* 324543.
(375) Pope, M. T. *Heteropoly and Isopoly Oxometalates;* Springer-Verlag: Berlin, 1983.
(376) Vallance, D. T.; Byrne, D. J.; Winder, A. F. *Clin. Chim. Acta* **1994,** *229,* 77.
(377) Yeang, H. Y.; Sunderasan, E.; Bahri, A. R. S. *J. Nat. Rubber Res.* **1994,** *9,* 70; *Chem. Abstr.* **1994,** *122,* 298992.
(378) Vaisanen, S.; Gavert, J.; Julkunen, A.; Voutilainen, E.; Penttila, I. *Scand. J. Clin. Lab. Invest.* **1992,** *52,* 853; *Chem. Abstr.* **1992,** *118,* 142933k.
(379) Umemoto, A. Japanese Patent JP 06109739 A2, 1994; *Chem. Abstr.* **1994,** *121,* 30522.
(380) Jones, R. M. U.S. Patent 5213965, 1993; *Chem. Abstr.* **1993,** *119,* 445653v.
(381) Toland, T. M.; Fugelsang, K. C.; Muller, C. J. *Am. J. Enol. Vitic.* **1996,** *47,* 111; *Chem. Abstr.* **1996,** *124,* 287635.
(382) Rohm, H.; Benedikt, J.; Jaros, D. *Food Sci. Technol.* **1994,** *27,* 392.
(383) Kelner, I. French Patent FR 1424481, 1966; *Chem. Abstr.* **1966,** *66,* 56888.
(384) Erbil, M. K.; Aykut, S.; Bingol, N. K.; Bilgi, C.; Ozkan, M. *Biyokim. Derg.* **1992,** *17,* 19; *Chem. Abstr.* **1992,** *118,* 142854k.
(385) Fialaire, A.; Postaire, E. *J. AOAC Int.* **1994,** *77,* 1338; *Chem. Abstr.* **1994,** *121,* 275930.
(386) Kroll, M. H.; Chester, R. *Clin. Chem. (Washington, D.C.)* **1994,** *40,* 389; *Chem. Abstr.* **1994,** *120,* 265140y.
(387) Belin-Geindre, S.; Chenu, C. *Rev. Inst. Fr. Pet.* **1994,** *49,* 5.
(388) Barnakov, A. N. *J. Microsc. (Oxford)* **1994,** *175,* 171.
(389) Yamashita, M.; Ide, M.; Murakami, Y.; Kubo, Y. *Igaku Kensa* **1995,** *44,* 1821; *Chem. Abstr.* **1965,** *124,* 140259.
(390) Aleksandrova, O. A. *Okeanologiya* **1992,** *32,* 583; *Chem. Abstr.* **1992,** *118,* 51585 g.
(391) Kiernan, J. A. *Biotech. Histochem.* **1996,** *71,* 304.
(392) Prentce, P. *Histochemistry* **1993,** *99,* 163.
(393) Shapiro, S. H.; Sohn, L. C. *J. Histotechnol.* **1994,** *17,* 125.
(394) Blasius, E.; Nilles, K. H. European Patent EU 73261 A1, 1983 (English equivalent, U.S. Patent 4460474); *Chem. Abstr.* **1983,** *99,* 12575.

(395) Blasius, E.; Nilles, K. H. European Patent EU 73262 A1, 1983 (English equivalent, U.S. Patent 4452702); *Chem. Abstr.* **1983,** *99*, 29780.

(396) Lin, Z.; Zhongqun, L.; Wenjun, C.; Shaojin, C. *J. Radioanal. Nucl. Chem.* **1996,** *205* (1, International Conference on Isotopes, Proceedings, 1995, Pt.1), 49.

(397) Deike, L. East German Patent DD 292433 A5, 1991; *Chem. Abstr.* **1991,** *115,* 235749.

(398) Pfrepper, G. East German Patent DD 264205 A1, 1989; *Chem. Abstr.* **1989,** *111,* 85952.

(399) Pfrepper, G.; Voigt, L. East German Patent DD 255879 A1, 1988; *Chem. Abstr.* **1988,** *110,* 84076.

(400) Kamoshita, M.; Fukazawa, T.; Kawamura, F. Japanese Patent JP 07280992 A2, 1995; *Chem. Abstr.* **1995,** *124,* 129636.

(401) Pfrepper, G.; Suess, M. East German Patent DD 152916 Z, 1981; *Chem. Abstr.* **1981,** *96,* 207275.

(402) Pfrepper, G.; Suess, M. East German Patent DD 137405, 1979; *Chem. Abstr.* **1979,** *92,* 30844.

(403) Fukazawa, T.; Nakamura, T.; Sasahira, A. Japanese Patent JP 05027090 A2, 1993; *Chem. Abstr.* **1993,** *119,* 190601.

(404) Yang, R. T.; Chen, N. U.S. Patent 5456892, 1995; *Chem. Abstr.* **1995,** *123,* 321039.

(405) von Wedel, W.; Weck, M.; Tarabocchia, J.; Schelbert, U.; Moeller, A. German Patent DE 4305344 A1, 1994; *Chem. Abstr.* **1994,** *121,* 211943.

(406) Fukuda, A.; Fukuda, Y.; Inoue, M.; Maki, M. Kaneko, Y.; Waki, M. Japanese Patent JP 04035716 A2, 1992; *Chem. Abstr.* **1992,** *117,* 117592.

(407) Bao, X.; Liu, L.; Wei, W.; Wang, X.; Shi, G.; Zhao, Y. *Huagong Yejin* **1996,** *17,* 144; *Chem. Abstr.* **1996,** *125,* 14791.

(408) Sebesta, F. Chech Patent 180789, 1979; *Chem. Abstr.* **1979,** *93,* 53243.

(409) Kuznetsova, L. I.; Fedotov, M. A.; Yurchenko, E. N.; Detusheva, L. G.; Lazarenko, T. P. Soviet Patent SU 1768251 A1, 1992; *Chem. Abstr.* **1992,** *119,* 253068.

(410) Myai, J.; Yanase, Y. Japanese Patent JP 08304377 A2, 1996; *Chem. Abstr.* **1996,** *126,* 108083.

(411) Ryazantsev, A. A.; Khakhinov, V. V.; Naidanov, O. A. *Tsellyul. Bum. Karton* **1992,** No. 5, 30; *Chem. Abstr.* **1992,** *118,* 218721n.

(412) Mueller, U.; Bayer, S.; Oetter, G.; Gehrer, E.; Ciesla, U.; Schueth, F.; Monnier, A.; Unger, K.; Stucky, G. European Patent EP 670286 A1, 1995; *Chem. Abstr.* **1995,** *123,* 203742.

(413) Hoelderich, W.; Hoelscher, M.; Schindler, G.-P.; Englert, U.; Zibrowius, B.; Arntz, D. German Patent DE 4424625 A1, 1996; *Chem. Abstr.* **1996,** *124,* 243576.

(414) David, L. D. U.S. Patent 4995942, 1991; *Chem. Abstr.* **1991,** *115,* 13720.

(415) Jackson, C. E. Jr.; Kasowski, R. V.; Lee, K.-S. World Patent WO 9420565 A1, 1994; *Chem. Abstr.* **1994,** *123,* 85873.

(416) Gall, R. D.; Hill, C. L.; Walker, J. E. *Chem. Mater.* **1996**, *8*, 2523.

(417) Akstinat, M.; Suter, W. World Patent WO 96311448 A1, 1996; *Chem. Abstr.* **1996,** *125,* 337188.

(418) Wall, G. German Patent DE 4001057 A1, 1991; *Chem. Abstr.* **1991,** *115,* 261849.

CR960398A