1976

Hypophosphite Photographic Emulsions

Randal A. Johnson

Recommended Citation

Johnson, Randal A., "Hypophosphite Photographic Emulsions" (1976). *Electronic Theses and Dissertations*. 4953.
https://openprairie.sdstate.edu/etd/4953

HYPOPHOSPHITE PHOTOGRAPHIC EMULSIONS

BY

RANDAL A. JOHNSON

A thesis submitted
in partial fulfillment of the requirements for the
degree Master of Science, major in
Chemistry
South Dakota State University
1976

HYPOPHOSPHITE PHOTOGRAPHIC EMULSIONS

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Advisor Date

Head, Chemistry Department Date

TABLE OF CONTENTS

LIST OF TABLES

INTRODUCTION

The purpose of this work is to study the sensitivity of emulsions of various hypophosphite salts to irradiation by photons in the x-ray region of the electromagnetic spectrum. This hypophosphite system bears little resemblance to the more common silver halide currently used in emulsions. Consequently, little is known about the reaction conditions necessary to make fast, sensitive emulsions or how to develop resultant latent images.

The project involves the synthesis and characterization of several compounds which have not been extensively characterized in previous work. Characterization of these salts involved the following techniques: Infrared Absorption Spectroscopy, Electron Paramagnetic Resonance Spectroscopy, and X-ray Diffraction.

The main objective of this work, however, is to prepare photographic emulsions of various compositions which, when irradiated with an x-ray beam for different durations, will produce a latent image. The latent images formed during the exposure are then amplified to permanent visible images of nickel metal by developing the emulsions using several techniques.

HISTORICAL

The first salts of hypophosphorous acid were characterized by P. L. Dulong in 1816. Although many of the salts that have been prepared were synthesized within a few years of the discovery of hypophosphites, few have been extensively studied or characterized at this time.

Methods of preparation of hypophosphites vary with the cation involved in the desired reaction. The first hypophosphites were made by boiling phosphorous with solutions of the alkaline earth hydroxides or by reaction of the alkaline earth phosphides with water.

Many of the salts are now made through the use of some of the alkaline earth hypophosphites in replacement reactions. Usually, if the hypophosphite is soluble, a salt is used which will form a precipitate. These include the reactions of sulfates with barium hypophosphite and carbonates with calcium hypophosphite producing the hypophosphites, most of which are soluble in water solutions, and insoluble barium sulfate or calcium carbonate. This method is quite often used with metals in higher oxidation states. For example, Iron (III) sulfate is dissolved in water and a solution of barium hypophosphite is added forming insoluble barium sulfate and iron(III) hypophosphite.

Another preparation which is currently more widely used is the dissolution of hydroxides or oxides, if they are soluble, in hypophosphorous acid. Many of the lanthanide salts have been made from their oxides recently. If the metal is easily reduced, however, an oxidation-reduction reaction will often occur under these conditions. These compounds can be made in this manner if the solutions are cooled properly or if the product is immediately precipitated.

The carbonates of metals have also been treated with hypophosphorous acid to give the desired salt and carbon dioxide gas.

The acid is strong enough in some cases to react directly with the metal. This method is used to produce the iron(II) salt. Some metals, however, catalyze the oxidation of the acid instead of reacting to form the desired product.

Hypophosphorous acid and the hypophosphite salts are quite easily oxidized. Impure hypophosphorous acid undergoes slow decomposition at room temperature. The pure acid and solutions of the acid decompose readily at temperatures over 130°C. The decomposition products of the acid are phosphine, phosphorous, phosphoric acids and some hydrogen along with other products.

When strongly heated, hypophosphite salts also decompose to give phosphine, red phosphorus, phosphites, and phosphates among other products.

As was previously mentioned, hypophosphorous acid and the hypophosphite ion are catalytically oxidized in the presence of certain metals in neutral aqueous solutions at room temperature. The metals that catalyze this oxidation include palladium, copper, cobalt, and nickel. Isotope studies have shown that the hydrogen evolved during the reduction is composed of equal proportions of hydrogen atoms from the hypophosphite and from the water. One proposed mechanism for this oxidation is:

$$H_3PO_2 \longrightarrow [H_2PO_2\cdot] + H\cdot$$

$$[H_2PO_2\cdot] + H_2O \longrightarrow H_3PO_3 + H\cdot$$

$$2H\cdot \longrightarrow H_2$$

Since they are so easily oxidized, hypophosphorous acid and alkali metal salts of the acid are powerful reducing agents. Many of the transition metal salts are reduced to the metal, the hydride, the phosphide, or a mixture of these products in the presence of the hypophosphite anion. Copper salts are reduced to the metal or the unstable hydride unless there are chloride ions present, when it forms copper(I) chloride.

Cobalt and nickel salts are reduced to mixtures of the metal and the metal phosphides even in the absence of catalysts. In the presence of palladium, however, the uncontaminated metal is obtained. The presence of ammonia also increases the amount of metal formed and accelerates the reduction in the case of nickel salts.

Two possible mechanisms postulated for the hypophosphite-induced reduction of nickel are:

$$H_2PO_2^- + H_2O \longrightarrow HPO_3^{-2} + 2H^+ + H^-$$

$$Ni^{+2} + 2H^- \longrightarrow Ni + H_2$$

$$H^+ + H^- \longrightarrow H_2$$

and

$$H_2PO_2^- \longrightarrow HPO_2^- + H$$

$$HPO_2^- + \cdot OH \longrightarrow H_2PO_3^-$$

$$2H + Ni^{+2} \longrightarrow 2H^+ + Ni$$

The first mechanism proposed was consistent with earlier data on the rate of hydrogen evolution during the reaction. The second mechanism involves the reaction of hydroxyl radicals from the metal surface with partly dehydrogenated hypophosphite. Very little has been done with the kinetics of these reactions.

Much work has been done with electroless deposition of nickel and alloys of nickel, iron, cobalt, chromium, and vanadium on various metal and plastic surfaces. Most of the work has dealt with improving the plating with different conditions or additives or improving the efficiency of the process.

The reduction of cerium(IV) to cerium(III) by hypophosphites is commonly used as an analytical determination of the hypophosphite, and the reduction of iron(III) to iron(II) by sodium hypophosphite has been used in determining either the iron or the hypophosphite concentrations in solutions.

Recently, it was found that the reduction of nickel hypophosphite in an ammoniacal emulsion could be induced upon irradiation with x-rays or an electron beam. The only published work in this area of application to date has been done by NASA. They have done some work in finding proper formulas for the emulsion and the developer for obtaining the best development of prints from this process.

The proposed mechanism for this radiation-induced deposition of nickel is:

$$\begin{aligned}
H_2PO_2^- &\xrightarrow{hv} H\dot{P}O_2^- + H\cdot \\
H\dot{P}O_2^- + Ni^{+2} &\longrightarrow Ni^+ + HPO_2 \\
2Ni^+ + H_2PO_2^- &\longrightarrow 2Ni + HPO_2 + H^+ \\
Ni^{+2} + H_2PO_2^- &\xrightarrow{Ni} Ni + HPO_2 + H^+
\end{aligned}$$

This mechanism is partially based on some electron paramagnetic resonance work done on γ-irradiated ammonium hypophosphite showing the formation of the $H\dot{P}O_2^-$ radical.

This method has been used to make permanent radiographs without the use of a dark room or fixer since the emulsion is insensitive to incident radiation and stable for long periods of time.

BIBLIOGRAPHY

A.A. Eldridge, et. al., "Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry," volume VIII, supplement III, Longman Group Ltd., London, 1971, p. 614-26, 1210-11, 1273-76.

M. Grayson, E.J. Griffith, "Topics in Phosphorus Chemistry," volume I, Interscience Publishers, New York, 1964, p. 121-27.

I.M. Kolthoff and P.J. Elving, "Treatise on Analytical Chemistry," part II, volume 5, Interscience Publishers, New York, 1961, p. 368-9.

A.T. Malinina, D.P. Shvets, and V.V. Serebrennikov, Tr. Tomsk. Gos. Univ., 192, 31-6 (1968); through Chem. Abst., 73, 72592(1970).

J.W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," volume VIII, Longmans, Green, and Co., Ltd., London, 1928, p. 870-90.

J.R. Morton, Mol. Phys., 5, 217 (1962).

NASA Tech. Brief, B72-10456 (1972).

C.Y. Peters, M.S. Thesis, South Dakota State University, Brookings, South Dakota, 1975.

J.R. Van Wazer, "Phosphorus and Its Compounds," volume I, Interscience Publishers, Inc., New York, 1958, p. 355-67.

EXPERIMENTAL

Preparation of Aluminum Hypophosphite

An excess of purified 50% hypophosphorous acid was added to a solution of basic aluminum acetate in water. The solution was heated at 80°C for 30 minutes to insure total reaction. During the heating, a white precipitate formed. The precipitate was filtered from the solution and washed with water and ethanol and allowed to air dry. The product was redissolved in a 3N hydrochloric acid solution and precipitated again to purify it further. The infrared spectrum was taken of a nujol mull of the sample (see Table I).

Preparation of Zinc Hypophosphite (this method was also used in the preparation of tin hypophosphite)

Excess zinc metal was placed in a dilute hypophorous acid solution and allowed to react until no more gas was evolved. The mixture was then filtered to remove the unreacted metal and the solution was allowed to evaporate to near-dryness on a steam bath. Ethanol was added to the solution to precipitate the product and the product was filtered and washed with ethanol. The white crystals and powder were allowed to air dry. The nuclear magnetic resonance spectrum was taken in deuterium oxide. The spectrum consists of peaks at τ -1.6, τ 5.0, and τ 7.3. The addition of a small amount of water showed that the peak at τ 5.0 was due to water. The infrared spectrum was taken of a nujol mull of the sample (see Table II).

A set of x-ray diffraction single crystal intensity data was taken using a four circle automated diffractometer.

The space group was found to be $P2_1/c$ with lattice constants of a = 7.95(7)Å, b = 7.38(2)Å, c = 10.50(3)Å, and $\beta = 104.(8)^\circ$. A Patterson map calculated from the reduced reflection data revealed the position of the zinc atom. The remaining atoms could not be located from subsequent least squares and electron density calculations. Various other indirect methods and multiple tangent formula calculations also ended in failure. A second crop of single crystals was sent to Iowa State University and additional data sets were taken but as yet the reason for the failure has not been diagnosed.

Analyses of both the crystalline and powder zinc hypophosphite samples were done using anhydrous cerium(IV) sulfate to oxidize the hypophosphite to phosphite. The excess cerium(IV) sulfate was then titrated with iron(II) ammonium sulfate using potentiometric methods (1,2,3). The following results were obtained.

calculated for $Zn(H_2PO_2)_2$: H_2PO_2, 66.54%
found in the powder: H_2PO_2, 66.31%

calculated for $Zn(H_2PO_2)_2 \cdot 3H_2O$: H_2PO_2, 52.12%
found in crystals: H_2PO_2, 52.23%

Preparation of Scandium Hypophosphite (4)

Scandium metal was dissolved in excess 6N hydrochloric acid and the solution was filtered to remove undissolved particles. Excess 50% hypophosphorous acid was added to the solution and a white precipitate formed immediately. The mixture was digested on a steam bath until the precipitate was filterable and the white powder was filtered out and dried. The infrared spectrum was taken of a nujol mull of the sample (see Table III). The x-ray diffraction powder pattern was also taken (see Table IV).

Preparation of Neodymium Hypophosphite (this method was also used in the preparations of thulium hypophosphite and gadolinium hypophosphite)

Neodymium oxide was added to a slight excess of dilute hypophosphorous acid solution and stirred until all the solid dissolved. The violet solution was allowed to evaporate until it was very concentrated and ethanol was added to precipitate the lilac-colored product. The infrared spectrum was taken of a nujol mull of the product (see Table V).

Preparation of Copper(II) Hypophosphite

Excess copper(II) oxide was added to a 50% solution of hypophosphorous acid which was being cooled in an ice bath. The mixture was stirred for several minutes and the unreacted copper(II) oxide was filtered off. The blue solution was again placed in an ice bath and ethanol was added to precipitate the product. The mixture was then filtered to remove the light blue precipitate which was washed with ethanol. The solid and solutions of this salt were unstable and tended to decompose to a copper-colored product within a few hours.

The infrared spectrum was taken of the nujol mull of the product (see Table VI).

Copper(I) oxide was also used in this preparation, and the same product was formed.

Preparation of Manganese Hypophosphite

Approximately equimolar proportions of manganese(II) carbonate and dilute hypophosphorous acid were mixed and allowed to stand until the effervescing had ceased and the solid was dissolved. The red solution was allowed to evaporate and ethanol was added to precipitate the product. The light pink product was filtered off and washed with ethanol. The infrared spectrum was taken of a nujol mull of the sample (see Table VII) and the x-ray diffraction powder pattern was taken (see Table VIII).

The electron paramagnetic resonance spectrum of the powder was run on a 9 gigahertz EPR spectrometer with a 5 kilogauss magnet assembled in the physics department. The sample was placed in a quartz tube in the cavity of the magnet and the magnetic field was swept from 2.125 kilogauss to 4.625 kilogauss ($g = 2$ is at 3.375 kilogauss). A single, broad peak was found centered at 3.375 kilogauss.

A crystal of zinc hypophosphite and 1% manganese hypophosphite was grown by slowly cooling the doped solution from 50°C to room temperature. This crystal was cemented to the bottom to a quartz tube and placed in the cavity of the magnet. Several sweeps were taken of this crystal at different angles of rotation. The spectrum was found to be a very complex pattern that changed with rotation and repeated itself every 180° of rotation.

Analysis of the hypophosphite present in the manganese hypophosphite through potentiometric titration gave the following results:

calculated for $Mn(H_2PO_2)_2$: H_2PO_2, 70.29%
calculated for $Mn(H_2PO_2)_2 \cdot H_2O$: H_2PO_2, 64.05%
found: H_2PO_2, 65.58%

This preparation was also used with nickel carbonate, barium carbonate, cobalt carbonate, lead carbonate, and cadmium carbonate. The infrared spectra of all products were basically the same except for characteristic splittings of the three main peaks for each metal and differing amounts of water present. The infrared absorptions for the nickel hypophosphite are given in Table IX.

The nickel hypophosphite was also analyzed and gave the following results:

calculated for $Ni(H_2PO_2)_2 \cdot 6H_2O$: H_2PO_2, 43.80%
found: H_2PO_2, 41.17%

Electron paramagnetic resonance spectra were taken of nickel hypophosphite powder, crystals, and crystals doped with 1% manganese hypophosphite, but no peaks were observed in any of these at room temperature.

Preparation of Iron(III) Hypophosphite

Hydrated iron(III) was dissolved in excess dilute hypophosphorous acid. A light pink residue which remained in the beaker was filtered off and washed with ethanol. The addition of the ethanol to the filtrate yielded more light pink powder which was filtered and washed with ethanol. The precipitates were allowed to air dry, and infrared spectra were taken on each precipitate. The spectra showed the first precipitate to be impure, but the second appeared to be the pure hypophosphite salt (see Table X).

Analysis was performed for the hypophosphite present in the product. The results were:

calculated for $Fe(H_2PO_2)_3$: H_2PO_2, 77.73%

found: H_2PO_2, 78.24%

Preparation of Emulsions

The emulsions which were prepared were all based on a previously determined formulation of a photosensitive nickel hypophosphite emulsion (5). All emulsions consisted of a metal hypophosphite, an agent to aid in the complexation or reduction of the metal, and a binding agent. The emulsion preparations have been divided into sections according to the basic metal in the emulsion and subdivided by the binder that was used.

Nickel Emulsions

Preparations Using Solid Gelatin as a Binder

The basic nickel hypophosphite emulsion consisted of the following proportions of components (5):

nickel hypophosphite (hydrated)	10 g
concentrated aqueous ammonia	18 ml
solid gelatin	10 ml

The nickel hypophosphite was dissolved in the concentrated ammonium hydroxide on a steam bath, and the gelatin was added and stirred with heating until a homogeneous solution was formed. This emulsion was then coated on a piece of filter paper while it was warm and the paper was allowed to air dry to make the completed film.

Several variations involving the addition of impurities to this emulsion formulation were also tried. These all used the same proportions of regular constituents, but included a trace (approximately 0.05 g) of other chemicals.

When copper(II) chloride was added to the emulsion, the normally green film became a dark blue-green color.

With cadmium hypophosphite as the added impurity, the film also changed to a blue color.

Silver nitrate added to the emulsion originally left the film a light green color, but upon standing for a few days, the film slowly turned darker and developed gray spots.

One other emulsion that was made up with a gelatin binder was not based on the original nickel film formulation. This emulsion consisted of 1 g of sodium hypophosphite, 1 g of copper(II) sulfate, and 5 g of nickel hypophosphite dissolved in 12 ml of concentrated ammonium hydroxide with heating. To this was added 7 ml of solid gelatin to complete the emulsion.

Preparations Using Only Mucilage as the Binder

Several films were made using mucilage as the binder in the emulsion instead of gelatin. These emulsions used the same proportions of components as the emulsions with the gelatin binder, that is, 10 g of nickel hypophosphite, 18 ml of concentrated ammonium hydroxide, and 10 ml of mucilage. It was not necessary to heat this emulsion as much as those with the gelatin binder since the mucilage dissolved easily. The film did take longer to dry than the gelatin emulsions, though.

The only other emulsion made with the mucilage binder was an emulsion with silver nitrate as an impurity.

Preparations Using Mixtures of Gelatin and Mucilage for the Binder

Emulsions were made using the basic nickel hypophosphite formulation except that instead of using 10 ml of gelatin, 5 ml of gelatin and 5 ml of mucilage were used. In these emulsions, the gelatin and mucilage were added to the nickel hypophosphite before the ammonium hydroxide was added. After the ammonium hydroxide was added, the mixture was stirred and heated until no more solid was evident on the bottom.

Another emulsion was made in the same way with a trace of silver nitrate added after the emulsion was ready for application to the filter paper.

Some emulsions were made with a saturated aqueous solution of disodium (ethylenedinitrilo) tetraacetate (EDTA) in place of the concentrated ammonium hydroxide solution. These emulsions were made by adding 5 ml of solid gelatin and 5 ml of mucilage to 10 g of solid nickel hypophosphite followed by the addition of 18 ml of the saturated EDTA solution. This mixture was heated and stirred on a steam bath until the solution was homogenous and there was no more evidence of any solids being present.

A mixture of 9 ml of the saturated EDTA solution and 9 ml of concentrated ammonium hydroxide was also used in the same procedure to make a film.

Preparations Using Dissolved Gelatin as the Binder

These emulsions were made using an aqueous solution of the solid gelatin as the binder. This solution was prepared by adding enough water to the solid gelatin to dissolve the particles when heated on a steam bath. The solution was heated until enough water evaporated to make the solution about the same viscosity as glycerine. The solution was kept at this viscosity through replenishment of evaporated water.

The same basic formulation was used except that 10 ml of the gelatin solution was used instead of 10 ml of solid gelatin.

Several other emulsions were made with various complexing or reducing agents used in place of the concentrated ammonium hydroxide. These emulsions all used the same ratios of components as the basic nickel hypophosphite formulation.

The saturated EDTA solution was again used as one of the replacements for the ammonium hydroxide. It resulted in a dark blue film.

A saturated aqueous urea solution resulted in a light yellow film.

The saturated hydroxylamine hydrochloride solution also resulted in a yellow film.

Replacing the ammonium hydroxide with an aqueous solution of 50% (by volume) ethylene diammine gave a violet-colored film.

Using a mixture of 9 ml of the saturated EDTA solution and 9 ml of concentrated ammonium hydroxide resulted in a dark blue film.

The following emulsions were made by mixing approximately 6 ml of the ammonium hydroxide replacement with 2.5 g of nickel hypophosphite and 3 ml of gelatin.

A saturated aqueous solution of lactose used as a reducing agent resulted in a light green film.

Using a saturated aqueous solution of hydroquinone also resulted in a light green film.

A 25 ml solution of dipyridyl was made by adding 0.8 g of dipyridyl to 20 ml of water and heating the mixture on a steam bath. Ethyl alcohol was then added until the dipyridyl had completely dissolved. The use of 6 ml of this solution in the emulsion again resulted in a light green film.

A 1,10 phenanthroline solution in the emulsion again resulted in a film that was yellow-green in color.

A saturated aqueous mannose solution resulted in a light green film.

A light green film also was formed by using a saturated aqueous galactose solution.

A saturated solution of tetracyanoquinodimethane (TCNQ) in a 30% ethyl alcohol solution resulted in a light blue film being produced.

An emulsion was made with EDTA and a trace of impure silver hypophosphite. The silver hypophosphite was made by adding hypophosphorous acid to a silver nitrate solution (6). The silver hypophosphite was added to 5 g of nickel hypophosphite dissolved in 9 ml of a saturated EDTA solution. When most of the silver hypophosphite had dissolved, 5 ml of gelatin solution was stirred in to complete the emulsion.

An attempt to make an emulsion with a trace of silver hypophosphite in an ammoniacal solution of nickel hypophosphite resulted in the reduction of the nickel and the evolution of a gas.

Preparations Using Glycerine and Gelatin Mixtures as a Binder

The basic nickel hypophosphite emulsion formulation was used except that about one-third of the solid gelatin was replaced by glycerine. The ammoniacal nickel hypophosphite solution was mixed before the gelatin and glycerine were added. Upon addition of the mixture the solution foamed and there was some reduction of the nickel hypophosphite.

Tetracyanoethylene (TCNE) was dissolved in a hot 30% ethyl alcohol solution to make a saturated solution. When 3 ml of gelatin solution was added to a solution of 2.5 g of nickel hypophosphite in 5 ml of the TCNE solution, a brown precipitate formed. Glycerine was added to the mixture until the precipitate had redissolved. The resultant film was yellow in color.

A saturated solution of triphenylphosphine in a hot mixture of ether, ethyl alcohol, and water was made and 5 ml was used to dissolve 2.5 g of nickel hypophosphite. When 3 ml of the gelatin solution was added to the solution, a precipitate formed. Glycerine and more ethyl alcohol were added to try to redissolve the precipitate, but it proved to be insoluble. A homogenous mixture of the precipitate in the solution was coated on filter paper.

Copper Emulsions

The copper emulsions were made very quickly with as little heating of the copper hypophosphite solutions as possible since the copper salt decomposed quite readily upon standing and faster upon heating.

Excess Copper(II) oxide was added to 50% hypophosphorous acid until the mixture heated up and a slurry was formed. Water was added to the slurry and the mixture was filtered. A supersaturated solution of EDTA was added to the filtrate and an especially thick gelatin solution was stirred in.

The same procedure was used to make a second emulsion with concentrated ammonium hydroxide replacing the EDTA solution.

Cobalt Emulsions

The emulsions with cobalt hypophosphite were made using the same procedure as many of the nickel hypophosphite emulsions. To a solution of 2.5 g of cobalt hypophosphite in 6 ml of concentrated ammonium hydroxide was added 3 ml of the gelatin solution. The resulting film was very dark brown.

Another emulsion was made with the saturated EDTA solution in place of the ammonium hydroxide. This film was light pink in color.

Iron Emulsion

A solution of 2 g of iron(III) hypophosphite in 5 ml of the saturated 1,10 phenanthroline solution was made with heating on a steam bath. The addition of 3 ml of the gelatin solution resulted in a slight precipitate, but the homogenous mixture of solution and precipitate was coated on filter paper anyway. The resultant film was light pink in color.

Exposure of Films

All the films were exposed with x-ray radiation produced by a copper x-ray tube. The current and voltage supplied to the tube varied from 15 milliamps at 35 kilovolts to 12 milliamps at 50 kilovolts.

The films with the solid gelatin binder were exposed by placing them directly over the x-ray port. These films were exposed for time periods of 1, 2, 3, 5, and 10 minutes to determine the sensitivity of each emulsion.

The remainder of the films were placed directly behind a collimator which was positioned against the port of the x-ray beam. The collimator was approximately 4 cm long and consisted of several thin metal plates which were parallel with the x-ray beam. The effect of the collimator was to produce a series of alternate light and dark strips on the film.

The films were all exposed for 10-minute and 5-minute time intervals, and some were exposed for 15 minutes.

Development of Exposed Emulsions

After the emulsions had been exposed, they were usually predeveloped with an exposure to ammonia vapor for about 5 minutes. The films were then usually developed in an appropriate solution. There were a few different developers used, but, as with the emulsion formulations, they were all based on a previously determined formula that had been found to work (5). The basic formulation for the developer is

0.1 M Nickel(II) chloride

0.2 M Sodium Hypophosphite

1.0 M Ammonium Hydroxide

Another solution that was prepared for use as a developer used nickel ammonium sulfate in place of the nickel chloride.

A solution of 0.1 M nickel chloride and 0.2 M sodium hypophosphite in water was used as a developer solution in some cases.

Another variation on the basic developer solution was to leave out both the ammonium hydroxide and the nickel chloride to give a 0.2 M sodium hypophosphite solution.

In the case of the copper hypophosphite films, copper(II) sulfate was used in place of the nickel chloride used in the basic developer solution.

An aqueous solution of a commercial developing agent used in the development of silver halide-based emulsions were also tried. The agent used was elon which is monomethyl-p-aminophenol sulfate.

Infrared Spectra

All infrared spectra taken for the compounds that were synthesized were taken on a Perkin-Elmer 700 infrared spectrophotometer using nujol mulls dispersed on sodium chloride plates. The spectra were compared with the spectrum of a sample of sodium hypophosphite purchased from J.T. Baker Inc., and with literature values (7-10).

Nuclear Magnetic Resonance Spectra

The proton nuclear magnetic resonance spectra were taken of synthesized zinc hypophosphite and sodium hypophosphite purchased from J.T. Baker Inc., on a Varian A-60A spectrometer at 60 MHz using tetramethyl silane as an external standard. The salts were dissolved in deuterium oxide and a small amount of distilled water was added to establish the position of the water peaks. The coupling constants for the peaks in the spectra were compared with values in the literature (8,10).

Electron Paramagnetic Resonance Spectra

The electron paramagnetic spectra were taken on an instrument assembled in the physics department by Dr. J.R. Tunheim and David Aaron. The instrument consisted of Hewlett-Packard wave guides, attenuator, frequency meter, magic T, and a model 716B klystron power supply; Varian 0-5 kilogauss field regulated magnet and power supply, and a 9.48 gigahertz klystron; a Princeton Applied Research model 128 lock-in amplifier; and a

Micro-Now Instrument Co. model 210 stabilizer.

Spectra were taken with an internal standard of diphenyl picrohydrazil.

X-ray Diffraction Patterns

X-ray diffraction powder patterns were taken on a Picker Nuclear, 6147 series, x-ray diffractometer with a copper x-ray tube. The d-values obtained were compared with those listed in the A.S.T.M. files.

Hypophosphite Analyses

The hypophosphite analyses were done with chemicals of analytical reagent grade using a Leeds and Northrup model 7415, pH-millivoltmeter to determine endpoints. Sodium hypophosphite purchased from J.T. Baker Inc., was dried and used as a standard.

RESULTS AND CONCLUSIONS

Syntheses of Hypophosphites

Many of the accepted syntheses for the hypophosphite salts used in this work employ starting materials that were not readily available. Therefore it was necessary to use syntheses for which the starting materials were available but which had not previously been used in the manufacture of these hypophosphites.

For example, nickel hypophosphite is made by reacting nickel hydroxide with hypophosphorous acid (11). Nickel hydroxide slowly decomposes upon standing, so it is necessary to synthesize it shortly before use. After noting the problems encountered by Peters in his attempts at this synthesis (12), it was decided that a method involving chemicals that were readily available would probably be better. The reaction with the carbonate appeared to be a very straight-forward reaction and it does seem to have worked quite well.

Some other reactions that were not previously reported were used in the synthesis of the hypophosphite salts of zinc, tin, iron(III), aluminum, and copper.

Infrared Spectra

The infrared spectrum of each compound was taken to insure that the compound was a hypophosphite and for a future reference of each salt's characteristic pattern. A hypophosphite salt is easily identified by the phosphorous-hydrogen stretching absorption at a frequency of about 2400 cm^{-1} and the PH_2 rocking mode at 800 cm^{-1}. Each salt has a characteristic splitting pattern of these two peaks and of the peaks between 1200 cm^{-1} and 950 cm^{-1} which are various phosphorous-oxygen and metal-oxygen vibrational modes.

X-ray Diffraction

The d-spacings obtained by x-ray powder diffraction data are also characteristic of each compound. The same values are found for a compound whether it is an uncontaminated sample or an impurity in another compound. The identity of or purity of a substance can therefore be determined through the use of accurate tables of d-spacings and intensities.

The listing of hypophosphite salts in the A.S.T.M. files is not at all complete, so a tabulation of some more d-spacings and intensities is useful.

EPR Spectra

The EPR spectra of the powders of the hypophosphite salts of various paramagnetic cations were taken to determine if the symmetries of the salts were such that the individual peaks in the spectra would be apparent. The resultant spectra show a single large peak in each case, so it is apparent that the symmetries are not the cubic symmetry necessary for a complex spectrum to appear.

Since the symmetry was not cubic, it was necessary to grow single crystals of the salts. Attempts to grow single crystals of manganese hypophosphite consistently resulted in powders, so it was decided to try other methods of obtaining the manganese in a crystalline form. Crystals of a nonparamagnetic substance are often doped with a small amount of a paramagnetic substance to aid in the study of their spectra. Therefore, the manganese hypophosphite was added to a zinc hypophosphite solution. Good single crystals were obtained with this method.

It is hoped that the symmetry of the zinc hypophosphite crystals can be determined by a rotational analysis of the signal obtained from the doped crystals. It is also hoped that it can be determined if the phosphorous and hydrogen atoms in the hypophosphite are participating in the splitting of the signal and to what extent.

NMR Spectra

The NMR spectra of the more soluble hypophosphite salts were taken to help characterize the compounds. It was also hoped that the characteristic coupling constants for some of the hypophosphite salts could be determined, but few of the salts that had been synthesized at that time were sufficiently soluble to obtain the spectra.

Hypophosphite Emulsions

The nickel hypophosphite emulsion used by Peters (12) and NASA (13) were used as a basis for the film emulsions used in this work. Various compounds and mixtures of compounds were investigated as substitutes for the components of the emulsion, and a few methods of image amplification were tried.

The original emulsion used by NASA employed mucilage as the binder whereas the emulsion used by Peters employed gelatin in the film. These binders as well as mixtures of the two, a solution of gelatin, and mixtures of gelatin and glycerine were investigated and compared to find the binder that gave the best results in development of an image and in ease of handling.

Generally, the manufacture of an emulsion involves heating the emulsion to dissolve the gelatin and keeping the solution warm until it is coated on the filter paper.

The use of solid gelatin in the formulation of photographic emulsions caused difficulties in obtaining uniform coatings of the emulsion of the filter paper. The solutions were generally too viscous to easily coat the paper with a uniform amount of emulsion before the gelatin hardened. Consequently, some pieces of film dried much faster than others and exposure times necessary for the development of a clear image varied considerably.

The mucilage binder caused the resultant films to be much more uniform in thickness. It was not necessary to heat this emulsion, so there was no risk of reducing the emulsion mixture through heating too strongly.

A mixture of mucilage and gelatin resulted in am emulsion that did require some heating and caused films to appear slightly less uniform than the mucilage emulsion, but the emulsion was still much easier to handle than the solid gelatin emulsion.

The use of the aqueous gelatin solution in the emulsion resulted in a film that was very similar to that manufactured with the gelatin-mucilage mixture.

The mixture of gelatin and glycerine caused the film to remain pliable when it dried instead of becoming rigid. Otherwise, the emulsion was similar to that of the gelatin solution.

The results of the irradiation and development of the various films are given in Table 1. All of the emulsions contain approximately the same proportions of components and all use the nickel hypophosphite-ammonium hydroxide formulation. The films were either exposed to the direct x-ray beam or to the collimated beam for the amount of time listed as the exposure time. After exposure, the emulsions were treated with ammonia vapors and, unless otherwise noted, the basic developer containing nickel chloride, sodium hypophosphite, and ammonium hydroxide.

The binder that appeared to give the most consistent positive results and the shortest exposure times necessary for the development of a visible image with the basic nickel emulsion was the aqueous solution of gelatin. The remainder of the compounds and mixtures used as binders did not consistently develop good images with shorter exposure times. It is possible that some of the binders would have worked better with different replacements for the ammonium hydroxide in the emulsion or with different

Table 1

Results Obtained for Emulsions using Various Binders with Nickel Hypophosphite and Ammonium Hydroxide.

Binder	Exposure Time (minutes)	Results	Comments
solid gelatin	2	good image	exposed to direct x-ray beam
solid gelatin	10	no image	exposed to direct x-ray beam nickel ammonium sulfate developer used
mucilage	10	no image	emulsion dissolved in the developer; exposed to direct x-ray beam
gelatin and mucilage	10	yellow discoloration	exposed to collimated x-ray beam; basic developer formulation brought about no further image development
gelatin solution	5	partial image	exposed to collimated x-ray beam
gelatin and glycerine	10	no image	exposed to collimated x-ray beam

developer solutions, but the gelatin solution appeared to be the best overall binder for the formulations that were tried.

The reduction of silver in silver halide films is greatly facilitated by the addition of certain ions. With the possible enhancement of the image formed by the nickel hypophosphite system in mind, several metallic cations were added to the emulsion to determine the effects upon the radiation-induced reduction of the nickel.

The impurities added to the emulsions containing solid gelatin as the binder were copper(II) chloride, cadium hypophosphite, silver nitrate, and both sodium hypophosphite and copper(II) sulfate. Silver hypophosphite was added to two emulsions with the gelatin solution as the binder. One of the emulsions was made with the usual ammonium hydroxide mixture, the other replaced the ammonium hydroxide with a saturated solution of EDTA.

The results of the exposure and subsequent development of the films are given in Table II. Unless otherwise noted, the films were exposed to the direct x-ray beam and treated with ammonium vapors and the basic developer solution to promote the development of a visible image.

As is shown by the results, the addition of traces of other compounds to the basic nickel emulsion did not produce the desired result of sensitizing the nickel emulsion. The effect of the addition was usually a decrease in sensitivity toward the x-ray photons. The only emulsion that was not adversely affected by

Table II

Results of Adding Impurities to the Emulsions

Impurity	Exposure Time (minutes)	Results	Comments
$CuCl_2$	15	good image	solid gelatin binder copper-colored spot appeared after exposure development formed nickel image
$Cd(H_2PO_2)_2$	4	light spot formed	solid gelatin binder development did not enhance image
$AgNO_3$	10	good image	solid gelatin binder
NaH_2PO_2 and $CuSO_4$	10	no image	solid gelatin binder
AgH_2PO_2	--	---	gelatin solution binder decomposed upon addition of impurity
AgH_2PO_2	10	good image	gelatin solution binder EDTA used to replace NH_4OH in emulsion developed with ammonia treatment alone exposed with collimated x-ray beam

the presence of an impurity was the EDTA emulsion. There was still no sensitization, however.

It was felt that the ammonium hydroxide was providing a medium that was aiding in the reduction of the nickel in the emulsion, so some compounds providing various environments for the nickel were tried. The compounds included some containing nitrogen, some that are complexing agents, and some that are easily oxidized and therefore provide a reducing medium.

The results of replacing the ammonium hydroxide in the emulsion with various solutions of compounds are given in Table III. Unless otherwise noted, the emulsions were all made with the basic formulation using a gelatin solution as the binder. The films were exposed to the collimated x-ray beam and placed in ammonia vapors and the basic developer solution to develop an image.

Several compounds were found which could effectively replace the ammonium hydroxide in the basic nickel emulsion. Many of these compounds improve the emulsion in that it is not necessary to make the emulsion in a well ventilated area and it is not necessary to use any kind of developer solution besides the ammonia vapors.

The compounds that will replace ammonium hydroxide in the emulsion fall into two major categories, the reducing sugars, and the complexing agents.

The reducing sugars included lactose, xylose, mannose, and

Table III

Results of Using Various Replacements for Ammonium Hydroxide

Emulsion	Exposure Time (minutes)	Results	Comments
NH_4OH	5	partial image	basic formulation; gelatin solution
EDTA	5	partial image	basic formulation had no effect gelatin solution
EDTA	10	good image	basic formulation had no effect gelatin and mucilage
EDTA	15	no image	EDTA formulation; gelatin and mucilage
EDTA and NH_4OH	10	no image	basic formulation; gelatin and mucilage
EDTA and NH_4OH	15	no image	EDTA formulation; gelatin and mucilage
urea	10	no image	basic formulation; gelatin solution
hydroxylamine hydrochloride	10	no image	basic formulation; gelatin solution
ethylene diammine	10	no image	basic formulation; gelatin solution

Table III (continued)

Emulsion	Exposure Time (minutes)	Results	Comments
hydroquinone	10	no image	basic formulation; the entire emulsion turned brown when exposed to ammonia
dipyridyl	10	partial image	basic formulation had no effect image composed of small dots
1,10 phenanthroline	10	partial image	basic formulation had no effect image composed of larger dots
TCNQ	10	good image	$NiSO_4$ and NaH_2PO_2; image had a bubbly texture; developer caused no further enhancement
TCNE	10	no image	basic formulation; glycerine was added to keep gelatin in solution
triphenyl phosphine	10	no image	$NiSO_4$ and NaH_2PO_2; glycerine was added to keep gelatin in solution
lactose	10	good image	basic formulation; bubbly texture; developer caused no further enhancement of image

Table III (continued)

Emulsion	Exposure Time (minutes)	Results	Comments
xylose	10	good image	basic formulation; bubbly texture formed; no enhancement of image by developer
mannose	10	fair image	basic formulation; no enhancement of image by developer
galactose	10	poor image	basic formulation; no enhancement of image by developer

galactose. These sugars are easily oxidized in the presence of a substance that is easily reduced such as ammoniacal silver nitrate. It is possible that these sugars provide a medium in the film that aids in the reduction of the irradiated nickel hypophosphite.

The remainder of the compounds used were intended to act as complexing agents. According to work done by Lingane and Kerlinger (13), the addition of a complexing agent such as pyridine or thiocyanate to solutions containing nickel(II) ions results in an increase in the ease of its reduction to the metal. It is possible that the complexing agents which developed good images in this work were affecting the reduction potential of the nickel so that it was more easily reduced after being irradiated with x-ray photons. The same article, however, states that the addition of ammonium hydroxide to a nickel(II) solution decreases the reduction potential slightly from the value for the water-coordinated complex. Therefore, the presence of ammonium hydroxides in the nickel emulsion should make the film less sensitive to reduction upon irradiation if this is a factor in the mechanism of reduction.

Some of the emulsions that did not develop an image could have been the result of poor formulations or improper developmental techniques. The complexing agents which were not soluble in water may form complexes which are soluble. If this is the case, it may be necessary to form the complex before placing it in the reducing medium and adding the gelatin.

Some of the metals near nickel in the periodic table were substituted for the nickel in a few emulsions. Copper, cobalt, and iron(III) hypophosphites were combined with some of the complexing agents that had produced image development with nickel hypophosphite. All emulsions were exposed to the collimated x-ray beam. The results of the various emulsions are given in Table IV.

These substitute emulsions appear to be affected by irradiation with x-ray photons. These results could be misleading, however. It is possible that a latent image is being formed in each case, but that the techniques of amplifying the image are unsatisfactory. This appears to be the case in dealing with the cobalt emulsion. Cobalt solutions are affected the same way as nickel solutions upon the addition of complexing agents (13). Apparently, cobalt forms a stable complex with ammonia which is not affected by x-ray irradiation.

The reason the iron(III) hypophosphite emulsion was only made with 1,10 phenanthroline was that iron(III) is reduced to iron(II) in the presence of sodium hypophosphite (14). It was hoped that the iron(III) hypophosphite would be reduced to iron(II) upon irradiation. Iron(II) forms a red-colored complex with 1,10 phenantholine which would be highly visible against the light pink film.

Table IV

Results of Using Various Metal Hypophosphites in the Emulsion

Metal Used	Complexing Agent	Exposure Time	Results	Comments
Nickel	NH_4OH	5	partial image	normal development procedure
Nickel	EDTA	5	partial image	normal development procedure
Copper	NH_4OH	15	no image	treated with ammonia and copper sulfate developer
Copper	EDTA	15	no image	treated with ammonia and copper sulfate developer
Cobalt	NH_4OH	15	no image	film turned brown with addition of NH_4OH
Cobalt	EDTA	15	no image	film turned brown upon treatment with ammonia
Cobalt	EDTA	15	no image	elon developing agent used
Iron(III)	1,10 phenanthroline	10	no image	treated with ammonia and a sodium hypophosphite solution

Treatment of the exposed film with ammonia vapors and a sodium hypophosphite solution resulted in no visible image being formed, however.

The effects of radiation on the various hypophosphite emulsions used in this study indicate that, with the emulsion and developer formulations tried, the nickel emulsions are the only ones suitable for photographic research at this time. It is possible that copper, cobalt, and iron could demonstrate photographic activity with different emulsion or developer formulations, but, since an effective formulation has already been found for the nickel salt, it may be more profitable to try to find a compound which will work to sensitize the photographic activity of nickel.

A sensitive photographic emulsion containing nickel hypophosphite instead of silver halides would have definite advantages over the conventional silver-based film in the field of x-ray photography. The insensitivity of the film to normal incident radiation would eliminate the need for darkroom facilities. The much lower cost of using nickel in large films necessary for x-ray work would make x-ray examination more feasible in many applications. There are very few applications for a photographic emulsion that must be exposed to a direct x-ray beam for 5 minutes to develop a picture, however. Much more work is necessary to develop this system into a good, sensitive, x-ray emulsion.

APPENDIX

Table I

Infrared Absorption Maxima for Aluminum Hypophosphite

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3480	w	1180	s
2460	m	1160	s
2430	m	1110	m
1660	w	1090	s
1200	s	840	s

Table II

Infrared Absorption Maxima for Zinc Hypophosphite

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3450	m	1130	s
3380	m	1090	s
3240	m	1080	s
2420	m	1050	s
2400	m	1030	s
2370	m	820	s
1630	m	800	s
1150	s		

Table III

Infrared Absorption Maxima for Scandium Hypophosphite

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
2390	m	800	m
1140	s	790	m
1080	s		

Table IV

d-values Obtained for the Most Intense X-Ray lines in Scandium Hypophosphite

d	Relative Intensity	d	Relative Intensity
5.99	40	3.31	15
5.54	35	3.19	95
4.99	35	3.08	15
4.10	30	2.98	15
3.90	35	2.90	10
3.53	100	2.74	30

Table V

Infrared Absorption Maxima for Neodymium Hypophosphite

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3610	w	1250	s
3290	w	1160	s
3000	w	1090	s
2420	m	1080	s
2390	m	1060	s
2360	m	1040	s
2330	m	980	m
2010	w	810	s
1950	w	8800	s
1620	w		

Table VI

Infrared Absorption Maxima for Copper Hypophosphite

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
2400	m	1060	s
1140	s	810	s
1080	s	800	s

Table VII

Infrared Absorption Maxima for Manganese Hypophosphite

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3450	w	1150	s
2380	m	1090	m
1630	w	1080	m
1220	m	1060	s
1200	s	1040	s
1170	s	800	s

Table VIII

d-values Obtained for the Most Intense X-Ray Lines in Manganese Hypophosphite

d	Intensity	d	Intensity
10.05	100	3.87	30
6.62	10	3.64	20
5.95	30	3.44	20
5.45	50	3.26	50
-	-	3.12	40
5.16	25	2.97	50
4.71	10	2.86	50

Table IX

Infrared Absorption Maxima for Nickel Hypophosphite

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
4100	s	1110	s
2420	m	1070	s
1650	w	1030	s
1150	s	800	m

Table X

Infrared Absorption Maxima for Iron(III) Hypophosphite

Frequency (cm^{-1})	Intensity	Frequency (cm^{-1})	Intensity
3480	w	1080	s
2400	m	1060	s
1620	w	1050	s
1140	s	810	m

REFERENCES

1. H.F. Walton and J. Reyes, "Modern Chemical Analysis and Instrumentation," Marcel Dekker, Inc., New York, 1973, p. 48.

2. M. Grayson and E.J. Griffith, "Topics in Phosphorous Chemistry," Vol. 1, Interscience, New York, 1964, p. 166.

3. Ed. A.A. Eldridge, et. al., "Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, suppl. III, Longman Group Ltd., London, 1971, p. 1273.

4. N.N. Greenwood, J. Chem. Soc., sect. A, 2878 (1969).

5. NASA Tech. Brief, B72-10456 (1972).

6. J.W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, Longmans, Green, and Co. Ltd., London, p. 1928.

7. D.E. Corbridge, and E.J. Lowe, J. Chem. Soc., 493 (1954).

8. Ed. A.A. Eldridge, et. al., "Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, suppl. III, p. 616 and 1211.

9. J.S. Ziomek, J.R. Ferraro, and D.F. Peppard, Journal of Molec. Spect., 8,212 (1962).

10. H.D. Gilman, T.E. Hass, Chem. Commun., 14, 777-8 (1968).

11. H. Rose, Ann. Physik., 2,12 (1828).

12. C.Y. Peters, M.S. Thesis, South Dakota State University, Brookings, South Dakota, 1975.

13. J.J. Lingane, and H. Kerlinger, Ind. Eng. Chem., and Ed., 13, 77 (1941).

14. A.A. Eldridge, et al., "Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, suppl. III, Longman Group Ltd., London, 1971, p. 624.