

THE UNIVERSITY OF MINNESOTA
GRADUATE SCHOOL

Report
of
Committee on Examination

This is to certify that we the
undersigned, as a committee of the Graduate
School, have given Winslow Samuel Anderson
final oral examination for the degree of

Master of Science

We recommend that the degree of

Master of Science

be conferred upon the candidate.

Charles S. Mann
Chairman

J. H. Reyerson

Frank F. Groat

M. C. Sneed

Date June 5 1923

THE UNIVERSITY OF MINNESOTA

GRADUATE SCHOOL

Report
of
Committee on Thesis

The undersigned, acting as a Committee of the Graduate School, have read the accompanying thesis submitted by Winslow Samuel Anderson for the degree of Master of Science.

They approve it as a thesis meeting the requirements of the Graduate School of the University of Minnesota, and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science.

Charles A. Mann
Chairman

J. H. Peterson

Frank F. Groat

Date June 2, 1923

UNIVERSITY OF
MINNESOTA
LIBRARY

AN ATTEMPT TO MAKE TRUE COLORED LITHOPONES

A Thesis

Submitted to the Graduate Faculty

of the

University of Minnesota

by

Winslow Samuel Anderson

In partial fulfillment of the requirements

for the

degree of

Master of Science

June

1923

MOM
9 Feb 1938

AN ATTEMPT TO MAKE TRUE COLORED LITHOPONES

324472

DEC 31 1938 (Std) 4, 17 m.

ACKNOWLEDGMENT

To Dr. C. A. Mann at whose suggestion and under whose direction this investigation was carried out, for his kind encouragement and sympathetic counsel, the author wishes to acknowledge his indebtedness and to offer his sincere thanks.

AN ATTEMPT TO MAKE TRUE COLORED LITHOPONES

Introductory

On February 10, 1874 an English patent was issued to J. B. Orr for an Improved Zinc White.¹ This Improved Zinc White we have come to know as lithopone. Until the discovery of zinc oxide there had been no white pigment other than white lead which had held the field without a competitor for over 2000 years.² Although lithopone was destined to become a dangerous rival of white lead, it, nevertheless, passed through many vicissitudes before coming into its own. Orr's process consisted, essentially, in mixing solutions of barium sulfide and zinc sulfate in molecular proportions, from which resulted a heavy flocculent precipitate containing about 70.5% barium sulfate and 29.5% zinc sulfide. This precipitate as such, however, possessed no body or covering power, and when dried was totally unfit for use as a pigment. Orr discovered in 1880 that by heating this precipitate to dull redness and suddenly plunging it into water, a pigment of better covering power than pure zinc oxide could be produced.³

With this discovery began the rise of lithopone. Many years usually elapse, however, before the paint manufacturers will accept a new pigment, hence the commercial importance of lithopone was not apparent until the year 1900 when the production was given as 920 tons.⁴ Even now it was not universally accepted

by the paint trade, for it had one great disadvantage; the tendency to darken in the sunlight. This "photogenic" property was studied by many famous chemists including Ostwald who, in 1905, produced a lithopone which he claimed was free of this tendency.⁵ It remained, however, for W. J. O'Brien to discover the real cause for this darkening.⁶ He showed it was due to the formation of zinc from the zinc sulfide. On the heels of this discovery came the issuance of a great number of patents for improved processes of making "light-proof" lithopone.

There is little doubt that lithopone of the present market is entirely free of any "photogenic" properties. In the last ten years the rise of this pigment has been rapid until in 1920 the production was over 100,000 tons. To-day the demand far exceeds the supply and its popularity seems to be steadily increasing.⁷

At the present time there is probably no paint manufacturer in America, who does not use lithopone in one form or another. It is used as a base in practically all of the so-called flat wall paints where it is mixed with colored inorganic pigments.⁸ Makers of oilcloth and linoleum as well as manufacturers of rubber goods make wide use of it. An increasing number of printing inks are now being made with lithopone as a base, and even face powders are not free from it. Improved processes are opening a new use of it in exterior paints.⁸ In fact the uses of lithopone are innumerable.

The great popularity of lithopone, its use with colored pigments in flat wall paints, and its wide application in the manufacture of linoleums and rubber goods has suggested the

possibility that lithopone made by replacing the zinc sulfide with a colored inorganic sulfide might prove useful as a colored pigment. With this point in view a search of the literature was made. It developed that in the electrolytic production of cadmium a solution of the sulfates of zinc and cadmium was obtained. H. R. Hanley⁹ has suggested that this solution might be used in producing cadmium lithopone. According to P. W. Webster¹⁰ this is possible, a yellow to orange pigment showing good covering power and high tinting strength being obtained. Late in 1921 a patent was issued to J. R. Marston,¹¹ which states that zinc dust containing cadmium is treated with sulfuric acid and the resulting solution precipitated with barium sulfide thus producing a pigment containing the sulfides of zinc and cadmium together with the sulfate of barium. As can readily be seen, this is analogous to the method suggested by Hanley and Webster reported above. A further search of the literature failed to reveal any other attempts to make colored lithopones although, undoubtedly, investigators have had this self-same idea and have perhaps applied it to other metals. It is the intention of the author to entirely replace the zinc sulfide of commercial lithopone with other colored sulfides.

It is, then, the purpose of this investigation to determine:

1. If, in accordance with the literature, a cadmium lithopone in which the zinc is entirely replaced can be produced.
2. If colored inorganic sulfides other than cadmium can be substituted for the zinc sulfide of commercial lithopone.

3. If a lithopone thus made will mix with oil and produce a paint of good covering power.
4. If a pigment of this type can be made without the customary calcining necessary in the zinc variety.
5. If such lithopones will withstand the effect of weak acids and alkalis.
6. If sunlight will affect these pigments to an appreciable extent.

Commercial Method

Lithopone sometimes called Orr's white, Ponolith, Griffith's white, Oleum white, Beckton white, and various other names is manufactured in this country on a large scale. According to A. S. Krebs¹² there are three steps in the commercial production of lithopone.

1. The preparation of the pure barium sulfide solution.
2. The production of the pure zinc sulfate solution.
3. The manufacture of the lithopone from these two solutions.

In making the barium sulfide solution, barytes is crushed, mixed with powdered coal and calcined in rotary kilns at 1200-1300 degrees Centigrade. The resulting black ash is then leached giving a barium sulfide solution of sufficient purity. The zinc sulfate solution is obtained by dissolving zinc wastes in sulfuric acid and purifying the solution by oxidizing methods. It is also made by roasting zinc ore and dissolving the mass in 20% sulfuric acid.¹³

The solutions are now heated with steam and the proper amounts run into wooden precipitating tanks. These tanks are equipped with agitators to insure thorough mixing and complete precipitation. The precipitate is removed by filtration and after thorough washing is dried and calcined at 480-500 degrees Centigrade. When uniformly heated it is taken out and immediately quenched. This quenched material is now ground, washed, dried, and pulverized when it is ready for use. Often the product is not a pure white, then some material having a complimentary color is added in order to make the final pigment a true white. For paint purposes, lithopone is usually ground in a mixture of rosin and China wood oil. As can be seen the method of manufacture is quite simple, although, it may be said that the average chemist unfamiliar with the theory and practice cannot make lithopone successfully. According to Toch³ the product depends very largely upon the materials used, while Jones¹³ states that the quenching is the key to the entire operation.

Theoretical

Lithopone is, as has already been stated, the precipitate resulting by double decomposition from the mixing of solutions of barium sulfide and zinc sulfate in molecular proportions, the reaction being represented by the simple equation:



In attempting the manufacture of true colored lithopones, it appears that by substituting a solution of the sulfate of some

metal for that of zinc we should obtain a product in which the zinc sulfide of our commercial lithopone has been entirely replaced. It happens, however, that often the sulfate of a metal we hope to use is either unknown or is insoluble. If such is the case, we can make use of some other soluble salt of the metal, say the chloride or nitrate, supplying the sulfate radical by the addition of sodium sulfate or sulfuric acid. The same methods, then, can be applied to the manufacture of colored lithopones as are used in producing the commercial pigment. In some cases, however, the sulfides may melt at rather low temperatures as arsenous sulfide which melts at 310 degrees Centigrade,¹⁴ or may have been used as pigments themselves without calcining as cadmium sulfide and antimony trisulfide, therefore the customary calcining and quenching used in making commercial lithopone may not be necessary in the colored variety. It was by using this procedure that the experimental work was carried out and, as will be shown, it is evident that true colored lithopones can be produced.

Experimental

As has been stated, the procedure for the making of colored lithopones will not differ very much from that used in the production of the commercial pigment. In obtaining the barium sulfide solution, the purified barium sulfide (Merck) containing 60 - 80 % BaS was added to water and the metallic sulfate was made by dissolving the pure chemical. Early in the work it was found that complete solution of the barium sulfide was not

necessary, in fact, it appeared that a larger yield was obtained when the barium sulfide was only partially dissolved before mixing the precipitating solutions. This is probably due to the fact that when barium sulfide is dissolved in water it does so by hydrolyzing with the formation of the hydroxide and the hydrosulfide.¹⁵ The precipitation of each lithopone was carried out in glassware. The specific amounts of material together with any modifications of the procedure will be considered under each lithopone.

Each experiment was repeated at least once in order to ascertain if the results could be duplicated. Often the procedure was varied and the effect upon the product noted. The problem was first attacked from the angle of color, but it seemed impossible to produce certain colors, therefore the experiments which follow will be arranged according to the sulfide used rather than by the color obtained. The treatment of the pigments after precipitation varied slightly as will be shown, but all were filtered and washed in a Buchner funnel by suction. Each precipitate was dried in an electric oven which was regulated to 90 - 100 degrees Centigrade.

In testing the pigments obtained, a modification of the procedure suggested by the Bureau of Standards¹⁶ was employed. The government specifications allow 68-72 parts of pigment to 32-28 parts of oil by weight in the finished paint. The author arbitrarily used 70 parts of pigment to 30 parts of China wood oil taking 14 grams of pigment to 6 grams of oil. The lithopones were first ground in an agate mortar until all would pass the 100 mesh screen and most pass the 200 mesh. They were then ground in oil in the

proportions given above. To determine the effect of sunlight the paint was applied to strips of high grade hard finish book paper instead of to glass plates as suggested in the government specifications. A part of each strip was covered with black paper and the whole exposed to the light for at least five days, thus clearly showing the effect of sunlight. Each pigment was also tested with 0.5 normal solutions of the common acids and alkalis by applying the reagent to the dry pigment.

Cadmium Lithopone

Experiment 1.

Cadmium lithopone, being the only one mentioned in the literature, was attempted first. To a solution containing 83 grams of cadmium sulfate was added with vigorous stirring a hot solution in which there were 50 grams of barium sulfide. The precipitate was first yellow, but rapidly turned to a deep orange. The equation below represents the reaction.



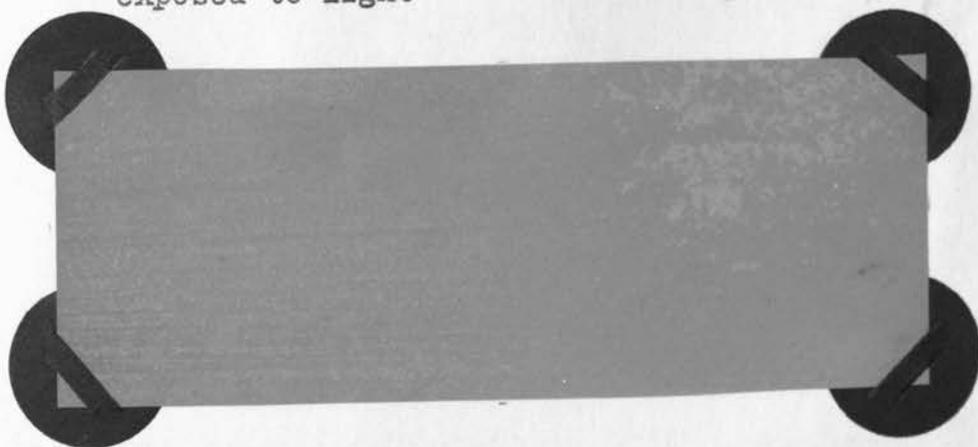
After the precipitate had been filtered through a Buchner funnel and thoroughly washed, it was dried at 90-100 degrees Centigrade in an electric oven. When dry the pigment was ground in an agate mortar to approximately 200 mesh. The yield was 73 grams which, considering that the barium sulfide was 60-80% active substance, appears to be very good. To form the paint, 14 grams of the lithopone was ground in a mortar containing 6 grams of China wood oil. The product had good covering power although it would have

been better if a little more oil had been used. It was found that weak acids, HCl, H₂SO₄, and HNO₃, react on the pigment to a slight extent, but weak alkalis, NaOH and NH₄OH, have no effect on it. After being exposed to the sunlight for eight days it showed no ill effects.

Sample of Cadmium Lithopone

exposed to light

not exposed



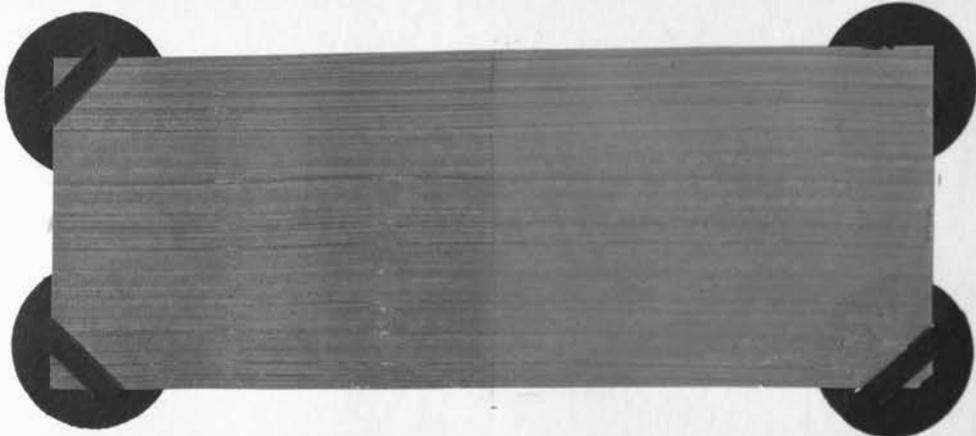
Experiment 2.

A second experiment was carried out in a similar manner except that the barium sulfide was added to the cadmium sulfate solution without first being dissolved. The precipitation took place in the cold. The yield was 112 grams, an increase of 38 grams. The pigment was of a stronger hue than before. The increase in yield is without doubt due to the fact that the barium sulfide was not hydrolized. No attempt was made to calcine the cadmium lithopone since cadmium sulfide is itself used without calcining as a pigment. The product was attacked by the weak acids but not by the weak alkalis. On exposure to light for eight days its color was very slightly changed. A sample of the paint produced will be found on the succeeding page.

Sample of Arsenic Lithopone

exposed to light

not exposed



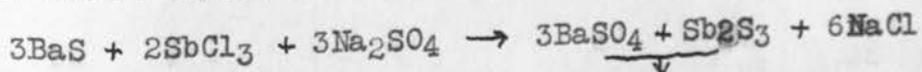
Experiment 4.

Experiment 3 was repeated with similar results. Arsenic lithopone was not calcined, for arsenic trisulfide melts at 310 degrees Centigrade.¹⁴

Antimony Lithopone

Experiment 5.

Hot solutions containing 45 grams of antimony trichloride and 95 grams of Glauber's salt were added to 50 grams of barium sulfide wetted with hot water insufficient for complete solution. A precipitate of 90 grams of a bright red product resulted. The equation below represents the reaction.



While drying the product the temperature was accidentally allowed to rise as high as 135 degrees Centigrade with the result that the pigment turned to a grayish purple in color. The reason for this is uncertain, for Smith¹⁷ states that the red Sb_2S_3 goes to the

black variety when heated to its melting point, 555 degrees Centigrade. Partington¹⁸ says that the red form heated to 200 degrees Centigrade in an atmosphere of carbon dioxide goes to a grayish black and if heated in nitrogen to 850 degrees Centigrade the vapor, if rapidly cooled, forms lilac colored globules of a third form. On mixing the pigment with oil a black paint was obtained. Although resistant to weak acids, HCl, H₂SO₄, and HNO₃, the alkalis destroy the color. Light on the other hand has no visible effect upon it. Several attempts were made to duplicate the purple color without success.

Sample of Antimony Lithopone

exposed to light

not exposed



Experiment 6.

A pigment obtained in a manner similar to experiment 5 was dried at 90-100 degrees Centigrade. The color remained a bright red. The product showed good covering power and exhibited a permanency toward light. Weak solutions, 0.5 normal, of HCl, H₂SO₄, HNO₃, NaOH, and NH₄OH had no effect upon it. The yield was 95 grams. A part of this precipitate was heated to 135 degrees in the electric oven in an attempt to duplicate the purple

variety but without success.

Sample of Antimony Lithopone

exposed to light

not exposed



Experiment 7.

Experiment 6 was repeated using cold solutions instead of hot ones. 93 grams of a product similar both in color and properties was obtained. A part of this product was also used in trying to duplicate the purple color, but the attempt met with no success. Since antimony trisulfide is a pigment in itself, calcining was not resorted to with antimony lithopone.

Sample of Antimony Lithopone

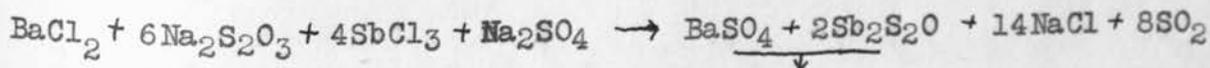
exposed to light

not exposed



Experiment 8.

According to Thorp¹⁹ if antimony trichloride is precipitated with sodium thiosulfate at 55 degrees Centigrade, a red oxy-sulfide of antimony which, according to Biedermann,²⁰ has the formula Sb_2S_2O results. With this in mind, solutions heated to 55 degrees Centigrade and containing respectively 50 grams of barium chloride, 50 grams of sodium thiosulfate and 50 grams of sodium sulfate were added simultaneously to a solution containing 92 grams of antimony trichloride. A brick red precipitate weighing 105 grams resulted. This reaction may be represented by the equation:



This precipitate was filtered and washed as in previous experiments and ground to 200 mesh. When mixed with oil this pigment produced a brownish red paint having good body and being resistant to light even after eight days exposure. Weak solutions of HCl, H_2SO_4 , HNO_3 , NaOH, and NH_4OH seemed to have no effect upon it.

Sample of Oxy-sulfide Lithopone

exposed to light

not exposed



Experiment 9.

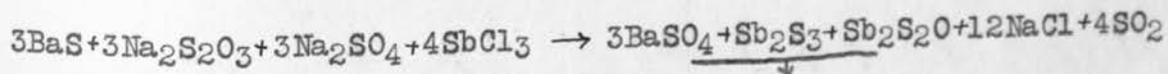
Experiment 8 was repeated with equal success.

Experiment 10.

A mixture of Sb_2S_3 and Sb_2S_2O was next tried. The raw materials consisted of:

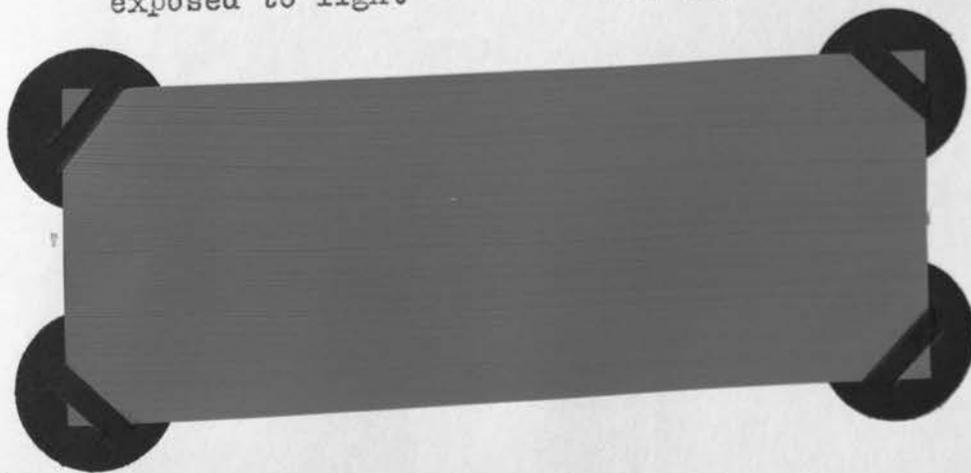
- 50 grams BaS
- 54 grams $SbCl_3$
- 73 grams $Na_2SO_4 \cdot 10 H_2O$
- 74 grams $Na_2S_2O_3$

Precipitation was brought about by adding the antimony trichloride, sodium thiosulfate and Glauber's salt solutions simultaneously to the moist barium sulfide. The precipitating solutions were all heated to 55 degrees Centigrade. The following equation, perhaps, represents the reaction.



When ground in oil it exhibited properties similar to the other red antimony lithopones except that it was of a slightly brighter shade

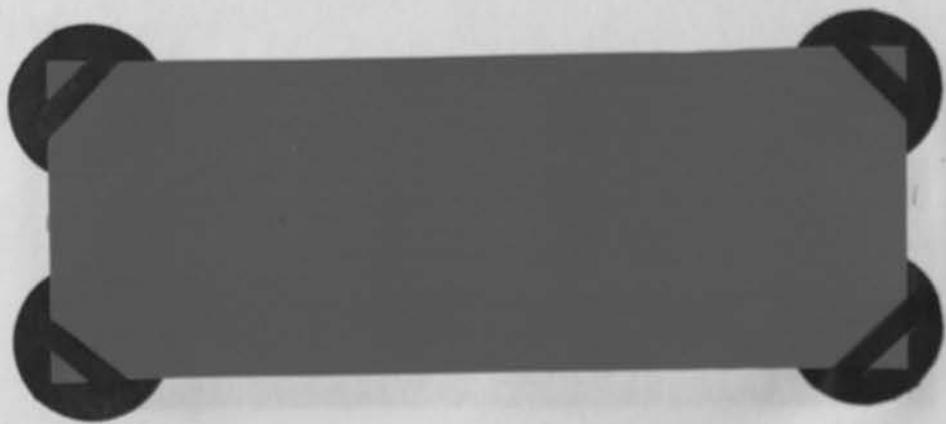
Sample of Mixed Antimony Lithopone
exposed to light not exposed



Experiment 11.

This was a duplication of experiment 10 with a somewhat larger yield, 125 grams.

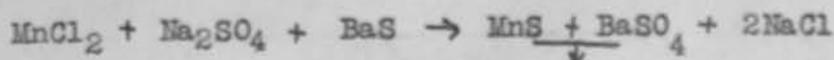
Sample of Mixed Antimony Lithopone
exposed to light not exposed



Manganese Lithopone

Experiment 12.

Hot solutions of 38 grams of $MnCl_2$ and 43 grams of Na_2SO_4 were added to 50 grams of BaS which was partially dissolved, and the whole was agitated until the reaction was as complete as possible. The precipitate formed was pink or flesh-colored. When washed, dried and ground to 200 mesh it produced a brown pigment of moderate shade. The yield was 80 grams. The equation given below represents the reaction.



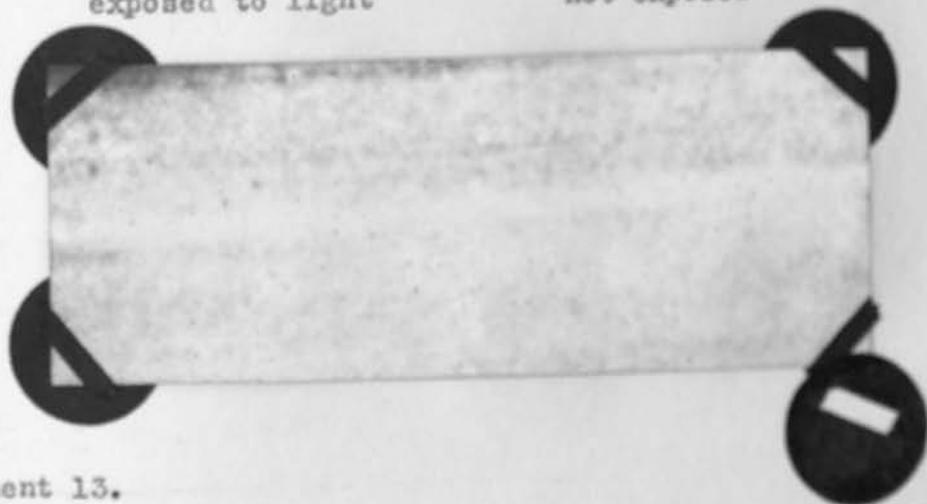
The sodium sulfate was used in place of sulfuric acid to supply the sulfate radical, because of its cheapness. On being ground with

China wood oil a dark brown paint having a fairly good body resulted. On being tested with 0.5 normal acids, hydrogen sulfide was evolved although the color seemed unimpaired. Alkalies have little or no effect upon it. The color was also permanent to sunlight.

Sample of Manganese Lithopone

exposed to light

not exposed



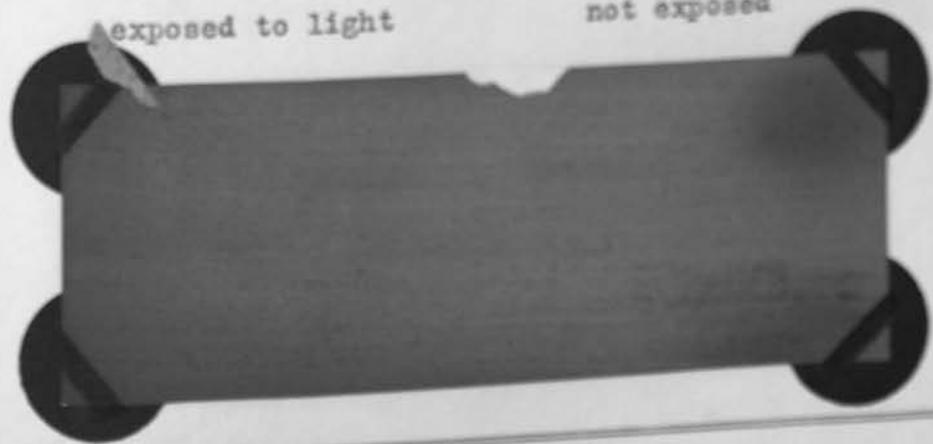
Experiment 13.

Experiment 12 was repeated except that the precipitation was done with cold solutions and with the barium sulfide added to the mixed manganese chloride and sodium sulfate solutions. The color was almost identical with that of experiment 12 as was the yield. The manner of precipitation appears to have little or no effect upon the final product.

Sample of Manganese Lithopone

exposed to light

not exposed



Experiment 14.

According to Roscoe and Schorlemmer²¹ when manganese sulfide is heated in the presence of ammonium sulfide to 300 deg. Centigrade, the pink colored form passes to the green crystalline type. Endeavoring to secure a green pigment, the manganese lithopone was precipitated in exactly the same manner as in experiment 12. As before the product was a pink which turned to a brown on being dried. This brown pigment of which there were 80 grams was then moistened in a porcelain crucible with strong ammonium sulfide solution until it formed a pasty mass. The crucible was calcined in a gas heated Segar furnace at a temperature of 650-700 degrees Centigrade for 1½ hours. On being removed the mass was immediately quenched in water, ground and thoroughly washed, and then dried in an electric oven as before. The product when removed from the Segar furnace and up to the time of drying was a dark olive green in color, but on being dried it rapidly turned to a brown. On grinding with oil it produced a dark brown paint similar to that of experiment 13. It had no better properties than that which was not calcined and as the green was not permanent, it is concluded that the calcining is not advantageous.

Experiment 15.

Roscoe and Schorlemmer²¹ also state that when ammonium sulfide is merely in contact with manganese sulfide, the green form results. Accordingly the brown lithopone was made as in experiment 13. The product was then ground in a mortar in the presence of an excess of ammonium sulfide solution producing a dark green pigment which after being washed and dried as before

turned to a brown having properties similar to the product of experiment 13.

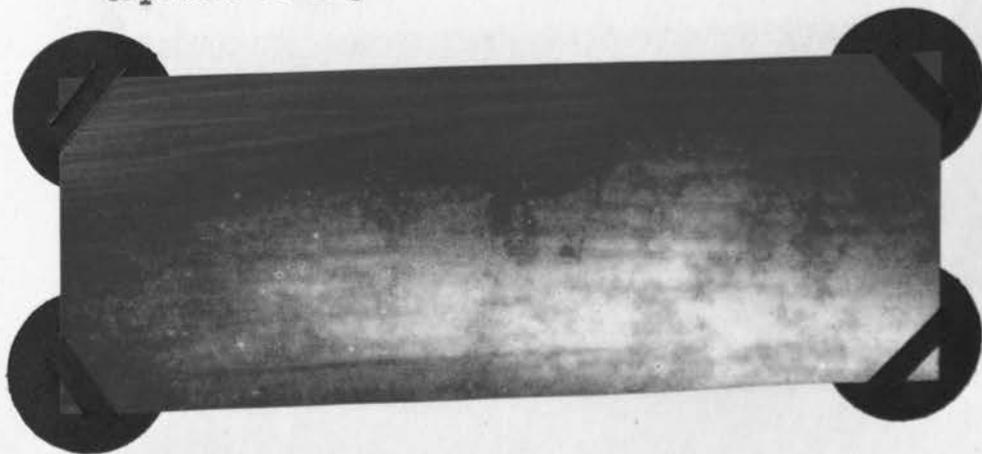
Experiment 16.

In this experiment the same amounts of materials were used, but mixed with the barium sulfide was 150 cc. of ammonium sulfide solution. The precipitate when first formed was pink in color, but after standing for eight hours the green variety appeared. The product was dried as before but with as small as possible surface exposed to the air. When the total mass was dry the interior had remained green while the exterior had turned brown. It would appear that this brown was due to oxidation on the surface. When ground in oil it gave a greenish brown paint which was resistant to the weak alkalis but not to the acids. It was, however, not affected by light.

Sample of this product

exposed to light

not exposed

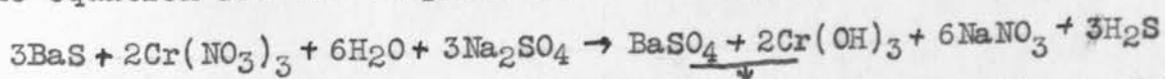


Chromium Lithopone

Experiment 16.

In preparing chromium lithopone cold solutions containing

45 grams of sodium sulfate and 79 grams of chromium nitrate were added simultaneously to 50 grams of moist barium sulfide. The mass was thoroughly stirred during precipitation. The precipitate formed was bluish green in color. On being ground with oil it gave a dark green paint which had poor covering power. It was, however, unaffected by either light, or weak reagents. This product probably does not contain any appreciable amount of chromium sulfide, for according to Prescott and Johnson²² chromic sulfide is not formed in the wet way. Partington²³ states that it is completely hydrolyzed by water with the formation of the hydroxide. The equation for the complete reaction is probably as follows:

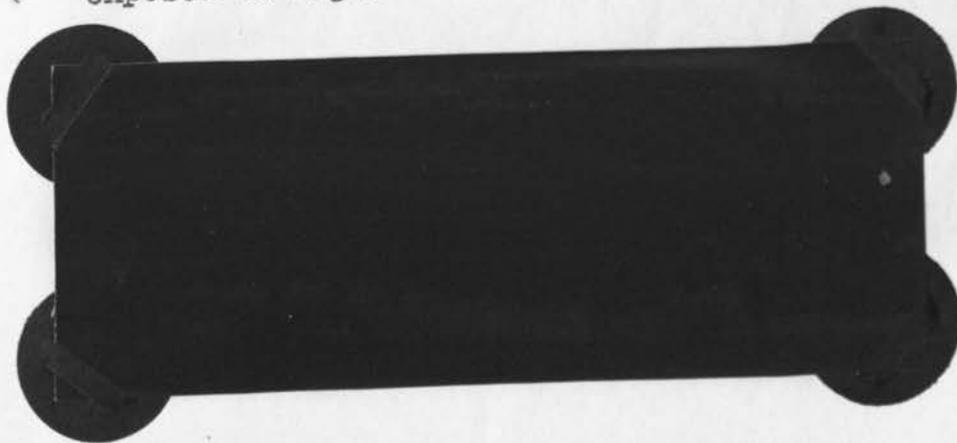


Since this product is not a true lithopone the experiment was not repeated.

Sample of this product

exposed to light

not exposed



Copper Lithopone

Experiment 17.

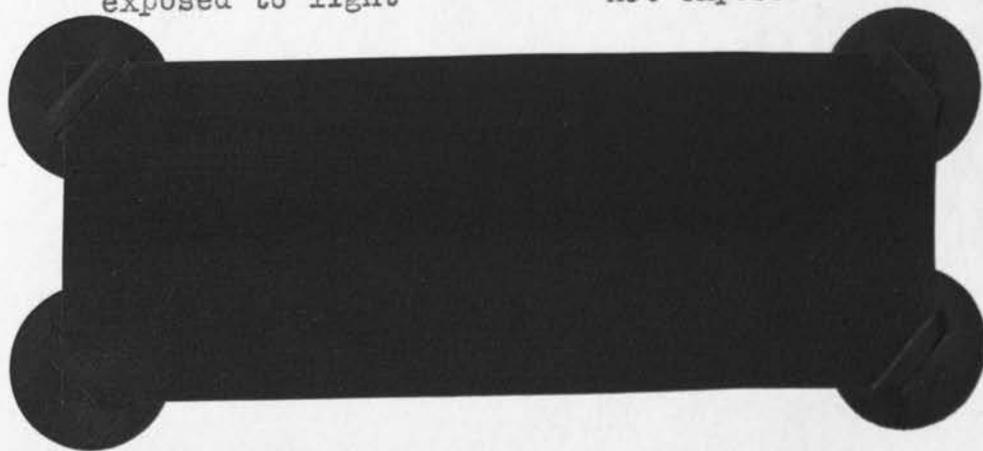
As copper sulfide is known to be black, it was thought that perhaps, if a sulfide of another color was mixed with the

black copper sulfide some shade other than black might result. Manganese sulfide precipitated together with copper sulfide by adding cold solutions of 19 grams $MnCl_2$, 25 grams of $CuCl_2$ with 73 grams of Na_2SO_4 to supply the sulfate radical simultaneously to 50 grams of previously moistened BaS. The precipitate was brownish black at first but on standing a short time turned to a very dark green. After being dried and ground, the pigment was mixed with oil in the usual proportions. The color appeared to be almost black with an undertone of green. The product seemed to have fairly good covering power and was resistant to the weak reagents. Likewise light had no bad effects upon it.

Sample of Copper Lithopone

exposed to light

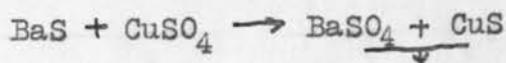
not exposed



Experiment 18.

In order to determine if the green shade was due to the presence of the manganese sulfide, a hot solution of 37 grams of cupric sulfate was added to 25 grams of barium sulfide. A black precipitate appeared at first but this soon turned to a dark green. The yield was 45 grams. On being ground with oil it gave a paint exactly like that of experiment 17 showing that the color was not

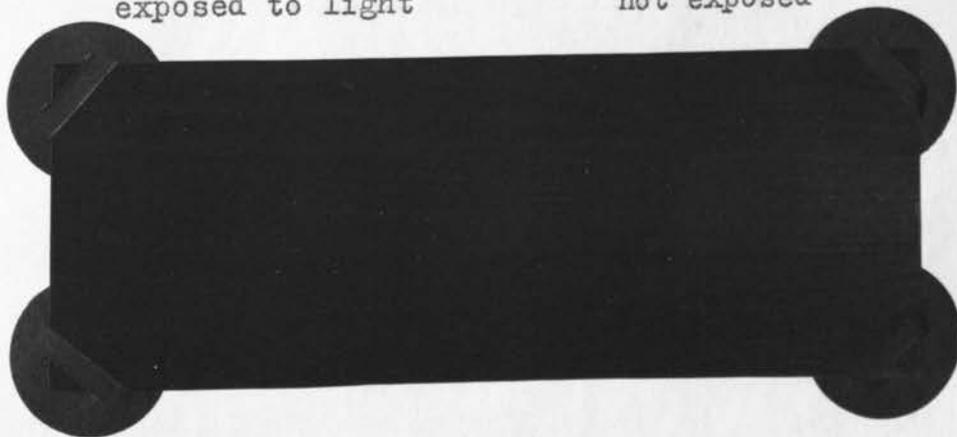
due to the presence of manganese sulfide. The reaction may be represented by the equation:



Sample of Copper Lithopone

exposed to light

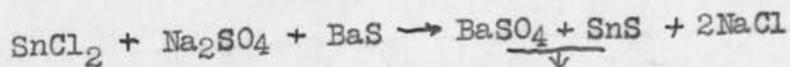
not exposed



Tin Lithopone

Experiment 19.

In preparing a tin lithopone 28 grams of stannous chloride were dissolved in a solution containing 22 grams of sodium sulfate and the whole added to 25 grams of moistened barium sulfide with constant stirring. The precipitation was carried out with cold solutions and a dark brown product resulted. This pigment was prepared for painting in the usual manner and gave a dark brown paint having fair covering power. It was resistant to the weak reagents but was readily affected by sunlight. The paint failed to dry well, however, therefore a sample is not included. The equation below represents the reaction.



Because of the adverse properties of tin lithopone a second experiment was not tried.

Mercury Lithopone

Experiment 20.

Mercury was tried next. A solution was made containing 94 grams of Glauber's salt and added together with a solution of 80 grams of mercuric chloride to 50 grams of barium sulfide in a moist condition. The temperature of the solution was kept at 45 degrees Centigrade during the precipitation. The precipitate with the resulting solution was digested at 45 degrees for eight hours with the hope of producing a red variety of mercuric sulfide, since Thorp²⁴ says that vermilion, HgS, is formed in the wet process by digesting 100 parts of mercury and 38 parts of sulfur in a solution of 25 parts of potassium hydroxide to 150 parts of water. This digestion should be carried out for eight hours. The black mercuric sulfide merely separated from the barium sulfate, because of the difference in density of the two. The yield was not determined, for the experiment was not a success.

Experiment 21.

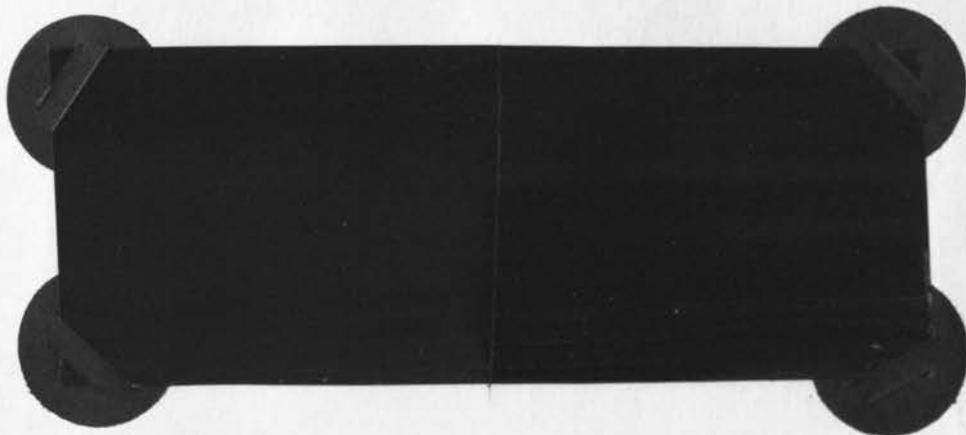
The black mercury lithopone was again precipitated exactly as above, but the entire mass vigorously stirred at intervals during the digestion. The mercuric sulfide remained incorporated with the barium sulfate, but the color was still black. The reaction may be represented by the following equation:



When ground in oil in the usual manner, a black paint having fair body was produced. It was resistant to 0.5 normal solutions of the common acids and alkalis. After being exposed to the sunlight for five days a slight change in color could be noticed. A sample

will show the change.

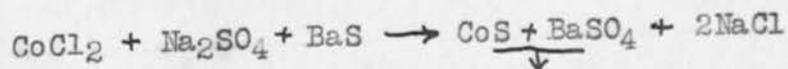
Sample of Mercury Lithopone
exposed to light not exposed



Cobalt Lithopone

Experiment 22.

Although expecting a black color, it was thought advisable to at least try one experiment with cobalt, therefore a solution containing 22 grams of sodium sulfate and 36 grams of cobaltous chloride was added to 25 grams of barium sulfide which was partially dissolved. The precipitation was carried out with cold solutions and a black product was formed. The equation for the reaction is given below.

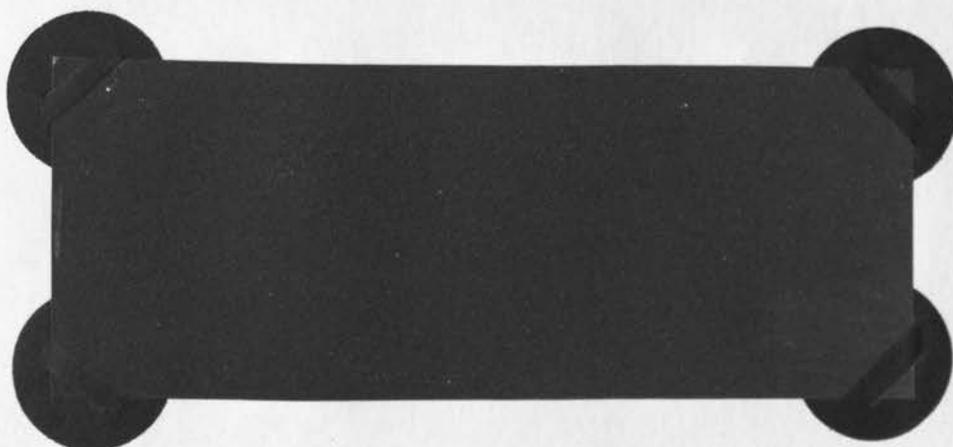


The paint produced proved to be resistant to sunlight as well as to the weak reagents. A Sample of the lithopone will be found on the next page. As the product was black a second experiment was not tried.

Sample of Cobalt Lithopone

exposed to light

not exposed



Iron Lithopone

Experiment 23.

Although ferrous sulfide is ordinarily black it also occurs in other colors, therefore an attempt was made to precipitate an iron lithopone. Cold solutions of 41 grams of ferrous sulfate and 25 grams of barium sulfide were mixed. A black precipitate was formed according to the equation:

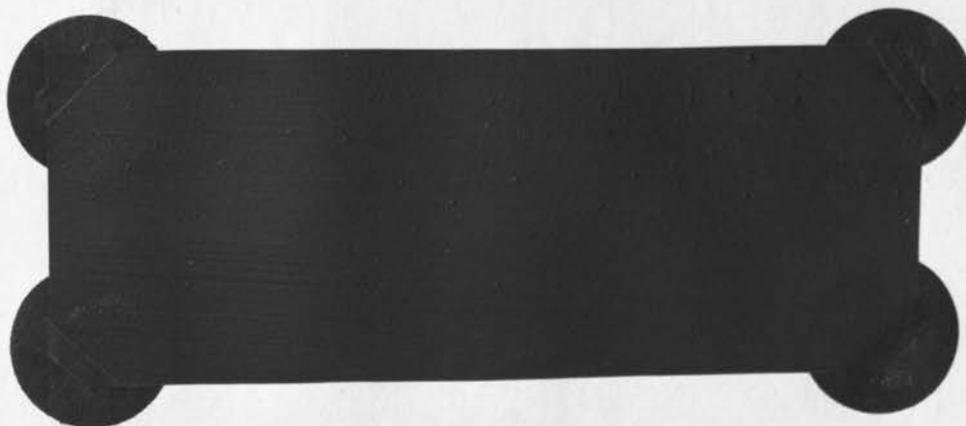


When ground and mixed with oil a brownish black paint was produced. This paint had fair covering power and seemed to be unaffected by sunlight even after five days exposure. Weak solutions, 0.5 normal. of HCl, H₂SO₄ and HNO₃ evolve hydrogen sulfide from it, but the alkalis have no effect on the color. As the product was black a second experiment was not tried. A sample will be found on the next page.

Sample of Iron Lithopone

exposed to light

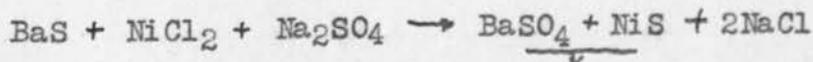
not exposed



Nickel Lithopone

Experiment 24.

Even though nickel sulfide is black, a nickel lithopone was tried with the view that perhaps a colloidal form might be precipitated. To a solution containing 22 grams of sodium sulfate were added 19 grams of nickel chloride and the whole added to 25 grams of moistened barium sulfide. A black precipitate was formed. The equation given below represents the reaction.



The precipitate was prepared for paint purposes in the usual manner. The black paint produced had fairly good covering power and was resistant to the weak reagents. After five days sunlight had no visible effect upon it. The yield was 43 grams. A sample of the paint is given on the following page.

Sample of Nickel Lithopone

exposed to light

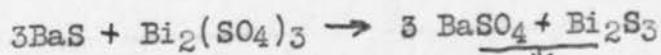
not exposed



Bismuth Lithopone

Experiment 25.

In this experiment a cold solution of 35 grams of bismuth sulfate was added to 25 grams of moist barium sulfide. A crystalline brownish black precipitate was formed. The equation below shows the reaction.



The yield was 20 grams. It was washed and ground as in the case of the other lithopones and mixed with China wood oil. The paint produced had good body but failed to dry. It was not affected by weak solutions of the common reagents as HCl, H₂SO₄, HNO₃, NaOH and NH₄OH. The sunlight, however, turned the paint to a jet black. A second experiment was not tried.

Conclusions

To one studying the foregoing experiments there are several deductions which are at once apparent. A capitulation of these conclusions is as follows:

1. A cadmium lithopone can be easily produced as stated by Hanley and Webster.
2. Colored inorganic sulfides other than cadmium sulfide can be substituted for the zinc sulfide.
3. The lithopones thus made will produce paints of good covering power.
4. In many cases a good pigment can be made without the customary calcining necessary in the zinc variety.
5. The lithopones formed will in general withstand the action of weak acids and alkalis.
6. These lithopones should not be discolored by hydrogen sulfide.
7. These lithopones are in most cases permanent to sunlight.
8. In precipitating a lithopone undissolved barium sulfide will give the best yield.
9. The cost of producing these lithopones would probably prohibit their immediate introduction unless they were incorporated with white lithopone.

Suggestions for Further Investigation

1. Testing the tinting power of these lithopones.
2. Determination of methods of lowering the cost either by improved methods of precipitation or by cheaper raw materials.
3. Determination of the oil figure of these lithopones, that is, the amount of oil necessary to produce the best paint.
4. Testing of the weathering properties of these paints.
5. A study of the uses to which colored lithopones might be put.
6. A study of the effect of calcining.
7. Analyses of the various pigments.
8. An investigation of the use of solid barium sulfide in precipitating lithopone.
9. The production of lithopones of a mixed zinc sulfide and colored sulfide composition.

Bibliography

1. Lithopone, H.S. Riederer; Jour. Soc. of Chem. Ind. vol. 28 page 403 (1909)
2. The Chemistry & Technology of Paints, Maximilian Toch; book 2nd ed. page 27
3. Ibid., page 46
4. Lithopone, A.S. Krebs; Chem. & Met. vol. 23 No. 22 page 1084 (1920)
5. German Patent 202,709 (1905) See C.A. vol. 3 page 725 (1909) William Ostwald
6. A Study of Lithopone, W.J. O'Brien; Jour. Phys. Chem. vol. 19 page 113 (1915)
7. Oil, Paint & Drug Reporter, vol. 103 No. 14 page 45 and vol. 103 No. 20 page 23 (1923)
8. Lithopone Production & the Zinc Industry, J. F. Williams, Jr.; Chem. Age (N.Y.) vol. 29 No. 8 page 333 (1922)
9. The Production of Electrolytic Cadmium, H.R. Hanley; Chem. & Met. vol. 23 No. 26 page 1257 (1920)
10. Advantages of Cadmium Lithopone, P.W. Webster; Chem. & Met. vol. 24 No. 9 page 372 (1921)
11. U.S. Patent 1,399,506 (Dec. 6, 1921) J.R. Marston See C.A. vol. 16 page 842 (1922)
12. Lithopone, A.S. Krebs; Chem. & Met. vol. 23 page 1083 (1920)
13. Making Lithopone at Collinsville, Ill., C. H. Jones; Chem. & Met. vol. 22 No. 11 (1920)

14. Van Nostrand's Chemical Annual, 4th issue page 138
15. General Chemistry for Colleges, Alex. Smith; book 2nd edition page 497
16. Circular 111, Bureau of Standards; U.S. Government Specifications for Flat Interior Lithopone Paint, White and Light Tints. 2nd ed.
17. General Chemistry for Colleges, Alex. Smith book 2nd ed. page 590
18. Textbook of Inorganic Chemistry, J. R. Partington page 937
19. Outlines of Industrial Chemistry, F. H. Thorp 3rd ed. page 245
20. Chemiker-Kalender 1920, R. Biedermann page 22
21. Treatise on Chemistry, Roscoe & Schorlemmer 3rd ed. page 924
22. Qualitative Chemical Analysis, Prescott & Johnson 2nd ed. page 149
23. Textbook of Inorganic Chemistry, J. R. Partington page 953
24. Outlines of Industrial Chemistry, F. H. Thorp 2nd ed. page 244