A STUDY OF
PHOSPHORESCENT ZINC SULFIDE

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FRANCIS PATRICK SOMERS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

FRANCIS PATRICK SOMERS

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DEGREE OF Bachelor of Science in Chemistry

B S Hopkins
Instructor in Charge

APPROVED: W. A. Noyes

HEAD OF DEPARTMENT OF Chemistry

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DISCUSSION

The terms phosphorescence, luminesence, and fluorescence have been used more or less as synonyms in previous publications, so it is necessary to define phosphorescence in order to prevent confusion of meaning.

A substance is said to phosphoresce when it emits light for a period of time after having been subjected to the action of light rays, of after heating, rubbing, or other mechanical excitation. A substance is fluorescent when it emits light only through excitation by light, cathode, radium or other light rays. Fluorescence ceases upon removal of the cause of excitation, but phosphorescence persists sometimes for as short a time as .001 of a second, other times for days. In both cases, the light is produced without the emission of heat, and without any visible evidence of a physical or chemical change in the substance. Bodies which fluoresce at ordinary temperatures are as a general rule phosphorescent at very low temperatures, and vice versa.

HISTORICAL AND THEORETICAL PART.

The history of phosphorescence dates from the year 1602 or 1603, when a shoemaker of Bologna, by name, Vincentius Casciorolus, heated some barytes in a charcoal furnace to obtain the noble metal which he thought it possessed on account of it's weight and luster. Upon cooling the barytes, he saw that it emitted a red light when taken into a dark place, after having been exposed to the sun. He called this material "Natural Phosphorus". Other materials were found that phosphoresced after calcination, and Kircher in 1631 advanced the first theory, namely, that "the stones after being made porous by calcination soaked up the light much as a sponge soaks up water."

In 1675, Baldewin or Balduinus as his name is latanized, published a paper on a phosphorescent compound which he made from chalk and potassium nitrate. However, being an alchemist he did not see fit to give the details of the preparation of the compound. After isolation of the element phosphorus in 1680, Baldewin's name persisted as one of the classifications of phosphorescent substances which were; 1-Bolognese Phosphorus, 2-Baldwinishe Phosphorus,(Blue), 3-Emerald Phosphorus (Green), 4-Elementary Phosphorus. In 1793, Homberg added another color by fusing one part ammonium chloride and two parts calcium oxide in a crucible and then casting in a copper mould. This mixture gave a grayish phosphorescence upon rubbing it.

Du Fay, in 1723, after preparing several phosphorescent substances from different materials by calcination with coal, stated that exposure to diffused light gave better phosphor-

escence than exposure to direct sunlight, that quenching in water did not affect the phosphorescence, that the color of the phosphorescence was variable and also that oyster shells and egg shells phosphoresced after calcination.

Dr. Von Hofmann in 1750 published the first known paper on Zinc Sulfide. He tried to isolate the phosphorescent part of Scharfenberger Zinc Blende by all known chemicals. Wilson in 1775, found that violet light excited phosphorescence better than any other color. Grotthuss in 1815, declared that phosphorescence was due to the creation of positive and negative poles, on the surface of the substance, through the action of the light to which it had been exposed. The reunion of these positive and negative charges gave the light which we call phosphorescence. E. Becquerel, in 1839, expressed practically the same views as Brotthuss had earlier. He also showed that the effect of the electric spark in activating the phosphorescence was due to the light given off and not to the heat. Later on, in 1843, he showed that it was the short wave lenghts of the spectrum which aroused phosphorescence. In 1857, he put forth the theory that bodies phosphoresce when their molecular equilibrium is displaced. He cites heat, mechanical means, electric discharges, and insulation as means to disturb this equilibrium. He further declared that the color of the phosphorescent light was a function of the duration and temperature to which the substance was heated, and not of the chemical composition. Further researches by him were mostly in the spectroscopic examination of phosphorescent bodies.

From the beginning, investigators found that there was trouble in preparing phosphorescent bodies by any formula. They never seemed to be able to obtain the same degree of phosphorescence by the use of the same materials and methods. The differences in the duration and heighth of temperature of the heating were blamed by most investigators. However, E. Becquerel found that materials which had been ground in an iron mortar would not phosphoresce. He also discovered that the presence of a small amount of impurity was necessary, and that manganese was the best to use. He called attention to the fact that the different colors and duration of phosphorescence might be explained by these impurities. Klatt and Lenard, in 1889, through spectroscopic examination of phosphorescent bodies, found that copper, bismuth, and manganese were active components, and that sodium chloride was also present in most phosphorescent bodies. Micheli, in 1901, and others showed the dependence of phosphorescence on temperature. Bodies which were not phosphorescent at ordinary temperature were phosphorescent at very low temperatures and likewise, bodies phosphorescent at ordinary temperatures lose this property at higher temperatures.

MATERIALS AND APPARATUS.

The materials used in the preparation of phosphorescent zinc sulfide must be pure and preferable soluble in water, and ammonium hydroxide. The zinc chloride used was dissolved in as little water as possible and ammonium hydroxide added until the precipitate first formed is redissolved. The solution then was allowed to stand over night or longer, and the ferric hydroxide was filtered off. This solution was made up to molar strenght with ammonium hydroxide and used as a stock solution. It is absolutely necessary that the iron should be precipitated and filtered off, because even the smallest trace, it was found later on, inhibited phosphorescence. Zinc chloride in sticks, although supposed to be almost iron free, was found to contain very appreciable amounts of iron.

As impurities, the chlorides of the metals were used as they were most readily available and gave comparative results. In the case of the non-metallic elements, the sodium salt was used for the same reason, although sodium itself gives a colored phosphorescence which would tend to cover any effect due to the presence of a non-metallic element.

The solutions of the compounds used as impurities were made up in one-tenth normal strength. Care was taken in each case to have these solutions as free from iron as possible.

The precipitation was carried out by hydrogen sulfide from a Kipp's Generator. The hydrogen sulfide was passed through a train of four bottles, two containing glass wool, and two containing distilled water, in order to wash out any foreign

material, especially suspended particles of iron-bearing vapor which might come over. Ammonium sulfide was used as a precipitating agent, but no advantage could be found in using it, and it had the disadvantage of increasing the chance of contamination by iron.

The precipitate was filtered through ordinary filter paper. Owing to it's rather flocculent state, it filtered very slowly, but this was an added advantage as it thereby was enabled to occlude more of the impurity and also more ammonium chloride. The precipitate should not be washed as washing weakens phosphorescence.

After filtering, the precipitate was removed from the paper, and transferred to a glass or porcelain dish, and then dried at 100-150° C, in an electric oven. It was found that the addition of a little ammonium hydroxide to the dish containing the precipitate before drying had a good effect in making the precipitate more homogeneous.

After drying, the residue was ground up to at least a 100 mesh degree of fineness, in a porcelain mortar. It is necessary to grind it this fine to obtain a uniform product after heating. On several occasions the wet precipitate or the unground residue was heated and a certain degree of phosphorescence was obtained in each case, but the product was not at all uniform. It is imperative that a porcelain spatula be used in each case, where it may be necessary to handle the precipitate, for any contamination of the precipitate with iron from a spatula or other instrument would inhibit phosphorescence.

The powdered residue was heated in a porcelain crucible of ten cubic centimeters capacity. In some cases, the crucible was covered. In others, the cover was left off. The results of the use or ommision of covers will be discussed later on.

EXPERIMENTAL METHODS AND RESULTS

Three methods were studied and tested for their possibilities in the production of phosphorescence. The first, that of Andrews[2], was abandoned because of the difficulty of obtaining any phosphorescence and also on account of the few compounds which could be prepared by that method. The method of Hofman and Ducea[3] was tried next. It gave a very brilliant phosphorescent substance, but it also was limited in it's application to two or three compounds. The method of McDougal, Stewart, and Wright[4] gave promise of being satisfactory, but contrary to expectation, only very slightly phosphorescent compounds were prepared in spite of every precaution taken to insure absolute accuracy of temperature measurements and duration of heating. In this method 10 cc. of a one thousandth normal solution of the substance to be used as impurity is added to 100 cc. of a normal zinc chloride solution in ammonia. The solution is heated to the boiling point, and enough ammonium sulfide is added to precipitate one half of the zinc as zinc sulfide. The solution is then poured into one hundred cubic centimeters of ice water containing one and one half grams of sodium chloride. The precipitate is then filtered off, dried at 100°C., and ground to a sufficient degree of fineness to pass through bolting cloth. It is then placed in a porcelain crucible and heated to about 750°C., for 1/2 to 1 1/2 hours. The resulting substance should then be phosphorescent upon exposure to light after cooling. However, very indifferent results were obtained by this method. The heating was carried

out in an electric muffle where the temperature was regulated very carefully. An objection to this method even if successful is that the occluded zinc chloride and ammonium chloride when volatilized, attack the resistance unites of the muffle, and in a short time destroy them. This method was modified so that instead of using an electric muffle, a common one inch Meeker burner was used. The crucible was covered loosely to prevent too rapid volatilization of the occluded chlorides, and instead of using any arbitrary length of time it was found that heating until practically all of the chlorides were volatilized, invariably gave a result which could be compared satisfactorily with other results. It was found also that hydrogen sulfide could be used instead of ammonium sulfide,, without impairing the value of the results. However, in this case, the method was changed so that instead of boiling the solution before precipitation, one hundred cubic centimeters of ammonium hydroxide were added, and after precipitation the solution was filtered without cooling with ice water. The results obtained by this method are comparative as a variation in the composition or quantity of impurity added will have an appreciable result on the degree or intensity of the phosphorescent product.

The effect of various quantities of impurities was observed by preparing four samples and using respectively, five, ten, twenty, and forty cubic centimeters of N/1000 $MnCl_2$ as impurity. The first three did not show any great difference in the degree of intensity of phosphorescence, but the latter was so strongly phosphorescent as the other three.

Sodium Chloride in the proportion of 1.5 grams to 100 cc. of the zinc chloride solution gave a strongly phosphorescent product, when another impurity was added it covered up the effect of the latter. For instance, $MnCl_2$ gives a yellow to pink phosphorescence, but when the solution contains the above noted amount of NaCl, the color of the phosphorescence is green just the same as if not $MnCl_2$ had been used.

The temperature to which the ground precipitate is heated may be as high as 1300° C., but not lower than 800°C. The heating should be continued until only a thin wisp of $ZnCl_2$ or NH_4Cl is seen arising from the crucible. The color of the phosphorescence will vary with the duration of the heating, varying from a light yellow to a pink for Manganese, and from a very light to a very dark green for copper or molybdenum.

The zinc sulfide may be activated by daylight, electric light, or electric spark between iron electrodes. In exposing the substance to daylight care should be taken not to leave it to die, as it were, and lose all power of phosphorescence. The sulfide changes from yellow or pink or green, or whatever color it had been, to a grayish color which is incapable of being activated. The phosphorescence in compounds should be kept either in the dark or in a diffused light.

, The chlorine ion is not necessary to phosphorescence, but it gives the best results. Cyanides, carbonates, and iron destroy phosphorescence. Fusion of a phosphorescent compound with borax or sodium chloride does not destroy the original phosphorescence. Copper does not increase phosphorescence.

It acts in much the same manner as sodium chloride. The presence of starch in the solution of $ZnCl_2$ is a detriment, as upon heating, it chars and gives a dirty gray product. Colloidal sulfur has no visibly beneficial effect in promoting phosphorescence.

Contrary to the findings of McDougal, Stewart, and Wright, it was discovered that grinding the product in water not only did not materially diminish phosphorescence, but even helped it, insofar as it removed any soluble deliquescent $ZnCl_2$ or other salts from the product leaving it a stable product after drying, and not subject to loss of phosphorescence through extraction of water from the air.

Higher oxidation compounds had no different effect as impurities than lower compounds.

The following table will show the relative intensity of the phosphorescence produced by different impurities, using Class I as the strongest and Class IV as the weakest.

I	II	III	IV
Tungsten	Sodium	Tin	Arsenic
Molybdenum	Potassium	Cadmium	Cobalt
Copper	Magnesium	Antimony	
Manganese	Lithium	Bismuth	
	Strontium		
	Calcium		
	Barium		

No phosphorescence could be obtained by using mercury, silver, nickel, or lead as impurities.

CONCLUSION.

It is evident from a study of the facts in the case, that the phosphorescence of zinc sulfide is dependent on the presence of a small amount of an impurity intimately united with the zinc sulfide. Furthermore, it is dependent on the occlusion of a likewise very small amount of zinc chloride, because if nearly all the zinc chloride is not driven off by heat, the product is not phosphorescent, and also if it is totally expelled by heat, the product is not phosphorescent. From the fact that washing the product did not kill the phosphorescence, we may conclude that the zinc chloride is held on the interior of the crystalline or probably semi-crystalline particles of the product. Evidently, in the presence of light, this zinc chloride sets up a strain and perhaps changes the molecular configuration of the exterior. Then, when the crystal is in the dark, it re-arranges itself giving off light or, on the other hand, by exposing the crystals to strong sunlight, the interior stain set up must wreck the molecular arrangement completely, so that the crystal being unable to resume it's former arrangement, loses the power to phosphoresce.

REFERENCES

1. Handbuch der Spektroscopie.
    H. Kayser.
    Vol. 4, 599-1214.

2. Andrews, W. S.
    Notes on Fluorescence and Phosphorescence.
    Science, 1904,-19,-435.

3. Hofmann and Ducea.
    Zum Kenntnis der phosphorescirenden Stoffe.
    Ber. 1904,-37,-3407.

4. McDougal, Stewart, and Wright.
    Phosphorescent Zinc Sulfide.
    J. O. C. 1917. 3,-663.