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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Red Zinc Oxide¹

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The physical properties of zinc oxide cause it to be classed as a covalence compound with some electrovalence characteristics. It involves tetrahedral bonding and is a semi-conductor. In view of the labile state of the electrons associated with the last mentioned property, it is not surprising to find that the compound, when heated, absorbs energy in the visible region of the spectrum, thus appearing yellow. This is a reversible phenomenon as is well known; the color disappears upon cooling to room temperature. In the present paper will be described a substance which by ordinary standards of analysis would pass for pure zinc oxide and which possesses a permanent² red³ color at room temperature. This color is lost upon heating at 300° and above and it does not return upon cooling. The present report will be concerned chiefly with the methods of preparation, the composition, some of the properties and the possible causes of the color of the material.

Red zinc oxide has been described in a cursory way by some previous workers. The mineral zincite is often found with a red tint and its color has been ascribed to impurities, chiefly manganese and iron.^{3a} Mylius and Fromm⁴ observed the formation of red zinc oxide when the hydrolytic products of an ammoniacal zinc nitrate solution were heated. Kutzelnigg⁵ prepared it by heating mixtures of zinc oxide and ammonium nitrate to the point of deflagration. He suggested that the color might be due to a nitrogen compound since his red zinc oxide con-

tained nitrogen in an "oxidized" form which he reported as 0.25% nitrogen pentoxide.

Preparation

Fusion of Zinc Oxide and Ammonium Nitrate.—Red zinc oxide was prepared for most of our experiments according to the method outlined by Kutzelnigg. The various factors which influence the preparation of the substance by this method were carefully studied in the hope of finding clues that might lead to an explanation of the color. Highly purified white zinc oxide, made by the method of Hüttig⁶ (thermal decomposition of zinc oxalate) and used as a standard of reference throughout this work, was mixed with thrice recrystallized c. p. ammonium nitrate in 25 × 200 mm. Pyrex glass tubes. About 15 g. of the mixture was usually taken. The temperature was raised until a sudden deflagration spattered the contents of the tube up along its walls. The contents of the tube were then washed into a casserole where, by elutriation with successive portions of water totalling two liters, residual ammonium nitrate and white zinc oxide were removed. The fact that red zinc oxide sinks faster than white when in water suspension permitted separation of these two. The yield of red zinc oxide was approximately 50% of the white taken. It is believed that the white zinc oxide, always found admixed with the red, was present because frothing carried some of the mixture up along the walls of the tube where it escaped the final vigorous action which brought on the red color. Some of the original mixtures also probably contained more white zinc oxide than was consumed in the reaction mechanism.

Extensive tests showed that the rate of heating of the original material could be varied within wide limits without detectable influence upon the composition of the red zinc oxide formed. Some experiments involved a uniform rate of heating over a period of two and one-half hours to the point of deflagration, others one and one-half hours, and still others ten minutes. Further, it was found that substitution of c. p. zinc oxide for the highly purified form caused no analytically detectable difference in the final product. Time-heating curves were plotted for the mixtures, using a tube filled with sodium chloride as a control. These were reproducible to within 0.5% as judged by the time required to reach a given temperature. The thermal behavior of the mixtures was thus highly reproducible.

The heating curves usually exhibited a pronounced halt around 100°, which is just above one of the transition temperatures for ammonium nitrate. Evolution of am-

(1) This paper is based on a dissertation presented by Arthur Greenstone in partial fulfillment of the requirements for the degree of Doctor of Philosophy, February, 1942.

(2) Ten years' exposure to ordinary light and atmosphere has produced no change in color. Similarly, two years' exposure to the weather in a paint has produced no change.

(3) The color, as determined by comparison with the Munsell color standards in accordance with the method of Judd and Kelly, *U. S. Bureau of Standards Research Paper 1239*, Vol. 23, Sept., 1939 is, *weak reddish-orange*.

(3a) Dittler, *Z. anorg. allgem. Chem.*, **148**, 332 (1925).

(4) Mylius and Fromm, *ibid.*, **9**, 155 (1895).

(5) Kutzelnigg, *ibid.*, **208**, 23 (1932); **221**, 46 (1934).

(6) Hüttig, *Kolloid Beihefte*, **39**, 286 (1934).

monia began at this temperature, a sign that reaction had begun even though the ammonium nitrate was still considerably below its melting point ($=169^{\circ}$). Another halt occurred at the latter temperature. In the neighborhood of 285° the vapors arising changed from basic to acidic in reaction toward litmus. The exact temperature at which this took place depended upon the original composition of the mixture as did also the temperature of the final deflagration which began with rapid evolution of fumes at $300-315^{\circ}$ and was followed by an abrupt rise in temperature of $30-40^{\circ}$ within ten to fifteen seconds. Copious evolution of fumes and a puff of white smoke marked this last stage of the reaction.

The composition of the starting mixtures influences not only the behavior during heating but also determines the depth of color of the final product. The 2:1 (NH_4NO_3 :ZnO) molar mixture produces the most intensely colored zinc oxide; it also undergoes the most vigorous deflagration and has the highest deflagrating temperature. With molecular ratios higher or lower than 2:1 the color of the product is less in proportion to the deviation from this ratio, *e. g.*, the 9:1 and 1:3 products are feebly pink. The 1:2 and 1:3 mixtures produce no deflagration, yet they yield a slightly colored oxide. Red zinc oxide made from the 2:1 mixture was used as a standard in the experiments to be described below. It is the most deeply colored oxide the authors have been able to make by any method.

Although the foregoing procedure describes a distinctly batch method of preparation, a continuous method based on the same reactions could be devised without difficulty.

Fusion of Zinc Oxide with Other Ammonium Salts or Analogous Compounds.—The technique employed in making red zinc oxide from zinc oxide-ammonium nitrate fusions (above) was applied to other ammonium and related nitrogen compounds with the results shown below. In each series the molar ratios ran in integral steps from 9:1 to 1:2 for the materials in the order given. In no case did the depth of coloration approach that found for the 2:1 NH_4NO_3 :ZnO mixture above; consequently these series were considered separately although the mechanism

$(\text{NH}_4)_2\text{SO}_4 + \text{ZnO}$	slight local coloration in the 1:1 and 1:2 mixtures only
$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 + \text{ZnO}$	all mixtures produce pink residues but these are soon discolored because of charring
$(\text{NH}_4)_2\text{CO}_3 + \text{ZnO}$	reddish residues produced in all cases; strongest coloration resulted from 1:2 mixture
$\text{NH}_4\text{Cl} + \text{ZnO}$	scattered red-brown patches in 2:1, 1:1, and 1:2 mixtures only
$\text{NH}_4\text{ClO}_3 + \text{ZnO}$	all mixtures produced residues that were sulfur-yellow when hot and white when cold
$\text{NH}_4\text{NO}_3 + \text{ZnCO}_3$	all residues colored pink
$\text{NH}_4\text{NO}_3 + \text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$	all residues colored pink
$(\text{NH}_4)_2\text{CO}_3 + \text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$	all residues colored pink; prolonged heating causes charring
$(\text{NH}_4)_2\text{SO}_4 + \text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$	no red coloration in any mixture
Acetamide + ZnO	no red coloration in any mixture
Urea + ZnO	pink colored residues in the 1:1 and 1:2 mixtures only

of these reactions may be rather similar to that of ammonium nitrate and zinc oxide.

In general, the deepest colorations, and, presumably, the greatest amounts of red zinc oxide, are formed when there are present, or readily formed in the reaction mixture, zinc oxide and ammonia.

Electrolysis of Fused Zinc Nitrate.—Lorenz⁷ prepared colored dispersions of metals in fused salts by electrolysis. The authors applied this technique to molten zinc nitrate, using zinc electrodes and a potential of approximately 10 volts. During the electrolysis the nitrate was gradually changed to oxide with evolution of oxides of nitrogen. The resultant decrease in fluidity ultimately made it impossible to keep the mixture molten. When the mixture encrusting the electrodes was removed, a red layer was found close to the anode and a yellowish one around the cathode. Attempts to collect and analyze the red material, which was probably zinc oxide, were abandoned when it was found impossible to remove from it small particles of zinc that had been dislodged from the electrode.

Exposure of Zinc Oxide to Zinc Vapor.—Rock salt and other alkali halides have been colored by exposure to alkali metal vapors.⁸ Numerous attempts by the authors to produce coloration in zinc oxide by heating it with zinc in sealed and evacuated tubes were unsuccessful. Heating zinc, covered with zinc oxide, in a covered 30-ml. porcelain crucible over a Meker burner for fifteen minutes resulted in the disappearance of the zinc and the formation of a thin layer of red zinc oxide on the surface of the white. More intensely colored material resulted when a zinc arc was struck under a cover of zinc oxide. This compared favorably in depth of color with the standard red zinc oxide mentioned above.

Composition

Chemical Analysis.—These analyses were performed on all samples of red zinc oxide (all molar ratios of NH_4NO_3 :ZnO) made from the nitrate. The results were so nearly identical that only those found for the 2:1 ratio, which yields the most deeply colored oxide, will be reproduced here (Table I). Since the work by Kutzelnigg had shown that nitrate and nitrite were present in red zinc oxide our efforts were laid in the direction of determining zinc, nitrate and nitrite as accurately as possible. The method employed initially for zinc was that of Lundell and Bee.⁹ Although its results were excellent, we turned to the volumetric modification of this method by Jamieson¹⁰ because of its greater speed. Nitrate was determined by the method of Pfeilsticker.¹¹ Nitrite was estimated in accordance with the method used in water analysis by the A. O. A. C.¹² The loss in weight of the zinc oxide on ignition was also determined. This treatment results in the destruction of both nitrate and nitrite. An examination of the table shows that the total composition always comes within 0.1% of the theoretical. The

(7) Lorenz, *Z. physik. Chem.*, **76**, 732 (1911).

(8) Rögner, *Ann. Physik*, **29**, 386 (1937).

(9) Lundell and Bee, *Trans. Am. Inst. Metals*, **8**, 146 (1914).

(10) Jamieson, *THIS JOURNAL*, **40**, 1036 (1918).

(11) Pfeilsticker, *Z. anal. Chem.*, **89**, 1 (1932).

(12) "Methods of Analysis of the Association of Official Agricultural Chemists," 3rd edition, 1930, p. 405.

TABLE I
COMPOSITION OF RED ZINC OXIDE MADE FROM THE 2:1
MIXTURE OF AMMONIUM NITRATE AND ZINC OXIDE

	Zn, %	ZnO, ^a %	N ₂ O ₅ , ^b %	Loss on ignition, %	Sum of compo- nents, %
A ^c	80.22, 80.18; 80.20 Av.	99.81	0.19	0.12	100.02
B	80.27, 80.19, 80.22; 80.23 Av.	99.85	0.16	0.15	100.03
C	80.17, 80.24; 80.21 Av.	99.82	0.13	0.15	99.99
	80.22 (Oct., 1936)	99.84	0.14	0.12	100.00
	80.23 (April, 1937)	99.85	0.12	0.13	99.99
	80.20 (Jan., 1938)	99.81	0.15	0.13	99.98
	80.21 (Dec., 1938)	99.82	0.13	0.13	99.97

^a Since it is shown below that there is 0.02% free zinc in the red zinc oxide, a correction has been made for this in calculating % ZnO from % Zn. ^b The percentage of nitrite nitrogen as N₂O₅ was 0.003 for all samples of the red zinc oxide made from the 2:1 mixture. ^c The letters A and B stand for red zinc oxides made by the method of slow heating, a period of two and one-half hours for A and one and one-half hours for B. The letter C stands for the rapid method of ten minutes.

sum involves zinc oxide, free zinc, nitric anhydride and nitrous anhydride. There is close concordance between the % N₂O₅ found colorimetrically and the % loss on ignition.

Determination of Excess Zinc by Distillation.—Since color in otherwise colorless materials has sometimes been ascribed to impurities in the form of free colloidal metal or to excess positive ions associated with *F*¹³ centers, the authors attempted to distill some such excess zinc out of red zinc oxide. By using pure white zinc oxide (Hüttig) as a control it was found that a metallic distillate was obtained from red zinc oxide at 335° and 6×10^{-3} mm. pressure while none was produced from the white. Distillation from a 4-g. sample was complete in four hours, the red oxide becoming practically colorless. The weight of the distilled zinc was found with a microbalance, and, after solution in acid, the zinc was also determined quantitatively by the method of Lott.¹⁴ This showed the distillate to be $99.6 \pm 0.5\%$ Zn for a series of fourteen samples obtained from red zinc oxides over a period of two years. These distillates demonstrate that the amount of excess zinc in red zinc oxide is $0.019 \pm 0.002\%$. During the distillations, while zinc condensed at one point, a white solid was obtained at another. Upon analysis this turned out to be N₂O₅ to the extent of 0.09% of the original sample. This may be compared with *ca.* 0.13% obtained by direct analysis (Table I).

Determination of Excess Zinc by Reaction with Standard Dichromate and Permanganate.—Eighteen samples of red zinc oxide, made both by the rapid and slow methods and from various source materials over a period of four years, were examined for reducing power by means of standardized dichromate or permanganate solutions. Correction was made for the reducing action of the nitrite present in the original samples. The remaining reducing qualities were ascribed to "free" zinc where this term was taken to mean either metallic zinc or excess zinc

associated with *F* centers. According to the determination with dichromate, the amount of free zinc in red zinc oxide was $0.0228 \pm 0.0001\%$. With the permanganate it was $0.0265 \pm 0.0007\%$. These results are in good agreement with that obtained in the distillation experiments.

Determination of Excess Zinc by Reaction with Bromobenzene.—The plan followed depends upon the fact that the reaction between a metal and a halogen substituted organic compound ultimately transforms the halogen to the ionic form. Bromobenzene was used for our purpose because of its stability to hydrolysis. Three samples of zinc oxide were refluxed in this liquid (b. p. 156°) for 1800 hours; one sample was standard red zinc oxide, another was white zinc oxide that had been heated over a blast lamp, the third was a sample of red zinc oxide that had been heated over a blast lamp for one hour until practically all of its color was gone. After refluxing, the bromobenzene from each run was filtered and divided into two parts. One part was evaporated to dryness and the residue taken up with water, the other was extracted five times with an equal volume of water acidified with nitric acid. Both extracts were tested for bromide ion. The results with white zinc oxide were negative, with the red that had been heated, doubtful. Bromide ion was estimated nephelometrically in the samples from the standard red zinc oxide and, on the assumption that two moles of bromobenzene react with one atom of the metal, the analyses showed the oxide to contain 0.011% free zinc. This is in reasonable accord with the results obtained by the methods already mentioned.

X-Ray Diffraction Analysis of Red Zinc Oxide.—X-ray analysis gives information with respect to phases present, solid solution, lattice deformation and imperfections, and particle size. Any of these could conceivably give rise to color. In consequence, samples of standard white and red zinc oxides were subjected to a diffraction analysis using Cu K_α radiation and Bohlin-type¹⁵ focusing cameras. No evidence of any phase other than the hexagonal zinc oxide was found. The *a*₀ values (*c*₁/*a*₀ = 1.609) calculated from the highest sin²θ reflections were: $3.243 \pm 0.007 \text{ \AA.}$ for the white oxide and $3.244 \pm 0.007 \text{ \AA.}$ for the red. There was complete correspondence also in the relative intensities and sharpness of the lines over the whole range of diffraction angles. This analysis suggests that any differences existing between the white and red zinc oxides along the lines mentioned at the head of this paragraph are of such magnitude as would not permit their detection with the X-ray apparatus at hand.

Properties

Color Value (Depth) as a Function of Excess Zinc in Red Zinc Oxide.—Any hypothesis attempting to ascribe the color of red zinc oxide to its free zinc or *F* center content would necessarily look for support to the relationship, if any, between depth of color and excess zinc. Table II arranges several different samples of red zinc oxide in decreasing order of color value. In juxtaposition is given the molar ratio of NH₄NO₃:ZnO used in preparing the sample and the percentage of excess zinc found in it. An

(13) de Boer, *Rec. trav. chim.*, **56**, 301 (1937).

(14) Lott, *Ind. Eng. Chem., Anal. Ed.*, **10**, 335 (1938).

(15) Westgren, *Trans. Inst. Min. Met. Eng., Inst. of Metals Division*, p. 13 (1931).

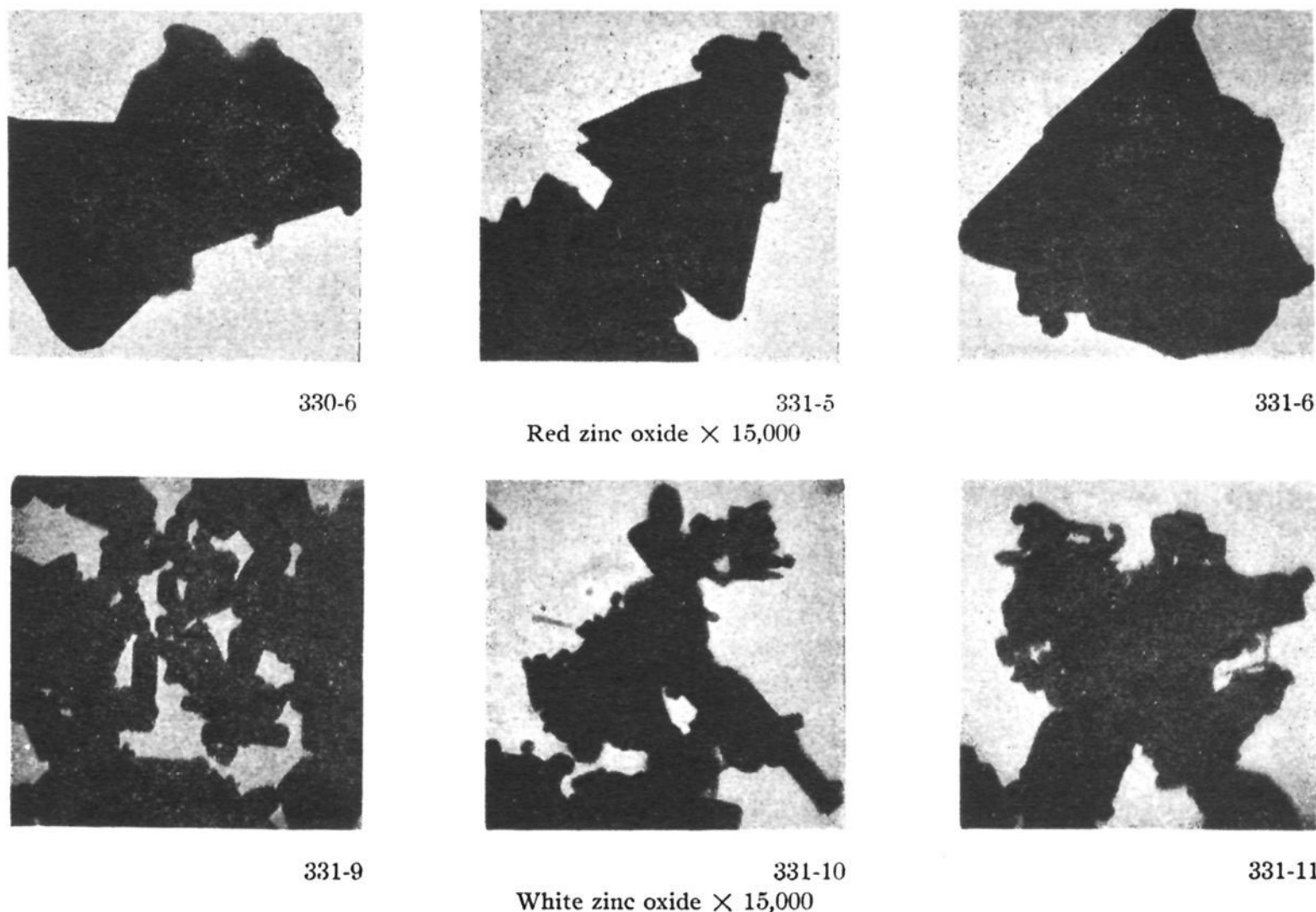


Fig. 1.—Electron microscope photographs of red and white zinc oxides.

unmistakable parallelism is seen between the first and last columns.

TABLE II
VARIATION OF COLOR WITH EXCESS ZINC IN RED ZINC OXIDE

Color value (1 > 2 > 3)	Mole ratio NH ₄ NO ₃ : ZnO	Excess zinc, %
1	2:1	0.022
2	3:1	0.016
3	2:1 ^a	0.011
4	7:1	0.005
5	1:2	<0.001

^a After refluxing with bromobenzene for 1800 hours.

Particle Size and Distribution.—Figure 1 shows electron microscope photographs¹⁶ of our standard white and red zinc oxides. The average particle size of the white is about 5×10^{-5} cm. whereas that of the red is about 10^{-4} cm. The lack of small particles in the sample of red oxide is due, at least in part, to the process of elutriation whereby it is separated from white zinc oxide during its preparation. Nothing in this study nor in any other microscopic studies we have made throws any light on the question of the distribution of color in or on the particles of red zinc oxide. We infer that the color is distributed uniformly throughout the particle because of the slow and progressive way in which the reducing action manifests itself (see under *Composition* above).

(16) The authors are indebted to Mr. A. L. Schoen of the Eastman Kodak Research Laboratories for these photographs.

Density.—The densities of red and white zinc oxides were determined pycnometrically with xylene. The sizes of the particles in the powder samples used lay between 200 and 325 mesh. Each density value given in Table III is for a different sample of oxide. The red oxides were made from the standard 2:1 mixture. It is obvious that, within the error limits of the method, there is no difference in the densities of red and white zinc oxides.

TABLE III
DENSITIES OF WHITE AND RED ZINC OXIDES AT 25° IN g./ml.

White ZnO (Hüttig)	Red zinc oxide		
	Series A ^a	Series B ^b	Rapid method ^c
5.64	5.65	5.63	5.66
5.66	5.67	5.65	5.67
5.65	5.66	5.65	5.64
5.67	5.64	5.66	5.63

^a Slow heating (two and one-half hours) to the point of deflagration. ^b Slow heating (one and one-half hours) to the point of deflagration. ^c Ten-minute heating period, room temperature to point of deflagration.

Comparative Solubilities of Red and White Zinc Oxides in Dilute Alkali.—In our early work with red zinc oxide we supposed that its color might be due to lattice imperfections. The latter had been shown to be accompanied by increase in solubility.¹⁷ For this reason we

(17) Fricke and Ackermann, *Z. anorg. allgem. Chem.*, **214**, 182 (1933).

measured the solubility of the standard red and white forms in dilute alkali (0.1357 *N* KOH) at 25°. The determinations were carried out in glass bottles coated on the inside with "Thermoseal"¹⁸ which was shown to be unaffected by alkali of the concentration here used. Zinc oxide remained the solid phase throughout these determinations as was shown by the wet residue method. Although Lott's¹⁴ method was used to check the progress of the solubility experiments, the more accurate method of Vosburgh¹⁹ (0.1%) was adopted for the final determinations. The solubilities of the red and white zinc oxides were found to be identical within the limits of error. It might be inferred from this that the two oxides have the same degree of lattice perfection and, therefore, the color of the red cannot be attributed to unusual irregularities in the lattice.

Photoconductance of Red and White Zinc Oxides.—Theoretically both forms of the oxide should show an increase in conductance when illuminated in the ultra-violet with frequencies that are strongly absorbed. Similarly, the red form should show enhanced conductance when irradiated with visible light of the frequency required to excite the *F* centers should they exist. Our experiments have been by no means thorough-going along these lines, but the results thus far obtained will be given nevertheless and their significance and the questions they raise will be discussed below.

The apparatus employed was that described by DuBridge and Brown²⁰ with modifications. Standard red and white zinc oxides were used and each had received a thermal treatment at 115° for eighteen hours. The powders were compressed between nickel electrodes in a vertical quartz tube of 21.3 sq. mm. internal cross-section. The pressure applied was that of a 1-kg. weight upon the upper electrode. The conductances of the red and the white oxides, in the dark or under room illumination, were of the same order of magnitude: 0.8×10^{14} mhos/cm. for the red and 1.1×10^{14} for the white. The average deviation of the readings from the mean was 10%. The conductance of the white oxide increased about ten thousandfold when exposed to the radiation from a quartz mercury arc whereas the red oxide showed only a fifty to one hundredfold increase. These changes were reversible and reproducible at will. Additional experiments with the white oxide alone showed that its conductance increased in a similar manner whether it was irradiated with the full mercury arc, with the frequencies less than 3000 Å., with white light, with white light >4360 Å., or with various ranges in the visible spectrum selected by filters. The range of frequencies to which the white oxide responded, as well as the magnitude of the response as compared to the red, was somewhat unexpected. Experiments designed to map the absorption spectrum of red zinc oxide, in order that its photoconductance might be effectively studied, have thus far been unsuccessful because of the marked scattering of the material. Further work along this line has been suspended because of other duties.

(18) This was supplied through the courtesy of the B. F. Goodrich Rubber Co., Akron, Ohio.

(19) Vosburgh, *et al.*, *Ind. Eng. Chem., Anal. Ed.*, **10**, 393 (1938).

(20) See Strong's "Procedures in Experimental Physics," Prentice-Hall, New York, N. Y., 1939, p. 418.

Discussion

It should be mentioned at the outset that Kutzelnigg's⁵ suggestion of a possible connection between the red color of zinc oxide and its nitrogen oxide content has not been supported by our experiments. Red zinc oxide was prepared in a number of ways involving no nitrogen compounds; it has even been prepared in the absence of the nitrogen of the air.²¹

All the methods of preparation of red zinc oxide suggested in this article, and others the authors have not mentioned, bring together zinc oxide and zinc, the latter either supplied as such or produced by electrolytic or chemical reduction. It may, therefore, be inferred that the coloration of the oxide is due to the presence of excess zinc. This extra zinc could produce color in one of two ways, either as colloidal particles or by creating *F* centers. In the present case the *F* centers would presumably be formed by a mechanism similar to that involved in the production of colored alkali halides by suspending them in alkali metal vapor. A slight alteration of the mechanism would also be sufficient to explain how colloidal particles might arise.

The experimental data available at the moment are not sufficient to permit a positive choice between these two hypotheses for color formation. The authors, however, incline toward one of them and it is for that reason that the several factors concerning each hypothesis are brought together for comparison in the following paragraphs.

There is no positive evidence for or against the hypothesis that colloidal particles of zinc are the cause of color in red zinc oxide. The idea should not be discarded, and should be further tested, for there are certain facts about the preparation and properties of red zinc oxide that are unlike those usually associated with substances containing *F* centers. These will be mentioned below.

In support of the *F* center hypothesis stand the several methods of preparation of red zinc oxide in which the white oxide was exposed to zinc vapor. It is easier to believe that this process leads to an atomic dispersion of zinc (as ions associated with *F* centers) than to a colloidal one. Also in support of *F* centers is the fact that the hue of the red zinc oxides is remarkably constant, almost independent of the method of preparation. The colors differ principally in value, *i. e.*, depth of

(21) Seacherl, *Coll. of Czechoslovak Chem. Comm.*, **10**, 223 (1938).

coloration. It is unlikely that this consistency in hue would arise through colloidal particles, for it would bespeak a similar distribution of particle size irrespective of the method of preparation. Still another line of reasoning which favors F centers is this: Colloidal particles of the dimensions generally required to produce red-colored sols (*ca.* 10^{-6} cm.) would lead to manifold structural defects when distributed in the grains of a powder whose particles were, on the average, 10^{-4} cm. in size. No such structural defects have been noted in our X-ray diffraction measurements.

It may be mentioned in passing that the fading of the color of red zinc oxide upon heating to 300° and above receives an explanation under either hypothesis. If the color is due to finely divided zinc, then decolorization should accompany heating because of the increased rate of diffusion of free zinc out of the oxide. If this happens in air, then the diffusion of oxygen into the zinc oxide may also contribute to the elimination of the free zinc. According to F center theory, an increase in the temperature of red zinc oxide, with the consequent increase in energy of the electrons constituting the F centers, should ultimately liberate the electrons trapped in the latter. This process is not reversed upon cooling because the conditions which originally led to F center formation no longer prevail.

There remain to be pointed out a number of facts which cannot, at present, be reconciled with the F center hypothesis. Firstly, the fact that red zinc oxide does not seem to fade upon standing nor when subjected to any sort of radiation. Also it apparently cannot be prepared by subjecting white zinc oxide to radiation (we have used the quartz mercury arc and the iron arc).²² Secondly, the remarkably slight increase

(22) Tafel, *Ann. Physik*, **11**, 613 (1903), observed that a stream of electrons caused zinc oxide to become colored. Our experiments in this direction have been inconclusive.

in conductance in red zinc oxide when illuminated in the region of the spectrum in which white zinc oxide exhibits strong photoconductance. If the color were due to F centers, one would expect an equal or greater photoconductance in the red oxide. It is possible that this anomalous effect is associated with particle size or with surface films on the oxides. Thirdly, the fact that Pohl's²³ method of producing color in alkali halides (by electron transfer from the cathode in conductance experiments) failed in our hands when applied to zinc oxide either as powder or single crystal.

The foregoing discussion leaves the matter of the cause of color in red zinc oxide unsettled. For the reasons given, the authors are inclined to favor the F center hypothesis as being more likely to lead to fruitful results in further experimentation to settle this question.

Summary

1. A report is made on several modes of preparation of a red-colored zinc oxide. The most generally suitable method is to heat white zinc oxide with ammonium nitrate.
2. The results of chemical and X-ray diffraction analyses of red zinc oxides lead to the conclusion that their common characteristic is an excess of zinc, of the order of 0.02%.
3. The following physical properties of red zinc oxide were measured: color values, particle size, density, solubility in dilute alkali, and photoconductance.
4. The possible causes of color in zinc oxide are discussed. The authors favor the F center hypothesis although no positive evidence for it is at hand.

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(23) Pohl, *Z. Metallkunde*, **26**, 217 (1934).