

ZINC OXIDE

Properties and Applications

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COVER NOTE:

Zinc oxide is produced in a variety of special grades to meet the requirements of a broad range of applications. Particle size may range from fine to coarse and particle shape from nodular to acicular. Of the acicular types, the experimental fourlings variation is illustrated on the cover, as photographed through an electron microscope.

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*To avoid duplication, this listing does not include the references cited in the text.

**The many papers and several patents on zinc oxide by Bell Telephone Laboratories over the past 20 years are listed together here because of their importance. They provide many significant contributions concerning the properties of zinc oxide. Many of the papers are already established as landmarks in their particular disciplines.

This collection illustrates how one institution persevered in its investigation of zinc oxide and discovered unexpected properties.

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Chapter Six

APPLICATIONS OF ZINC OXIDE

ADHESIVES, MASTICS, SEALANTS

The versatility of zinc oxide and its derivatives is evident in the complex fields of adhesives, mastics, and sealants, which comprise a variety of compositions to meet the requirements of many types of applications. Certain of the properties contributed by zinc oxide and its compounds are:

Adhesiveness	Setting time	Heat stability
Tack	Shelf-life	Fire resistance
Tack retention	Suspension	Water resistance

Zinc oxide and its compounds perform the following functions in adhesives, mastics, and sealants:

- a. Setting the binder
 - Curing
 - Crosslinking
 - Catalysis
 - Resin formation
- b. Reinforcement of the binder
 - Structure-bonding of the zinc oxide
- c. Reactivity with other ingredients of the compositions
 - Formation of zinc compounds



Fig. 6-1. Electronic devices of ferrite (nickel-zinc-iron oxide compound) are more efficient than similar parts based on iron. (Photo-Indiana General Corp.)

In adhesives, mastics, and sealants, a variety of elastomers, resins, latexes, and other materials are utilized as major binders. Zinc oxide and its derivatives are compatible with many of those binders. Judging from the patent references (below), zinc compounds contribute significantly to the properties of the resulting compositions. The following examples are classified into two types of compositions:

(a) New types in which zinc oxide is an essential component and (b) improved compositions in which zinc or its derivatives are specified.

a. New types of compositions in which zinc oxide is an essential component:

- Conventional polysulfide adhesives were marketed as a two-package system, to keep separate the polymer and the curing agent (PbO_2). Allied Chemical¹ found that by compounding polysulfide with 2-17% zinc oxide and 10-25% carbon black it could be marketed as a one-package system.

- To avoid cold flow in maleic anhydride ester adhesives, Johnson — Johnson⁴ used to advantage the pronounced crosslinking properties of zinc oxide which are utilized extensively in the vulcanization of rubber compounds. Incorporation of 40-50% zinc oxide in the maleic anhydride adhesives developed structure-forming crosslinks by reacting with available carboxyl groups. The resulting adhesives retained their tack properties over the 10-month test period at 120°C.
- North American Rockwell⁷ developed a single-package system for neoprene cements by eliminating sulfur and conventional accelerators and using only ZnO and MgO. Example: 1600 parts Neoprene W, 80 parts ZnO, 64 parts MgO and >50% toluene. The product, suitable for application to many substrates, provides longer shelf-life and better adhesive strength than the sulfur-containing type.
- In ammonium solutions zinc oxide reacts to form zinc-ammonium complex ions and salts with higher solubility, depending upon the pH of the solution. Rohm & Haas¹⁰ utilized some of those properties of zinc oxide in the development of a special release coating. The latter consists of a mixture of zinc oxide and polymer dispersions. One of the two polymers is an ammonium salt of methyl methacrylate.
- Tervakaski Oy¹⁵, Finland, utilized the favorable dielectric properties of fine particle size zinc oxide in the development of an adhesive for condenser insulation. The product, consisting of methyl cellulose 100 and zinc oxide 200 (average particle size 0.74 μ m), retained a charge of 5,400 volts at 50 Hz compared with 2,425 volts without zinc oxide.

b. Improved compositions in which zinc oxide or its derivatives are specified:

- The reactivity of zinc oxide with H₃PO₄-epoxide mixtures forms an antisetling additive for caulking compositions, according to a Lubrizol patent⁶.
- Neoprene adhesives are improved by the addition of both phenolic resins and zinc compounds, the reaction products imparting special properties such as high heat resistance, high bond strength, improved peel and shear-stress resistance, and stability to settling of neoprene solution adhesives. The zinc compounds specified: zinc dibutyldithio carbamate for antisetling², zinc resinate and zinc oxide for high cohesive strength and good contact properties when bonding Formica to wood⁸, zinc resinate and zinc oxide for improved adhesion at 120°C^{11,12}.

- Zinc oxide has long been a major constituent of surgical and industrial tapes based on natural or synthetic rubber as it is outstanding in retention of tack during shelf-aging. Examples of the composition of such adhesives, based on recent patents, are as follows:

1. Natural rubber 17, polyisobutylene 17, polyterpene resin 26, polybutylene 3, zinc oxide 28.5, starch 8, and antioxidant 0.5 parts. To this mixture add zinc dibutyldithiocarbamate and zinc 2-mercaptobenzo-thiazole¹³.

2. Pale crepe 23, polyisoprene 65, styrene-isoprene 28, zinc oxide 95, starch 24, lanolin 5, and antioxidant 1 part. Add tackifiers¹⁴.

3. Natural rubber 34, zinc oxide 10, wool fat 6, mineral oil 2 parts. Add resins.³ This adhesive is for tape used at low temperatures.

- Zinc oxide is also specified in various adhesives based on synthetic polymers. Kuraray⁵ reported improved adhesive strength and water resistance on addition of zinc oxide and diisocyanate adduct to an ABS copolymer latex. Prodesco⁹ noted good shelf-life and fire resistance of carpet-backing adhesive compositions based on a methacrylate latex, zinc oxide and dodecylsuccinic anhydride.
- The U.S. Department of Agriculture¹⁶ has been granted a patent entitled, "Mastic adhesive compositions containing a zinc salt of a formaldehyde-modified rosin." It utilizes the reactivity of zinc oxide with rosin to form an adhesive with strong adherence to plywood surfaces. Preparation: Heat gum rosin with paraformaldehyde and zinc oxide. Dissolve in toluene-hexane with SBR rubber, clay, and asbestos fiber.

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AGRICULTURE

Zinc in Plants

Zinc plays a necessary role in the cultivation of major farm crops and in the feeding of various farm animals. As a constituent of several metalloenzymes, zinc catalyzes a number of vital biological processes, including metabolism and respiration.

Zinc was proved essential to plant life in 1926. It was successfully applied to field and vegetable crops in Florida in 1927 and to tung in Texas and citrus in California in 1932. Later, considerable impetus was given to the use of zinc as a crop nutrient when its supplementation was found to increase the yields of corn in several major producing states. In some western states, zinc is now regarded as second in importance only to nitrogen as a nutrient.

Unlike the major nutrients ordinarily supplied in mixed fertilizers, zinc is required in only infinitesimal amounts. For example, an acre of healthy oats contains only about one ounce of zinc. Yet without that essential ounce, there would be no crop.

Because of the small amounts needed by crops, zinc is classed as a micronutrient. Even though that element is required in only minute traces, many soils do not supply it in sufficient quantity for healthy growth and high yield of crops. Treatment of such soils with a few pounds of zinc an acre frequently restores fertility.

Although the exact function of zinc in plants is not completely understood, it appears to play an important role in enzyme systems which regulate plant growth. In recent years zinc has been found to be an essential component of a variety of metalloenzymes in plants. A number of these show such sensitivity to zinc deficiency that metabolism can be strongly and specifically affected²¹.

Zinc deficiency in crops is a worldwide problem. Deficiency of zinc and other micronutrients is increasing because of increased use of chemical fertilizers, the rise in crop yields, increased cultivation of marginal land, and decreased use of animal manures. In the United States, zinc deficiency of one or more crops occurs in more than 40 states at the present time. At least eight states suffer deficiency on large acreage and often on more than one crop. Although zinc treatment was used on citrus crops and vegetables in Florida half a century ago, only in recent years has the need for zinc supplementation been recognized in corn, beans, and other major field crops.

Soil applications of zinc are by far the most common and generally successful method of application for a number of crops. Comparison of the effectiveness of soil applications of zinc involves many factors such as source of the element (type of zinc compound), type and condition of soil, and modifications of soil chemical properties.

Classification of soils by a zinc availability index, for example, has been developed by Alley et al.¹. The use of

EDTA, they found, is the most effective means for selective extraction of available zinc. The clay content of soil can significantly reduce the availability of zinc, Keefer, et al.,¹² observed. In a study of the fate of isotope ⁶⁵Zn applied to soils as ZnSO₄ and Zn-EDTA, they established that zinc can adhere to clay in soil so strongly that it is not available for plant use. Chemicals in soil can markedly affect zinc availability, favorably as well as adversely, according to Lindsay, et al.¹⁶. With zinc applied in two forms of chelates, EDTA and DTPA, they studied the equilibrium relations of zinc with ferric, calcium and hydrogen ions. Lindsay¹⁷ has recently covered many aspects of zinc in soils and its effects on plant nutrition in a comprehensive review, including 186 references, on this extensive subject.

In the following pages, accordingly, the abstracts of papers on the use of zinc to aid plant nutrition will be limited to a single major crop, corn. The papers will cover the period 1965-1974; patents will cover the years 1960 to 1974. References to all other papers over the past 20 years will be found in Further References.

Zinc in Corn

Papers (1965-74)

Investigators report progress in their efforts to identify and offset the factors limiting the full availability of zinc plant nutrition. Granulation, Brown, et al.,⁴ noted, markedly reduced the effectiveness of ZnSO₄, Zn(NH₄)PO₄ and a Zn polyflavonoid on sweet corn, but ZnEDTA was not affected. In the absence of granulation, ZnSO₄ and ZnEDTA provided equal response to sweet corn. Such factors as light intensity, temperature and phosphorus content of soil can seriously affect the uptake and translocation of zinc by corn seedlings, Edwards⁵ reported. Of these three, phosphorus is the only one subject to control, but it continues to present serious problems for availability of zinc. Several investigators have reported on the adverse effects of phosphorus, so far as the uptake of zinc is concerned: Giordano, et al.,⁷ Keefer, et al.,¹³ Langin, et al.,¹⁴ Penas,²⁰ and Stukenholtz, et al.²⁴.

In a series of studies on zinc fertilization of corn, pea beans, sugar beets and potatoes, the Michigan Experimental Agricultural Station^{3,11,25} found various zinc compounds effective on those crops. ZnO, ZnSO₄ and ZnEDTA produced high response, but slag and ZnSO₄·(NH₄)₂SO₄ were inferior as sources of Zn. Residual effects of Zn were reported to last at least three years.

Relative effectiveness of various sources of Zn for corn is dependent on many factors. Schnappinger, et al.,²² noted that ZnSO₄ was more effective than ZnEDTA on Litz silt loam soil, but ZnEDTA was superior on a Westmoreland silty loam clay soil. On the latter, more than 13.6 kg Zn/ha as broadcast ZnSO₄ was required to correct the Zn deficiency

of corn. In another comparison of soils, Hoeft, et al.,¹⁰ observed that a Zn frit-CSP mixture in comparison with ZnSO₄ was less effective on a calcareous sandy loam but equal to ZnSO₄ on a neutral soil. In both field and growth chamber studies in Kansas, Gallagher⁶ compared the effectiveness of ZnO and ZnSO₄ as a source of Zn for corn when applied as a coating on AOP, APP and CSP. Equal levels of Zn were found in plants receiving applications of these forms of Zn.

The relative efficiency of several zinc sources for corn was reported by Shukla²³, in studies based on Norfolk soil. ZnO and ZnSO₄ proved equal or superior to Zn chelate or Zn (polyflavonoid) in increasing the Zn content and uptake of corn on the basis of the Zn contents applied. Zn (polyflavonoid) was the least effective. Liming and high P fertilization were highly instrumental in decreasing Zn uptake of corn.

In pot culture studies with Dinuba fine sandy loam, a Zn-deficient soil, Wallace, et al.,²⁶ investigated the effect of various Zn sources. The tests revealed that the chelates were superior to ZnSO₄ in Zn uptake of Golden Bantam corn, but high levels of the chelates (EDTA and NTA) decreased the levels of Fe, Mn, and Ni in the plants.

Berzina of Russia² has taken a step beyond uptake studies and has investigated biological effects of micronutrients. He reported that Zn enhanced the ascorbic acid content in corn leaves, and Cu increased the protein content in corn grain.

The effects of weather conditions as well as types of soil have been the subject of investigation. Lindsay, et al.,¹⁵ have reported that soil incubation temperatures are directly related to availability of indigenous zinc. Placement of the Zn compounds is another factor for consideration, whether broadcast, band, drills, or foliar applications. Hibberd⁹, for example, reported that the application of ZnO or ZnSO₄ in drills near the seed was especially effective in overcoming Zn deficiency in irrigated maize grown on black earth soil at Darling Downs, Queensland. Dusting or pelleting the seed with ZnO was also effective.

The availability to corn of Zn applied with various macronutrient fertilizers is the subject of several papers by Giordano and Mortvedt of TVA^{8,18,19}. Their tests, conducted in greenhouse pots, revealed that the effectiveness of inorganic Zn is low when applied as a mixture with NH₃ fertilizers. ZnO and ZnSO₄ were more effective in their tests when applied to soil. NH₄NO₃ in particular was an inferior carrier for ZnO when the latter was pressure-granulated with the nitrate.

Patents—1960-74

The following patent abstracts are not limited to the use of zinc oxide and its derivatives for application to corn acreage; they cover all types of crops unless otherwise specified.

Zinc compounds can be applied as coatings on fertilizer granules to prevent caking, form a hydrophobic surface, or other improvement. American Cyanamid²⁷ developed a

free-flowing, non-caking fertilizer by moistening the granules with ZnCl₂ solution, adding powdered ZnSO₄, and heating to dryness. The product contained 10-15% Zn, distributed more uniformly than by mixing of the constituents.

TVA^{33,34} covered by patent a method of coating granular fertilizers with a moisture-resistant coating. Example: A mixture of NH₄NO₃ with 10% ZnO is reacted to form Zn₅NH₄(NO₃)₂(OH)₉·3H₂O, which is a moisture-resistant coating.

To prevent the blowing away of Zineb and other agents against plant pathogens, Dorst²⁹ developed adhesives for addition to such agents. The adhesives are soluble in water but become insoluble on evaporation of the water. Of the several types covered in the patent, one is a complex of NH₃ and a Zn compound.

Dow³⁰ has covered by patent a series of plant-growth regulators based on carbamate-alkanolamine complexes with metallic elements such as Zn, Fe, Mn, Ni, Co, or Cu. The most effective of these complexes contained at least 30 mole % Zn. These products serve two functions inasmuch as they inhibit the growth of lower plant forms such as fungi while increasing the growth of higher plants.

Zinc compounds are also prominent constituents in complexes for more effective uptake by plants. Chemische Werke Albert²⁸ developed such complexes based on Fe, Zn, Cu, or Mn. They are water-soluble but yield no ions in solution. A typical product consists of Na-Metal-NH₄ complexes of straight-chain condensed phosphoric acids containing at least 3 P atoms/mole.

For control of iron chlorosis and for improving alkaline soils, Geigy³¹ patented the preparation of chelates, those of Fe, Mn, Zn, and Co, in particular.

Texaco³⁵ has covered by patent a micronutrient prepared from petroleum coke and a zinc compound. The product is a slow-release micronutrient carrier prepared by oxidizing coke with oxygen in the presence of water and reacting it with ZnCl₂ for 16 hours. The final carrier contains 0.59% Zn and resists leaching by water.

Purdue Research Foundation³² developed a method for preservation of silage which inhibits or prevents the growth of undesirable putrefactive microorganisms without affecting desirable forms of fermentation. The method consists of addition of 1-50 grams/ton of Zn bacitracin to the silage.

Zinc in Animal Feed

Zinc is now recognized as an essential mineral for all animal feeds. Such recognition, however, is relatively recent. The first instance of zinc deficiency in a farm animal was reported by Tucker and Salmon^{24a} in 1955. Such deficiency, they discovered, is the cause of parakeratosis, a common disease at that time in pen-fed swine. That disorder was also prevalent in poultry, and the resultant losses incurred among swine and poultry totaled millions of dollars before it was identified as zinc starvation. Zinc deficiency

has since been recognized in cattle and sheep, and to correct it or prevent occurrence of the deficiency, feeds are frequently supplemented with additional zinc.

All feed ingredients, fortunately, contain some zinc, but sometimes too little for normal growth. When levels of zinc in feeds are too low, animals are stunted and unthrifty. They show poor feed efficiency; sometimes they do not survive. The amounts of zinc required for animal life are so low that zinc is classed as a micronutrient. For example, a typical level of zinc in feeds is 50 ppm (equal to 0.005% zinc by weight, 50 grams of zinc per metric ton, or 1.6 ounces of zinc per short ton of feed).

Zinc is effective in such small quantities because it forms part of the enzyme systems that regulate biological processes throughout the body. It is sometimes present as an integral part of the molecule, as in metallo-enzymes, and sometimes in loose association in a metal-enzyme complex. Some of the enzymes that require zinc for proper functioning are carbonic anhydrase, active throughout the body, necessary for proper bone formation and, among other roles, important in the formation of eggshells; carboxypeptidase, found in the liver; and lactic dehydrogenase, found in skeletal muscles.

Several factors can contribute to a deficiency of zinc in animal diets. The particular feed supplied may have a naturally low content of zinc. Feed ingredients contain widely different amounts of zinc. For example, barley, corn, and most roughages fed to cattle contain only 22 ppm or less of zinc. Some feeds may also be low in zinc because they were grown on a zinc-deficient soil. In other cases zinc may be present in feed ingredients in ample amounts but in a form that cannot be utilized. Sometimes other components tie up zinc in unavailable form. The phytic acid in soybean meal, for instance, apparently inactivates some of the zinc in the ration, making it unavailable to swine and poultry.

The amount of zinc required in a feed varies with the amount and kind of other minerals in the ration. Abnormal amounts of calcium in the diet cause a marked increase in the zinc requirement of poultry and swine. Similarly, abnormal levels of cadmium also raise the zinc requirements of turkeys and chicks.

Most animals pick up a certain amount of zinc from galvanized equipment or from the soil. However, a soil may have a high content of zinc and still be a poor source of this element for animals. The compounds in which zinc is found in the soil greatly affect its availability to animals. The zinc in zinc oxide, zinc sulfate, zinc carbonate, and zinc metal is relatively available; whereas, the zinc is not readily available in franklinite and sphalerite zinc ores.

In the United States zinc-supplemented feeds always list zinc oxide or any other zinc compound used, on the feed bag or label. However, the level of zinc is not generally specified. Pre-mixes of zinc and other micronutrients may be added to feeds, and they generally contain from 0.5 to 10 per cent zinc.

Where zinc is added directly to feeds, various zinc compounds may be used; however, zinc oxide is often preferred because of its high purity, insolubility, and low cost. Water-soluble zinc salts such as zinc sulfate or zinc chloride may also be used, the former being preferred.

Note: The above information was obtained from the following publications:

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AMMONIUM NITRATE EXPLOSIVES

Zinc oxide is a highly effective inhibitor of the thermal decomposition of ammonium nitrate used for explosives.

Over the past two decades a mixture consisting of 94.5% prilled ammonium nitrate and 5.5% fuel oil has become the major explosive produced in the United States. This product, termed AN-FO, has replaced dynamites to a large extent in such blasting operations as salt mining, quarrying, and ore mining. The lower cost, ease of manufacture, and suitability for mechanical loading of AN-FO have markedly contributed to that replacement.

Ammonium nitrate for this application analyzes higher in nitrogen content than fertilizer grades and thus is more susceptible to thermal decomposition. This subject has been explored by several investigators. Fosse², in an extensive report covering tests over a 4-year period, observed that nitrates containing 33-34% N "had a definite tendency to explode under pressures close to atmospheric and at temperatures lower than or close to 250°C. Agricultural-grades tested (22.5 and 26% N) were much less hazardous.

Kerdivorenko, et al.,³ found that pure NH₄NO₃ starts to decompose at 170°C after a one-hour induction period, and at 195°C after a one-minute period. Various metal chlorides (Ca, Mg, & Pb) catalyze the rate, concentrations of 0.01-0.2% Cl content being particularly dangerous.

The mechanism of thermal decomposition of NH₄NO₃, as conceived by Rozman^{4,5}, consists of four essential stages: (a) hydrolysis, (b) thermal decomposition of HNO₃ formed in stage "a," (c) reaction of NO₂ with NH₃ formed in "a," and (d) decomposition of NH₂NO radical.

- a. $\text{NH}_4\text{NO}_3 \rightarrow \text{NH}_3 + \text{HNO}_3$
- b. $2 \text{HNO}_3 \rightarrow 2\text{NO}_2 + \text{H}_2 + \text{O}_2$
- c. $\text{NH}_3 + 2\text{NO}_2 \rightarrow \text{NH}_2\text{NO} + \text{H} + \text{NO}_3$
- d. $\text{NH}_2\text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O}$ (x = radical)

The NO₂ formed in the second stage is considered by Rozman as the basic agent of the autocatalysis, forming ignition centers for reaction of NH₄NO₃ with organic constituents such as paper packing materials. The role of an inhibitor of this thermal decomposition is to check the initiation of the autocatalytic process by combining with the HNO₃ and the NO₂ formed in the above reactions.

On testing several groups of substances, Rozman found that urea and the oxides of Ca, Mg, Cd, Zn, Pb, and Ni were suitable inhibitors, urea and zinc oxide being outstanding. The effectiveness of ZnO he ascribed to formation of the complex $[\text{Zn}(\text{NH}_3)_4](\text{NO}_3)_2$.

Cominco⁷ approached the stability of NH₄NO₃ from a different concept, namely, prevention of the orthorhombic pseudotetragonal phase transition at 32°C. They found the addition of even minor amounts (0.8-1.3%) of zinc oxide highly effective in stabilizing the nitrate.

The addition to NH₄NO₃ explosive of zinc nitrate as well

as zinc oxide is covered by a patent issued to Chemical & Industrial Corp.⁶. $\text{Zn}(\text{NO}_3)_2$ serves as an NH_4NO_3 transition-rate modifier; whereas, ZnO is effective, they point out, as a nucleating agent for production of prilled NH_4NO_3 .

Zinc oxide in NH_4NO_3 is not only an inhibitor; it contributes to the safety of blasting by decreasing the activity of the charge, according to Forshey, et al.,¹ of the U.S. Bureau of Mines Explosives Research Center, Pittsburgh.

Sumimoto Chemical⁸ aids the flow of NH_4NO_3 for explosives by preventing the caking of that nitrate. Their patent indicates that this can be accomplished by addition of the reaction product of zinc oxide with octadecylamine.

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BATTERIES, FUEL CELLS, PHOTOCELLS

The chemical, electrochemical, catalytic, and photocatalytic properties of zinc oxide can be utilized to advantage in many types of applications in batteries, fuel cells and photocells. Examples from technical papers and patents are presented below:

Dry Batteries

• Zinc-carbon dry cells

Yung-Nien Ch'in⁷ reports that, in dry cells using CrO_3 as an anticorrosive agent, replacement of the CrO_3 by an equal weight of zinc oxide provides superior anticorrosive properties.

• Zinc-silver oxide batteries

The electrolyte in these batteries consists of zinc oxide in a strongly alkaline solution. Dirkse,³ of Calvin College, active in this field for many years, presents an informative paper on the interaction of zinc oxide and zinc hydroxides with alkaline solutions.

• Nickel oxide-cadmium batteries

In sealed, alkaline, NiO -Cd batteries the evolution of hydrogen is completely suppressed by the presence of Zn , ZnO or $\text{Zn}(\text{OH})_2$ in the electrolyte. That finding is the basis of a patent issued to Electric Storage Battery Co.⁸.

Secondary Batteries

• Negative plates

The nickel-zinc secondary battery BB-674, designed and developed by Eagle-Picher¹, passed its qualification test program successfully. The positive plates consist of the standard type: sintered nickel powder. The negative plates, especially developed for this battery, are Teflon-treated zinc oxide.

Negative plates of 75% zinc oxide and 25% zinc powder in silver-zinc batteries are improved in self-discharge and other electrical characteristics by incorporation of a PVC binder, reported Volkov, et al.,⁶ of Ivanovo, U.S.S.R.

Hitachi Ltd. & Tokyo Electric Power Co.⁹ have developed and patented a zinc electrode for an alkaline storage battery. It consists of a paste of 1 mole ZnO and 0.25-1.5 moles $\text{Ca}(\text{OH})_2$ plus Pb powder applied to a grid of iron or nickel.

A mixture of zinc compounds and $\text{Ca}(\text{OH})_2$ for the negative plate of storage batteries has been patented by the Rheinisch-Westfaelisches Elektric Co.¹².

• Electrolyte

A 21% KOH solution saturated with zinc oxide is the electrolyte in an experimental Zn-O_2 cell under study by Thacker⁵ of General Motors Research.

Fuel Cells

• Electrode material

A mixture of zinc oxide and silver powder was the effective electrode material developed by Chambers,² of Sonder Place Research Institute, Dorking, England, for use in a fuel cell designed for operating on sludge-digestion gas.

• Cathodic material

Zinc oxide doped with Al_2O_3 or ZrO_2 provides relatively high electrical conductivity as a cathodic material for solid-electrolyte fuel cells, Takahashi, et al.,⁴ found. The maximum conductivity at 1,000°C was 9.5 mho/cm for $\text{ZnO:3\% Al}_2\text{O}_3$ and 8.8 mho/cm for ZnO:5\% ZrO_2 .

● Fuel element

A silvered zinc oxide electrode as the fuel element in a fuel cell has been patented by National Research Development Corp.¹¹. At 600°C it produces 0.044 amp/sq. inch at 0.7 volt during oxidation of CO to CO₂.

Photocell

● Solar energy cell

Korsunovskii¹⁰ has developed a device for conversion of solar energy into an electric current. In this solar cell the photocatalyst is zinc oxide sensitized by a thiazine dye.

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CATALYSTS

The inauguration of synthetic methanol production over zinc oxide as catalyst by BASF in the early 1920's marked the first commercial use of an oxide catalyst. Extensive research through the years has developed many new roles for oxide catalysts. Zinc oxide, for example, has been found effective in a variety of other industrial catalytic processes

such as alkylation, dehydrogenation, hydrogenation, oxidation, and miscellaneous processes, as indicated by the following patent references:

Alkylation

Alkylation catalysts based on boron and aluminum compounds are improved by addition of zinc compounds. American Oil³ has patented the addition of zinc fluoborate for alkylation of ethylene and isoparaffins. Ashland Oil & Refining⁴ has covered the addition of zinc oxide to such catalysts for alkyl transfer of alkyl aromatics.

Unsaturated hydrocarbons are removed from alkylation feed by mild polymerization over a zinc pyrophosphate catalyst, according to M. W. Kellogg⁴³.

Monsanto⁴⁷ reported high yields in acylation of aromatic ketones catalyzed by zinc oxide. A yield of 88%, for example, was obtained in the production of 3,4-dimethylbenzophenone.

The addition of zinc oxide to catalysts based on silica and phosphoric acid has been patented by Societe Francaise des Produits pour Catalyse^{57,58}. Such catalysts, they point out, are useful for oligomerization of olefinic hydrocarbons (heptenes, for example), as well as for alkylation and polymerization of olefinic and aromatic hydrocarbons.

Dehydrogenation

In the removal of hydrogen from compounds, zinc oxide is used as catalyst in both pure and modified forms, depending upon the specific operation involved. Utilization of the pure type is patented by BASF^{5,10} for dehydrogenation of low-boiling by-products to produce 3-heptanone and for treatment of straight-run naphtha and sulfur-containing aliphatic cuts to produce high-octane fuel by dehydrogenation and cyclization.

For an unusual application, Dow Chemical²⁵ has developed a dehydrogenation catalyst with specific electrical resistivity. It consists of a mixture of ZnO, Cr₂O₃, Fe₂O₃ and MgO, and is for the preparation of vinyl monomers in reactors heated by electrical resistance.

Zinc oxide doped with copper ions is covered as a dehydrogenation catalyst by Emel'yanov, et al.^{31,32}. It is useful, they report, in formation of cyclohexanone from cyclohexanol. Esso³⁴ likewise has patented a special zinc oxide catalyst. It is for dehydrogenation of secondary alcohols to ketones, specifically methylethyl ketone. This catalyst, like the one used in the standard method for MEK, consists of approximately 94% ZnO and 6% Na₂CO₃. The major difference is the use of Al(OH)₃ as the base instead of calcined coke in the standard method.

To convert aliphatics to aromatics, Mobil Oil⁴⁶ has patented as catalyst a ZSM-5 synthetic aluminum silicate molecular sieve impregnated with Zn(NO₃)₂. On calcination at 1,000°F, the nitrate is converted to zinc oxide.

Zinc oxide can be modified to form catalyst pellets of high strength, according to Phillips Petroleum ^{48,49}. The procedure consists of calcining ZnO with Al₂O₃ for up to 30 hours at 800-1200°C. This catalyst, they find, is useful for dehydrogenation of n-butane to olefins and diolefins.

Hydrogenation

Zinc oxide and its derivatives contribute to the effectiveness of catalysts in an array of hydrogenation processes. Depending upon the particular operation, they may increase the rate of reaction or the yield, or they may contribute some special feature. British Gas¹⁴, as an example, found that a catalyst consisting of ruthenium 9, ZnO 37 and Al₂O₃ 54 % (the Al₂O₃ serves as the support) is resistant to sulfur poisoning and can be regenerated. These features are in addition to the usefulness of the catalyst in the gasification of naphtha to CH₄.

For the reduction of organic compounds containing oxygen, marked differences in catalysts are evident. Type of feed is responsible for some of the differences. In the preparation of alcohols by reduction of carboxylic acids, esters, ketones, or aldehydes, it should be noted that Bayer AG,¹² patented a catalyst of Cr₂O₃-CuO containing as much as 35% ZnO by weight of the CuO. CSR Ltd.¹⁵, however, in hydrogenation of invert sugar to mannitol, patented a process based on the presence of Ni and ZnO. As other examples, Japan Gas-Chemical³⁹ selected a ZnO-CuO catalyst for hydrogenation of dimethyl maleate. Kao Soap⁴² developed a ZnO-CrO₃-CuO catalyst for the dehydration-hydrogenation of maleic anhydride. Mitsubishi Chemical⁴⁵ found a Ni-ZnO catalyst useful in the hydrogenation of (AcOCH₂CH)₂ to 1,4-diacetoxybutane.

For hydrogenation of petroleum fractions and other hydrocarbons, zinc oxide and its derivatives are the basis for catalysts in a number of patented processes. Such a catalyst developed by Chevron Research¹⁹ consists of approximately equal weights of palladium metal and ZnO on synthetic clay. Texaco^{63,64}, as another example, has patented hydrorefining catalysts based on ZnO with ZnO·Cr₂O₃.

Zinc oxide and its derivatives are also involved in new developments in special areas of hydrogenation of hydrocarbons, including the hydrocracking of coal. Du Pont²⁷ has developed new oxide compositions for the hydrogenation of ethylene. They are of the type Pt₃MO₄ (M is a metal atom: Zn, Ni, and others) and are of particular interest in that they possess an orthorhombic crystal structure.

In the conversion of coal to gasoline, several processes based on molten zinc salts as catalyst have been patented. One of the patents, assigned one-half to Consolidation Coal²¹ and one-half to the U.S. Department of Interior, covers molten ZnCl₂ containing ZnO. Shell Oil⁵¹⁻⁵⁵ has developed several hydrofining and hydrocracking processes for petroleum fractions as well as coal and were based on molten zinc salts, ZnI₂, ZnCl₂, and ZnBr₂.

Methanol Synthesis

Recent patents on zinc oxide catalysts for methanol production reflect changes in types of feedstock and processing modifications as well as advances in catalyst design and preparation.

BASF's patents^{7,8} cover catalysts to meet the requirements of changes in feedstocks. Each of the two catalysts consists of a ZnO-CuO base modified by addition of other metal compounds, chromium and manganese in one, aluminum in the other. The aluminum-modified catalyst is for use with synthetic gas of the following composition: H 71, CO 23, CO₂ 6 and CH₄ 0.7 vol. %. The catalyst formula is: Cu_n Zn_m Al₂(OH)₁₆CO₃·4H₂O in which n = 1-3, m = 3-5, and n + m = 6.

Two other large methanol producers offer catalyst modifications. Shell International⁵⁶ covers the addition of silver oxide to a ZnO-CuO base, while Du Pont²⁶ presents a method of preparation of a ZnO-CuO catalyst which introduces semiconductor properties in the ZnO by means of a special reduction with hydrogen under high pressure. In this process zinc nitrate is converted to the carbonate, to which is added CuO in various proportions. The mixture is calcined two hours at 400°C and then reduced with 5% H₂ in N₂ at 275°C and 70 atmospheres.

Two catalyst producers have been granted patents on ZnO-CuO catalysts modified for use on different methanol processes. Catalysts & Chemicals¹⁶ modify the catalyst with Al₂O₃ for its application to low-temperature methanol synthesis. Topsoe⁶⁵ offers a ZnO-CuO catalyst containing Cr₂O₃ for use on low-pressure processes for methanol production.

Oxidation

Zinc oxide-containing catalysts are effective in several types of oxidation processes, including the important Oxo process for production of higher primary alcohols from lower olefins. The types include both catalytic and photocatalytic oxidation of hydrocarbons, oxidation of numerous chemicals, oxidation of motorcar exhaust gases, and a new process for production of hydrogen for use as synthesis gas in the production of methanol and ammonia.

The photocatalytic oxidation of gaseous C₂₋₄ hydrocarbons was conducted by Agence National de Valorisation de la Recherche¹ over ZnO and other selected metal oxides at room temperature under a broad range of ultraviolet wavelengths, 2200-3900 Angstrom units (220-390 nm).

The aldehyde or alcohol recovered in the Oxo process has one more carbon atom than the parent olefin. Addition of zinc acetyl acetonate as promotor to the conventional catalyst, however, results in production of varying amounts of dimeric alcohol product having twice the number of carbon atoms of the monomeric alcohol, Esso³³⁻³⁶ reported. They also noted that the use of ZnO and other zinc compounds in the conventional Oxo process, followed by hyd-

rogenation, produced alcohols of high molecular weight. In another study they found that zinc salts are highly effective promoters when applied to a nickel-kieselguhr catalyst in a process for producing such alcohols.

The production of higher molecular weight mono- and polyfunctional alcohols was also covered by Deutsches Hydrierwerk Rodleben VEB²³. Their catalyst consisted of ZnO supplemented by CuO and Cr₂O₃.

In the oxidation of hydrocarbon compounds other than olefins, zinc oxide and its derivatives aid the catalytic operation. Bayer AG,¹¹ found that ZnO was one of several metal oxides useful in the oxidation of propylene to acrolein. In the oxidation of hydrocarbons to alcohols in the presence of a zinc promoter, Shell International⁵⁶ patented a list of ten zinc compounds that were effective promoters. As another example, Standard Oil of Indiana⁶⁰ found ZnO a desirable activator of a vanadium-phosphorus catalyst for the oxidation of butane to maleic anhydride.

A variety of organic chemicals can be oxidized to useful products over catalysts containing zinc oxide or its derivatives. Interesting examples are these: BASF⁶ formed anthraquinone by oxidation of 1-methyl-3-phenylindan over a ZnO catalyst prepared by calcining at 450°C a mixture of zinc nitrate, ammonium vanadate and pumice grains. Daikin Kogyo²² prepared trifluoroacetic acid anhydride by heating 20 grams CF₃COC1 with 6 grams ZnO 9 hours at 40°C in a stainless steel autoclave.

In the preparation of 1-cyanocyclobutene from 1,2-dicyanocyclobutane, Du Pont²⁸ pointed out that a basic oxidation catalyst was used. Such catalyst consisted of a mixture of ZnO and MgO preheated one hour at 400°C.

As another variation, Maruzen Oil⁴⁴ prepared 5-methylheptan-3-one over ZnO containing approximately 1% of a noble metal (rhodium). In the formation of organic hydroperoxides, Ruhrchemie AG,⁵⁰ reported that ZnO was one of the metal oxides effective as catalyst. ZnO was also patented as a catalyst by Shell Oil⁵³ for the preparation of cyclic ethers.

Purification of motorcar exhaust gases is currently the subject of extensive research, and zinc oxide is already demonstrating its catalytic properties in some of those programs. Toyota Motor⁶⁶, for example, removed 96% of the C₃H₈ pollutants in exhaust gases with a catalyst composed of ZnO 10, Al₂O₃ 100, and palladium 0.17 parts. They titled that composition as a "heat-resistant palladium-zinc catalyst."

A similar type of catalyst developed by Societe Procatalyse⁵⁹ reduced carbon monoxide from 29 to 0.52 grams/mile. Hydrocarbon output in the exhaust gases was lowered from 4 to 0.10 grams/mile. The composition consisted of two granulated catalysts: (1) platinum or palladium on Al₂O₃ and (2) oxides of Zn, Cu, Ce and Co on Al₂O₃. The two catalysts were combined in the proportion of 4 parts of the second to one part of the first.

An oxidation process of particular interest has also been developed for the production of an important synthesis gas, hydrogen. Bethlehem Steel¹³ has patented such a process based on the catalytic oxidation of carbon monoxide and water. The gas is useful as feed for the production of methanol or ammonia. The catalyst consists of ZnO-CuO, ZnO-Cr₂O₃ or Fe-Cr oxides. An important feature of the process is that it forms no methanol, although it is similar to the process for that alcohol. This selectivity may be attributed in part to the catalyst. An example of the latter, cited in the patent, consists of ZnO-CuO prereduced for 30 minutes at 250°C under 320 atmospheres pressure.

Other Catalytic Processes

The broad spectrum of catalytic applications of zinc oxide and its derivatives is further illustrated by the following patent abstracts:

American Cyanamid² has found zinc oxide useful as catalyst in urea and melamine molding compositions.

Distillers Ltd.²⁴ can convert alkanes to olefins over a catalyst consisting of vanadium and zinc oxides.

DuPont^{29,30} has covered the use of zinc oxide as catalyst in preparation of tetrachlorobenzenedithiols, and Zn-Cu chromites for the addition of HCN to butadiene to form pentenenitriles.

Henkel G.m.b.H.³⁷ has developed a mixture of ZnO and Cr₂O₃ for preparation of amines.

Hoechst AG.³⁸ prepared (2-chloroethyl)phosphonic dichloride by photosensitized chlorination of ethyl-POCl₂ with Cl₂ at 0-10°C over ZnCl₂ as catalyst.

Kali-Chemie AG.⁴¹ has patented ZnCl₂ as catalyst for telomerization of pentafluoroiodoethane with tetrafluoroethylene. One feature of the process is that it operates without the formation of tar.

Standard Oil of Indiana⁶¹ found ZnCl₂ an effective catalyst for water-soluble, baking-type resins.

Universal Oil Products⁶⁸ converted ROH alcohols to organic halides and ethers by treatment with Zn-Cu chlorides.

Zinc Catalysts, Preparation

As catalyst performance is influenced by its method of preparation as well as its composition, the following patent abstracts are pertinent:

BASF⁹ found a complex zinc compound useful as catalyst for organic reactions. The formula: (Ph₃P)₂NiZn(CN)₄.

Chemetron^{17,18} developed a method for stabilization of pyrophoric ZnO-CuO catalysts. Composition: ZnO 60-70, CuO 25-40, Al₂O₃ 0-25. The method: Treat with gas containing O₂ in step-wise manner from 0.2 to 1 volume % of O₂ at 107°C. Such catalysts, they point out, are for water-gas conversion.

Continental Oil²¹ prepared ZnEt₂ as catalyst for production of organozinc and organocadmium compounds by reaction of ZnCl₂ and trialkyl aluminum.

Japan Kenkyusho⁴⁰ activated ZnO powder by bombardment with atomic nuclei, alpha particles, or xenon ions to introduce lattice defects. This improved the sintering properties and also the usefulness of the ZnO as catalyst for hydrogenation of heavy oils.

Texaco⁶² reduced the regenerating time for ZnO and ZnO·Cr₂O₃ catalysts by addition of antimony oxides. Such catalysts, they reported, are useful for reforming of petroleum products.

Union Carbide⁶⁷ formed a coating of ZnO on zeolite molecular sieves for catalytic applications by heating the zeolite with metallic zinc at 650°C for 4 hours.

Vahala & Vyrnol⁶⁹ prepared a ZnO of high adsorption activity by forming a Zn(OH)₂ precipitate of fine particle size at 8.5-9.0 pH, drying the pulp and calcining for 40-60 minutes.

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CEMENT, PORTLAND

The beneficial effects of zinc oxide additions to portland cement have long been known—retardation of setting and hardening (to reduce the rate of heat evolution), improvement in whiteness and final strength. Recent technical papers from Germany and Russia, in particular, are concerned with the reactions responsible for the effects of additions of zinc oxide and other compounds.

Addition of only ½% zinc oxide increased whiteness 6% and 7-day strength by 18%, Kramanovich, et al.,¹ found in their tests on portland cement. In a study of admixtures enhancing the strength of such product, Kurumada, et al.,² noted that zinc hydroxide retarded the rate of setting by its moderating effect on the rate of hydration of one of the specific components in cement, the "alite" phase with the composition 54CaO·16SiO₂·Al₂O₃·MgO.

Liebau, et al.³, of the University of Kiel approached the problem of retardation in setting of portland cement by an x-ray analysis of the crystal structures formed. They reported that zinc oxide additions formed a hydrated complex which retarded setting. Composed of special groups such as $\text{Zn}(\text{OH})_4$ tetrahedrons, the formula of the crystals was: $\text{Ca}[\text{Zn}_2(\text{OH})_6]_2\text{H}_2\text{O}$.

Retardation of setting was also caused, Lieber, et al.,⁴ observed, by intercalation of zinc oxide into hydrated calcium silicate, one of the major contributors to the setting and hardening of portland cement. Lieber, et al., likewise noted that zinc oxide imparted higher strength.

Zinc chloride, too, reacts with constituents to decrease the rate of setting and increase strength, according to Ved, et al.,^{5,6} of Kharkov, but in a different manner than does zinc oxide. They reported that it modifies the setting by reacting with $\text{Ca}(\text{OH})_2$ to form a gelatinous $\text{Zn}(\text{OH})_2$, which accumulates around the grains of tricalcium silicate. The latter is considered the principal active hydraulic compound of cement. Around tricalcium aluminate grains, ZnCl_2 forms a difficultly soluble form of $\text{Zn}(\text{OH})_2$, which increases the strength of high-aluminate cement, they found.

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CERAMICS

The large, highly diversified field of ceramics, a substantial consumer of zinc oxide, continues to explore means for utilizing some of the properties of that oxide in the upgrading of present products and in the development of new ceramics. Nearly 200 technical papers and patents, covering more than a dozen classes of ceramic products, were found in the literature search for this section. Of particular interest were

the properties imparted by zinc oxide to some of the newer applications such as electronic glass, low-melting glass for metal-to-glass seals, thermistors for use as lightning arresters, and devitrified glasses of low thermal expansion.

Zinc oxide has a long history in ceramics. It was formally introduced to the glass industry at the London Exhibition of 1851¹¹ in the form of a dense zinc flint glass used for crystal. A short time later (1860) the first U.S. patent on the use of zinc oxide in a ceramic product was issued to Wetherill³⁰. It was for a lime-free glass with high zinc oxide content of the composition 33.4 ZnO , 16.6 Na_2O and 50 weight per cent SiO_2 . This radical departure from the typical soda-lime-silica glass stimulated extensive investigations to explore the properties of this promising new additive in glass.

It was soon discovered that zinc oxide imparts a unique combination of properties when used in glass. Zinc oxide reduces the coefficient of thermal expansion, imparts high brilliance and luster and high stability against deformation under stress. As a replacement flux for the more soluble constituents, it provides a viscosity curve of lower slope. The specific heat is decreased and the conductivity increased by the substitution of zinc oxide for BaO and PbO .

A one per cent addition to tank window glass lowers the devitrification temperature and improves the chemical resistivity, while maintaining good forming properties (workability). Zinc oxide is used consistently in high-grade fluoride opal glass in which it greatly increases opacity, whiteness and luster by inducing precipitation of fluoride crystals of optimum number and size. It is used in optical glasses of high barium content to reduce their tendency to crystallize on cooling. The resistance of phosphate glasses to chemical attack is improved by the presence of zinc oxide. The phosphate glasses are coming under consideration as a bonding agent in bio-medical applications. A ten per cent zinc oxide addition assists in the development of the characteristic color of cadmium sulfo-selenide ruby glass which is used for neon signs.

The first large-scale use of zinc oxide in ceramics was based mainly on its low coefficient of thermal expansion. The product was the heat-resistant, chemical-resistant laboratory glassware introduced in the 1890's by Jena Glassworks⁷, Germany. The glassware contained 6 - 11 per cent zinc oxide. Popularity of that product resulted in annual consumption of substantial quantities of the oxide. Numerous other applications of zinc oxide followed, many of them being based on the properties outlined above.

For decades, zinc oxide has been used in amounts up to 2 - 3 per cent in transparent raw or fritted glazes for artware or dinnerware, and in somewhat larger amounts in semitransparent glazes for stoneware. In Bristol glazes for earthenware products, for example, zinc oxide in combination with alumina produces opacity and whiteness in low lime compositions. In tile glazes, the use of zinc oxide is very general, its content in certain types being 10 per cent or more. The higher

percentages are used for the development of a matte finish. Crystalline glazes are produced by loading with zinc oxide to such a high degree that supersaturation occurs. The value of zinc oxide in crystalline glazes can be attributed to its unusual property of crystallizing as a silicate instead of an oxide.

Zinc oxide has many interesting and unusual properties for ceramic applications, as is evident from the following abstracts of technical papers and patents.

Glass Systems

Replacement of only 5% SiO_2 by ZnO in certain light-sensitive glasses and photo-sensitive glass-ceramics markedly lowers the coefficient of thermal expansion and increases light sensitivity and optical density of the glasses by 20-fold. The ZnO also imparts lower dielectric loss. The composition of the system is: SiO_2 68, Al_2O_3 5, Li_2O 24 and K_2O 3 mole %, reported Berezhnoi¹. He further noted that the glass structure with ZnO consolidates and beta-spodumene crystallizes provided there is no separation of Zn compounds.

Deev, et al.,³ studied the effect of ZnO concentrations on the physicochemical properties of fluxes of the following composition: (a) $\text{Na}_2\text{CO}_3\text{-Na}_2\text{B}_4\text{O}_7$ and (b) Na_2SiF_6 . ZnO increased the viscosity and surface tension of the melts, but decreased their crystallization temperature, they noted.

Glass-forming regions were found by Dusil, et al.,⁵ in the system $\text{ZnO-Al}_2\text{O}_3\text{-SiO}_2$. The boundaries are: $\text{Al}_2\text{O}_3 \leq 25$, $\text{SiO}_2 \geq 40$, and $\text{ZnO} < 60$ mole %. Demkina, et al.,⁴ explored the elastic properties of certain types of glasses to determine the effect of addition of ZnO . They reported that ZnO decreased the elasticity of crown glasses and imparted higher elasticity to Pb silicate flints.

In studies on the structure of glasses, Ermolenko, et al.,⁶ established a relation between selected properties and the strength of the bonds in the metal oxides. With the system $\text{SiO}_2\text{-ZrO}_2\text{-Al}_2\text{O}_3\text{-MgO-ZnO}$, they observed that microhardness, for example, increased with the strength of the metal-to-oxygen bonds of the four metal oxides in that system.

The structural role of ZnO in glasses in the system $\text{Na}_2\text{O-ZnO-SiO}_2$ was investigated by Hurt & Phillips^{8,9}. They confirmed the decrease in coefficient of thermal expansion and increase in index of refraction as ZnO content was raised to 35 mole %. A detailed study of infrared absorption of the test glasses showed, they reported, the presence of both 4 and 6 coordinations for oxygen ions in ZnO .

Low-melting glasses in the $\text{SiO}_2\text{-ZnO-B}_2\text{O}_3\text{-Na}_2\text{O}$ system possess many interesting properties, according to Karadzova, et al.¹⁰. The best combination of properties was exhibited by the composition ZnO 60, B_2O_3 25, SiO_2 10 mole % and the balance consisted of Na_2O . Major properties: softening point of 520°C , coefficient of thermal expansion (linear) of 70×10^{-7} , and good chemical stability in water. This

stability could be increased by raising the ZnO and SiO_2 contents.

The structural framework of glasses in the system $\text{La}_2\text{O}_3\text{-B}_2\text{O}_3\text{-P}_2\text{O}_5$ and the effect of ZnO on the properties were studied by Kutukova, et al.¹², and yielded unexpected results. The introduction of 5 - 10 mole% ZnO or CdO in place of La_2O_3 gave glasses with abnormally high transmission, with only slight lowering of the refractive index. More substantial lowering had been expected. They explain these results in this manner: they represent a sequence of change of the polarizing effect and the entry of Zn and Cd into the structural framework of the glasses.

In alkali-free alumina-borosilicate glasses, ZnO and CdO gave the lowest coefficient of thermal expansion, PbO and CdO gave the lowest softening point, and BaO imparted the highest electrical resistivity, reported Kutznetsov¹³.

Crystal growth studies in $\text{ZnO-Al}_2\text{O}_3\text{-SiO}_2$ glasses, conducted by McMillan, et al.¹⁴, produced an unusual ZnO phase which they designated as a "stuffed keatite crystal." The composition was essentially $\text{ZnO} \cdot \text{ZnO} \cdot \text{SiO}_2$ with a minor quantity of Al_2O_3 .

The resistance to breakage of the popular refrigerator-to-oven ware, based on beta-spodumene glass, is improved by addition of zinc oxide, Mueller, et al.,¹⁵ reported. A 6% ZnO addition provided substantial improvement in strength properties.

The elastic properties of glass, as measured by the Poisson ratio, may relate to resistance to breakage, as well as to factors responsible for the structural framework of glasses. Phillips, et al.,¹⁶ reported on the effect of ZnO and other metal oxides on the elastic properties of glasses containing soda and SiO_2 .

Glass with sufficient toughness to serve as binder for a tool can be prepared from a crystalline glass based on ZnO . Ralko, et al.,¹⁷ in a study of the glass system $\text{PbO-B}_2\text{O}_3\text{-ZnO-SiO}_2$, observed that compositions containing 22.5 - 32.5 mole % ZnO and 15 - 20 mole % B_2O_3 attained complete crystallization, which improved toughness. Shortly thereafter they¹⁸ found such glass suitable as binder for a tool made from cubonite (cubic boron nitride).

The kinetics of crystal growth promoted by ZnO was investigated by Rogers, et al.,¹⁹ in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$. They found that crystallization and crystal growth increased as the square of the concentration of ZnO .

Crystalline glasses of low thermal expansion and based on ZnO have been studied by several teams. Sugimura, et al.²⁰, developed such a glass in the system $\text{ZnO-Al}_2\text{O}_3\text{-SiO}_2$. The crystals consisted of an unusual ZnO type: Zn indialite with the composition $2\text{ZnO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$. The crystals were relatively long, approximately 500 microns. The indialite precipitated when glasses of the composition $2.16 \text{ ZnO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ were heated at $870\text{-}1000^\circ\text{C}$. Above the

latter temperature the indialite decomposes to gahnite and SiO_2 . The thermal expansion coefficient of the indialite glass is low: 11×10^{-7} .

In a study of reactions between ZnO and selected oxides of elements of Groups IV and V, Brown and Hummel², discovered a phase, $2\text{ZnO} \cdot 2\text{Nb}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$, of unusual interest because of its very low thermal expansion characteristics.

Patents

Corning Glass Works has developed a variety of ceramic articles in which ZnO is a prominent constituent: (a) Articles containing 20 - 50 weight % Zn spinel crystals (less than 0.1 micron diameter) but no silicate crystals maintain transparency at 1000-1200°C. With a thermal expansion coefficient $25-40 \times 10^{-7}$, they are useful as envelopes for electric lamps operating at high temperatures.²¹; (b) Stable boron silicate opal glass contains about 8½ % ZnO, has low thermal expansion and improved chemical resistance.²²; (c) A thermal-shock-resistant ceramic material contains ZnO^{23} ; (d) A transparent, semi-crystalline ceramic body contains 0-12% ZnO^{24} ; (e) A low-expansion Zn Petalite-8-quartz glass-ceramic article²⁵.

A series of partially or wholly devitrified glasses containing substantial percentages of ZnO have been patented by English Electric, Ltd: (a) $\text{ZnO-Al}_2\text{O}_3\text{-SiO}_2$ glasses were devitrified to a sharply defined depth of 100-200 microns. The devitrified zone consists of willemite ($2\text{ZnO} \cdot \text{SiO}_2$) crystals formed by the annealing process described in the patent. The glasses are transparent, stress-free, high strength, and readily workable. Typical ZnO content: 36-50%²⁶; (b) They developed a process for devitrifying zinc borosilicate glass-ceramics. Typical ZnO content: 22 weight %²⁷; and (c) a completely devitrified ceramic glass of the system $45\text{ZnO} \cdot 36\text{SiO}_2 \cdot 9\text{Al}_2\text{O}_3$ was stress-free and showed good mechanical and electrical properties.²⁸

Lower intrinsic radioactivity, higher transmittancy to 350 nm rays, and good machinability were developed in a devitrified borosilicate glass by Jenser Glaswerk²⁹. It contained 5-8% ZnO.

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Electrical Glass

Zinc oxide imparts a wide array of electrical and semiconductor properties to glasses and ceramics for such applications as printed circuits, capacitors, resistors, and electroconductive articles. Selected examples are described below; additional examples are listed in Further References.

Patents

High-energy sparkplug bodies can be prepared by pressing and sintering at 1400°C a mixture of semiconductor ZnO and 0.5% kaolin, as disclosed by Bern-Werk Albert Ruprecht¹.

Corning Glass^{2,3} developed a semiconducting fused ceramic by modifying Zn₂SiO₄ with an activator consisting of In₂O₃ or Ga₂O₃. They also patented a process for depositing a metal oxide film of variable electrical conductivity on a ceramic body. In this process a solution of ZnCl₂ and SbCl₅ in 37% aqueous HCl is sprayed on borosilicate glass heated to 800°C to give a ZnO-Sb₂O₃ film of approximately 390 m micron thickness. The electrical conductivity may be varied from 236 ohms to 10¹¹ ohms by varying the Zn-to-Sb concentration ratio in the solution.

Pyroelectric glasses with a stored charge capacity of 1 x 10⁻⁶ coulomb/cm² were developed by Deutsche ITT Industries G.m.b.H.⁴ by heat treatment of a mixture of ZnO 52 and P₂O₅ 48 mole %.

Du Pont⁵⁻⁷ patented a series of compositions in this field. (1) Glass for printed circuits was prepared from a composition such as ZnO 24, SiO₂ 30 weight % with minor constituents. This material was fritted and dispersed in a lacquer binder. (2) An electrical-resistance film was developed by heating to 900°C a mixture of 84 parts V₂O₄ and 16 parts borosilicate glass containing 27% ZnO and forming as a thin film or other shapes. (3) Capacitor dielectric compositions with Q-values of 320-800 and less than 1% electric charge loss at 75-110°C and 1 KHz comprised the following compositions: SiO₂ 13-25, B₂O₃ 15-29, ZnO 22-27, PbO 15-26, Al₂O₃ 5-10% by weight. Melting point: 1100-1400°C.

IBM⁸ patented a method of preparing microminiaturized capacitors of good resistivity, damping and dielectric properties by combining a semiconductor composition (87% ZnO) with a ferroelectric (87% BaTiO₃). Ratio: 4 parts semiconductor to 1 part ferroelectric.

Ceramic semiconductor resistors composed of high-purity ZnO plus modifiers in small proportions were developed by Minnesota Mining⁹. Operating at 925°C, they have a resistivity of 0.1 ohm/cm.

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Low-Melting Glass

Some of the thermal properties of zinc oxide are utilized in glasses of low melting point and low thermal expansion which are useful as adhesives, insulating materials and sealants, particularly in electronics.

Patents

An insulating coat of glass was developed by English Electric¹ to serve as a covering on metallic thread or analogous material. Composition of the glass: P₂O₅ 40-60, ZnO up to 45, BaO up to 50, and MgO to 10 weight %.

General Electric²⁻⁴ has a series of patents covering glass coatings for electrical devices; the compositions carry a high percentage of ZnO. Composition: ZnO 60, B₂O₃ 25, SiO₂ 9, and PbO 2 weight %, plus minor constituents. A similar composition can serve as a binder for abrasive tools, judging by a patent of the Ukrainian Scientific-Research Institute⁵.

Owens-Illinois^{6,7} reported a coefficient of thermal expansion (0°-425°C) of 45 - 65 x 10⁻⁷ and a fiber softening point below 600°C for the following composition: ZnO 34-46, PbO 11-29, B₂O₃ 18-32, SiO₂ 7-14 and CuO 8-16 weight %. Using a ZnO-V₂O₅ base the expansion and softening point were reduced. The composition: ZnO 40-60, V₂O₅ 5-30, B₂O₃ 20-40 and CuO 1-10 weight %.

Philips Electric N.V.⁸ patented a composition for sealing ceramics to Fernico: ZnO 55, SiO₂ 20, B₂O₃ 20, and Li₂O 5 weight %. Properties: Thermal expansion coefficient: 49 x 10⁻⁷, upper annealing point: 515°C, and sealing temperature: 1100°C.

Union Carbide⁹ developed a glass for use as an oxidation-resistant coating on steel, and as infiltrant for ceramics and costume-jewelry stones. The base composition: 3SiO₂·Al₂O₃·2MO, in which MO can be an oxide of selected elements. Example cited in the patent shows 20-40% by weight of ZnO.

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Optical Glass

Zinc oxide contributes to optical glass a variety of properties in addition to high refractive index, as indicated by the following patents.

American Optical¹ has patented for use on laser equipment a cladding glass of one-inch thickness and containing P₂O₅ 68, ZnO 12, Al₂O₃ 7, La₂O₃ 9 weight % and minor constituents. In another patent² they disclose a glass composition for goggles for welding which is superior to those of silica-base since the new glass has a much narrower spectral band, which produces purer and sharper colors. The composition: P₂O₅ 64, ZnO 18, Al₂O₃ 9, CuO 3½, and MoO₃ 5 weight %.

Optical borate glasses with a refractive index of 1.72 - 1.81 were developed by Heindorf³ of East Germany. An example: B₂O₃ 20-32, ZnO 18-36, PbO 2-32, WO₃ 2-18, La₂O₃ 0-20 and TiO₂ 0-15 weight %.

The transparency of ZnO in the infrared region is used to advantage in a glass filter patented by Hoya Glass Works⁴. The filter is designed for "transmitting in the infrared region but blocking visible light." The composition: SiO₂ 28-53, B₂O₃ 1-10, ZnO 28-48, CaO 1-12, Na₂O 10-30 weight %, together with these color-forming components: CdS 2-4, Se 1-3, and Te 0-3.

Hoya Glass⁵ also noted that the high absorption of ultraviolet light by ZnO minimizes many difficulties in coloring and they suggest the use of a "large amount of economical ZnO to absorb u.v. light to produce optical glass of excellent transparency at less cost." An example cited in their patent contains CdO as well as ZnO. The composition: B₂O₃ 23-9, La₂O₃ 23-9, ZnO + CdO 20-40 weight %. Refractive index: 1.71-1.75. Ratio of CdO to ZnO is maintained below 0.5 to provide "high chemical durability and polishing properties." Details are provided on means of preventing devitrification.

Potassium-zinc silicate glass optical filters with CdS and ZnS color centers absorbing at 3800-4750 Angstroms were covered in a patent issued to Jenser Glaswerk.⁶ The composition: SiO₂ 51, B₂O₃ 4, K₂O 22, ZnO 20, ZnS 1.6 and CdS 1.0 weight %. This glass is annealed at 580°C to form ZnS and CdS color centers. The position of transmission cutoff can be varied by change in composition or by modification of the annealing temperature.

Stable crown glass containing only minor quantities of La₂O₃ and BaO were developed by Ernst Leitz G.m.b.H.⁷. They have excellent chemical resistance and good optical properties. The composition: B₂O₃ 19-55, SiO₂ up to 30, CaO or MgO 12.5-38, ZnO or CdO 10-46, ZrO₂ up to 17.5 weight% and up to 12% of oxides of Sr, Ba and La.

An optical glass containing no CdO is the basis of a patent by Minolta Camera⁸. Refractive index is high, 1.82407. Example of the product: ZnO 27, B₂O₃ 20, SiO₂ 5, La₂O₃ 25, Nb₂O₅ 20 and ZrO₂ 3 weight %.

Low crystallization capacity is a feature of optical glass developed by Mukhin, et al.⁹ Composition: ZnO 29-32, B₂O₃ 26-30, La₂O₃ 26-9, SiO₂ 6, ZrO₂ 29-32 and Ga₂O₃ 5-10 weight %.

Pittsburgh Plate Glass¹⁰ utilized both ZnO and TiO₂ to

provide refractive index of 1.52-55 in an optical glass. The composition: SiO₂ 63-73, ZnO 5-18, TiO₂ 1-8 and alkali metal oxides 8-20 weight %.

High transparency in infrared light, high chemical resistance and refractive index of 1.67 - 1.83 are the special characteristics of an optical glass of Saale-Glas¹¹. The composition: B₂O₃ 22-47, ZnO or CdO 45-72, WO₃ or MoO₃ 2-25 weight %.

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Glazes

A high proportion of the following papers bear upon the practical rather than the theoretical aspects of the use of zinc oxide in glazes.

Papers

ZnO and MgO impart craze-resistance to low-lead borosilicate glazes for artware and also enhance the hardness, Quazi, et al.,⁶ reported. Up to 0.2 mole equivalent they likewise improve the gloss and texture, but beyond that limit gloss is adversely affected. The crawling of glazes can be influenced by the reactivity of the zinc oxide used, according to Reising⁷. Any formation of gelatinous Zn(OH)₂ by reaction of ZnO with water is detrimental and can be minimized by use of a coarse particle size ZnO.

ZnO as a mill addition in glazes contributes substantially to craze-resistance, and, Wanie^{8,9} observed, in lead glazes ZnO enhances color. One of the examples cited by Wanie consisted of a mat glaze containing 24% ZnO. Groessel⁴, however, has pointed out that ZnO requires special treatment when used in high proportions in mat glazes for Seger cone 05a. To minimize shrinkage of the glaze, he suggests that the oxide be pre-calcined or fritted with wollastonite or a mixture of CaCO₃ and quartz.

The texture of ZnO opaque glazes may be dependent, in part, on the type, quantity, and particle size of the opacifying agent, Kato, et al.,⁵ found. In an opaque Bristol glaze they detected the spinel ZnO·Al₂O₃ as the opacifier. For good texture and opacity, the average particle size ranged from one to three microns and the quantity represented 4-16%. In a siliceous opaque glaze they reported that the particles were

non-crystalline and immiscible with the bulk of the glaze. For best optical properties, the size of the particles was 0.2-0.3 micron. Opacity decreased with reduction in size of particles below 0.2 micron.

With ZnO and TiO₂ as modifying agents, Bierbrauer² developed an attractive variety of white and colored engobes based on a Seger cone 03a lead glaze for whiteware bodies. Most of the engobes, he commented, were glassy due to the fluxing action of ZnO.

In glazes for ceramic bodies, ZnO can contribute electrical properties. Examination of a ZnO-Fe₂O₃ conducting glaze by Binns³ revealed the presence of a spinel and a hematite phase, the latter being present in only minor amounts. The spinel phase is mainly responsible for the electrical conductivity; its formation is dependent upon the ZnO content. Additions of 1 - 9% ZnO produced 2 - 16% spinel phase. In glazes for zirconium porcelains, Alvarez, et al.,¹ were able to increase dielectric constant from 7.9 to 14.5 by additions of ZnO, ZrO₂, BaO, and K₂O.

In a study with tagged atoms of the interaction of glazes with the ceramic body, Zavarzina¹⁰ found that the addition of ZnO, Na₂CO₃ or PbO strengthened the bond; borax and Fe₂O₃ were less effective.

Patents

A low-melting-point glaze patented by Augustinik, et al.,¹¹ of Novocherkassk contains a higher content of ZnO than of any other metal oxide. The composition consists of: SiO₂ 52-8, Al₂O₃ 9-11, ZnO 11-12, CeO₂ 8-10, CaO 5-6, Li₂O 2-4, Na₂O 2-4, La₂O₃ 1-2, and MgO 0.6-1 weight %.

Crystalline mat glazes developed by Szilikatipari Kozponti Kutató¹⁵ are based mainly on ZnO, higher than 60 mole %. These glazes are for application to china and can be produced in a range of attractive colors, such as blue crystals on a yellow background.

Kukolev, et al.,¹² of Karkov incorporated ZnO into a glaze for face tiles to obtain improved thermal stability. The composition: SiO₂ 40-44, Al₂O₃ 4-7, B₂O₃ 5-10, ZnO 7-10, ZrO₂ 8-14, CaO 4-7, Na₂O 2-5 and minor constituents.

Glazes for electrical ceramics such as insulators have long relied on zinc oxide for its special properties, and new applications continue to appear. In a semiconducting glaze for high-voltage ceramic insulators, Nigol¹⁴ found that the addition of only 1% ZnO reduced the effects of firing on variations in resistivity. And Matsushita Electric¹³ has covered by patent a ceramic glaze to which is applied an aqueous coating. The ceramic is glazed with Al(H₂PO₄)₃ and then coated with a sodium silicate solution containing Ca(H₂PO₄)₂ and Zn(FeO₂)₂. The coating is air-dried.

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Thermoelements

Zinc oxide plays an important role in semiconductor ceramic elements for operation at elevated temperatures or high voltages. Such thermoelements can be produced to cover a broad range of thermal and electrical properties.

Papers

Uses for 13 industrial types of semiconducting thermistors produced in the U.S.S.R. were described by Turkulets³. He also presented their compositions, properties and many tables of working parameters. The starting materials included ZnO and various other oxides and silicon carbide.

A new (1963) type of thermoelement investigated by Valeev, et al.,⁴ consisted of an oxide ceramic with unique nonlinear-resistance characteristics under high-voltage conditions. Based on ZnO, SiO₂, Al₂O₃ and ZrO₂, they had good stability with respect to short current pulses (20-40 micro-seconds), Valeev, et al., reported. (This type of thermoelement, now known as a varistor, has been the subject of many patents in recent years. Varistors are composed of semiconductor ZnO modified by other oxides. Developed

for use as lightning arresters and high-voltage surge arresters in electric transmission lines, they are based on a unique electronic property of semiconductor ZnO, nonlinear resistance.)

The voltage nonlinearity of ZnO ceramics is dependent upon the formation of segregation layers, formed by modifiers, at the grain boundaries, reported Matsuoka et al.^{1,2} of Matsushita Electric. Dopants having an ionic radius larger than that of Zn²⁺ (0.74 Å) produce such layers, they pointed out.

The kind and quantity of modifier with ZnO, and conditions of synthesis, offer wide possibilities for controlling the nonlinear properties of such ceramics, noted Voronkov, et al.³

Patents

Addition of minor quantities of selected metal oxides to ZnO, Hitachi Ltd.⁶ found, increases the electrical breakdown voltage. Example: ZnO 91, Bi₂O₃ 3, Sb₂O₃ 3, Cr₂O₃ 1, CoO 1, MnO₂ 1/2, B₂O₃ 1/2 weight %.

ZnO varistors have high-temperature stability and resistance to humidity, electrical load, and current shocks, reported Matsushita Electric^{7,8}. A composition suitable for lightning arresters consisted of: ZnO 98% plus Bi₂O₃, and CeF₃ and was sintered 5 hours at 1200°C.

A varistor ceramic composition having large nonlinearity coefficients and high varistor voltages was patented by Tokyo Shibaura Electric⁹. Example: ZnO 87, Bi₂O₃, 0.5, La₂O₃ 12, and CaF₂ 1 mole %.

(Matsushita Electric has been particularly active in the development and patenting of ZnO-based varistors. Many of its patents in this area are listed in Further References.

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Other Ceramics

A number of references were found covering the properties contributed by zinc oxide to several other types of ceramics. They are listed under the following headings in Further References.

- Ceramic colors
- Glass coatings for steel
- Glass fibers
- Porcelain
- Miscellaneous

COATINGS, SPACECRAFT

During development of the recent aerospace program, the National Aeronautics and Space Administration (NASA) found that a white coating was essential on the exterior of their manned spacecraft to provide thermal control of the interior of the crafts. In the environmental conditions of outer space, absorption of only a minor fraction of the sun's radiation is sufficient to provide comfortable temperatures within a craft; the major portion of the rays must be reflected. The development of a white coating to provide such thermal control without itself being severely degraded by the intense radiation of the sun became a NASA project.

Some of the results of the research activities generated by that project have appeared as technical papers and patents. The coating developed in those studies was patented by NASA⁷. It consisted of a stabilized zinc oxide in a silicone polymer binder. Stabilization of the pigment was necessary in order to minimize reflectance loss (yellowing) induced by solar radiation in outer space (Born, et al.¹).

Several methods of stabilization of zinc oxide were developed. Sklensky, et al.⁴, reported that degradation was minimized by doping the pigment with copper ions. The latter act as "hole" traps in zinc oxide crystals and thereby reduce the occupancy of O-vacancy defect states or adsorbed O states. Zerlaut, et al.⁶, found that a silicate treatment on zinc oxide inhibited degradation by preventing formation of "magnetic centers" by irradiation. The oxide can also be stabilized by modification with titanium dioxide at 900°, according to a NASA patent⁸ covering the use of such a modified zinc oxide in a silane binder. Markowitz, et al.², in studies on degradation of spacecraft coatings during bombardment with 10¹⁶ protons/cm², found that potassium silicate coatings with zinc oxide had lowest initial solar absorbance followed by some degradation. Modification of ZnO with ZrO₂ inhibited degradation. Of these methods of stabilization of zinc oxide, the silicate surface treatment was the one covered in the NASA patent⁷, which also specified a silicone polymer binder for the coating.

During the period of the above studies, the United Kingdom Atomic Energy Authority was likewise engaged in the development of suitable thermal-control coatings for space-

craft. A comparison of their results with those of NASA is of interest. Their investigations centered around methods of stabilization of potassium silicate coatings containing zinc oxide. Rhodes³ reported that such paint applied over a white acrylic primer retained its high reflectance for more than a year in space. Walker, et al.,⁵ modified the oxide's particle size, semiconductor properties, and surface characteristics. These modifications were accomplished by producing zinc oxide of larger particle size (to impart crack-resistant films), by heating the oxide 30 minutes at 800°C, and by coating the oxide's surface with potassium silicate. The Authority's patent⁹ on silicate paints covers the modification and use of the zinc oxide.

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CORROSION PREVENTION

The element zinc, with its high positive electrode potential, inhibits the corrosion of metals of lower potential by repressing their ionization. Some of those metals are iron and its alloys, and copper and its alloys. An outstanding example is the widespread use of galvanizing to protect iron and steel fabrications. The zinc coating provides sacrificial protection by means of its higher potential.

In aqueous systems the zinc ion (Zn^{2+}) is readily available by addition of water-soluble zinc salts and, in acidic conditions, by addition of zinc oxide. The inhibitive properties of the zinc ion are frequently enhanced by additives. These may increase protection by forming coatings, by modifying the pH of the system, by providing synergistic properties, or by other means. Illustrative of these are the following extracts from papers and patents:

Papers

Carbon steel in Albian-Cenomanian water was afforded a measure of protection, Efremov, et al.,² found by selected corrosion inhibitors. From potentiokinetic curves they noted that H_3PO_4 and also $H_3PO_4 + ZnCl_2$ were among those effective.

The Zn, PO_4 , and Cr ions are prominent in corrosion inhibition in aqueous systems and Comeaux¹ of Humble Oil has reported on the chemical basis by which they provide inhibition.

Modified zinc phosphates, too, can provide effective inhibition. Hatch and Ralston³ studied the effect of aminomethylenephosphonate-zinc mixtures for control of corrosion of steel in flood waters. They found that this zinc compound provided optimum effect at pH 8.5 compared with pH 7 for zinc polyphosphate.

Patents

The use of sodium gluconate with $ZnSO_4$ provides a synergistic effect as a corrosion inhibitor in water-carrying systems, Applied Chemicals Pty.⁴ disclosed. A synergistic effect is also imparted by the use of aminodiphosphonates with the zinc ion, Calgon Corp.^{6,7} noted and patented. Other compounds of zinc and diphosphonates are useful, they reported, as inhibitors of steel corrosion and boiler-scale formation. Addition of 100 ppm of one of these to tap water lowered corrosion of steel strips in such water from 83.1 mg/dm²/day to 0.1 mg.

An inhibitor of corrosion and boiler-scale deposits in cooling systems was developed by Drew Chemical⁹. It contains 2-50 ppm Zn or Cd ion and 0.5-100 ppm lignosulfate mixed sugar aldonate polymer.

Monsanto¹⁵ has patented a synergistic mixture of the Zn ion and an epoxyethanepolyphosphate as an inhibitor of corrosion of Fe, Cu, Al and their alloys in water systems.

Zn, sulfamate, and phosphate ions in a mole ratio of 3:2:2, respectively, are the basis of inhibitor compositions developed by Murray¹⁶⁻¹⁸ for use in closed water systems. They passivate the pipe surface by depositing a film of $Zn_3(PO_4)_2$ which prevents diffusion of dissolved oxygen.

A mixture of $ZnCl_2$ 20ppm, P_2O_5 20ppm and a copolymer of acrylic acid-isopropylacrylate 40ppm was patented by Rhone-Progil²⁰ for corrosion prevention in cooling water.

In developing corrosion inhibitors for ammonia-refrigerating equipment, Ges. fur Linde's Eismaschinen A.G.¹⁴ utilized the complex-forming properties of Zn, Cd and Cu in ammonia. A 2% solution of the oxides of those metals is added to the equipment.

Corrosion of stainless steel (type 347) and aluminum (type 61S) by fuming HNO_3 is inhibited by addition of 0.1-10% Zn [as ZnO or $Zn(NO_3)_2$] Phillips Petroleum¹⁹ reported. Moreover, when the acid thus treated is used as a rocket-

engine fuel oxidant, the Zn also serves to increase the ignition delay.

Sodium phosphate with admixtures of 0.5-5.0% Zn, Ca, Ni, and Al (as their oxides) is superior to sodium polyphosphate as an antirust agent for iron and steel, Japan Organo¹⁰ found.

Zinc compounds also contribute to the corrosion-inhibitive properties of aqueous coatings, slips, and slurries applied to iron and steel surfaces, as indicated in the examples below.

A mixture of zinc dithiophosphate and calcium salts of mahogany sulfonic acids was developed as a rust preventative by Barker⁵. Zinc dialkyldithiophosphate mixed with organic compounds was patented by Kohblank¹¹ as a water-displacing corrosion inhibitor. It provided 12 months of protection of iron and steel in storage in a high-moisture atmosphere.

ZnO, H₃PO₄ and fatty amines, either simply mixed or reacted, are the basis for slushing compositions developed by Koppitz, et al.,¹² for protection of metals against corrosion.

Zinc chromate 1,000, anhydrous Na₂SO₄ 50 and calcium stearate 10 parts is a solid corrosion inhibitor patented by Kurita Industrial Co.¹³

Sinclair Refining²¹ developed a lube oil coating for application to the interior surfaces of metal tanks to protect them from corrosion by both salt and water. To the lube oil was added barium mahogany sulfonate, zinc dithiophosphate and an alkylphenyl phosphate.

Surfaces to be coated by the electrophoresis process require special protection from corrosion and Dainippon Paints⁸ developed a product for that application. It consisted of a solution containing the ions of the following metals or radicals: Zn, Al, As, Ni, PO₄, F, NO₃ and NO₂.

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COSMETICS

The optical and biochemical properties of zinc oxide and its derivatives impart special features to a variety of cosmetic preparations for care of the hair and skin. In powders and creams it protects the skin by absorbing the ultraviolet sunburn rays; in burn ointments it aids healing.

Simple salts of zinc provide astringent and skin-conditioning properties to creams, while more complex salts furnish fungistatic properties which contribute to the effectiveness of deodorants, soaps, antidandruff and antiseborrheic preparations.

Papers

A survey of the chemical and biochemical properties of zinc compounds in cosmetics was prepared by Fryer¹. He presented information on such applications as zinc oxide in face powder, zinc salts as astringent-deodorants and zinc soaps in cold cream. His paper included 20 references as sources of more detailed information.

In another survey in this field, Maisano, et al.,⁶ reviewed the composition and properties of inorganic antiseptic compounds. It covered the compounds of many metals, including zinc, and listed 71 references.

A subject of particular importance in the cosmetics field is the extent to which compounds are absorbed through the skin. In experiments with radioactive ⁶⁵Zn, Micaneck, et al.,⁷ showed that on white rats "even water-insoluble zinc compounds are absorbed through the skin." The type of ointment base, they noted, was not a factor in the absorption.

A new principle of deodorization was announced by both Lowicki, et al.,⁴ and Schrader⁸. It is based on the synergistic action of zinc ricinoleate with zinc salts of polyhydroxy fatty acids. Their activity is considered due to clathrate formation. The compositions are useful for depilatories and shampoos as well as deodorants.

Gerstein² of Revlon Research Center prepared a clear zinc pyrrithione compound and complexed it with various organic

amines to form water-soluble complexes for use in rinses, grooming agents, antidandruff preparations and conditioners. Solubility ranged from 700 to 20,000 ppm.

The exceptional efficacy of zinc oxide in protection of the skin from exposure to sunlight was discussed in at least two papers. Knox³ and Macleod, et al.,⁵ compared the effectiveness of TiO₂ and chemical sunscreens as well as zinc oxide.

Patents

A burn ointment consisting of ZnO 35, lanolin 27, ZnO₂ 12, petrolatum 26, and starch 12 weight % was patented by Bayart⁹.

The biochemical properties of zinc compounds were utilized by several laboratories for cosmetic applications. Bayer¹⁰ incorporated ZnCO₃ or Zn₃(PO₄)₂ or the zinc salt of dimethyl dithiocarbamic acid in white, solid soaps to improve the bactericidal and fungicidal activity.

Zinc 2-pyridimethiol-1-oxide was patented by Contier¹² as a component of lotions and shampoos with antiseborrheic properties.

Zinc cysteine complexes are useful in combatting zinc-deficiency diseases. Laboratories Pharmascience¹³ reported. That compound showed good compatibility with skin and no unfavorable effect on acatization.

Procter & Gamble¹⁶ discovered a synergistic effect when the zinc salt of hydroxy-2-pyridinethione was used with halogenated salicylamides in bacterial soaps and detergents.

Detergent compositions containing 1-5 per cent C₁₂₋₂₂ fatty acid salt of zinc showed low skin irritancy, Lion Fat & Oil¹⁴ disclosed.

Useful for deodorization, granulation, and skin treatment in the cosmetic and pharmaceutical industry are, according to Pek, et al.,¹⁵ water-soluble chlorophyll preparations containing zinc. The zinc is introduced as a replacement for the magnesium ion in chlorophyll to produce greater stability of the chlorophyll.

Hair-bleaching compositions containing zinc phthalocyanine, together with H₂O₂, MgCO₃, MgO, K₂S₂O₈ and (NH₄)₂SO₄ were patented by Bruce¹¹.

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DENTAL APPLICATIONS

Many advances have been made in dental cements since their inception a century ago. Zinc oxychloride, the first cement, was formed by the reaction of zinc oxide with hydrochloric acid. Zinc oxide and its derivatives have continued to contribute special properties in this field, and recent literature and patents reveal considerable activity involving zinc compounds.

Papers

A mixture of a zinc oxide cement and gutta percha is not only effective as an immediate root filling composition for dogs but also furnishes definite aid in healing of the tissues, Barker, et al.,¹ reported.

Micronutrients, including zinc, may play a role in prevention of dental caries. That was the subject of a paper presented by Hardwick⁶; it included 50 references.

Of the several types of zinc dental cements that have found extensive use, the ZnO-eugenol type has been the most important in recent years, followed by the ZnO-H₃PO₄ type. Many papers and patents have appeared on methods for modifying the eugenol type; they were not included in this survey. A new type of binder for dental cements consists of various acrylic resins, and zinc compounds are also effective with them.

Tissue reactions to improved ZnO-eugenol cements were studied by Cook, et al.,³ and significant differences were found in several mixtures tested.

Addition of ZnO-Zn₃(PO₄)₂ mixtures effectively reinforced butyl alpha-cyanoacrylate mixtures for dental work, reported Civjan, et al.,² of the Walter Reed Army Medical Center. They compared the properties of these compositions with those of ZnO-eugenol and Zn₃(PO₄)₂ cements.

The sealing, bacteriostatic, hemolytic and protein-

precipitating properties of phosphate, eugenol and polyacrylate cements were investigated by Ehmer, et al.⁵ The eugenol product was a modified type (EBA) consisting of o-ethyloxybenzoic acid, eugenol, ZnO, quartz and rosin. All three types of cements were found to be bacteriostatic, and disks of 1.5 mm thickness were impermeable to bacteria. Permeability tests with dyes showed that only the ZnO-PO₄ cement was quite dye-permeable, indicating the permeability to drugs in root-canal fillings.

The physical and mechanical properties of zinc polyacrylate dental cements were studied by Powers, et al.,⁷ and compared with those of five commercial cements.

Infrared spectroscopy of dentifrice polishing agents shows that the relative effectiveness of ZnO, MgO, Al(OH)₃, SnO₂, CaCO₃, SiO₂, pumice and kaolin is in accordance with the Beer law, according to De Freitas⁴.

Patents

Improved dental cements are covered in the following patents: Biorex Laboratories Ltd.⁹ developed two types: (1) 90% ZnO and 10% hydrogenated rosin, and (2) 84% ZnO, 6% hydrogenated rosin, and 10% SiO₂.

A self-hardening, high compressive strength cement is formed by the reaction of ZnO with poly(maleic acid) or poly(itaconic acid), ESPE Fabrik¹³ revealed.

Zinc orthophosphate tetrahydrate is a new compound with interesting properties for dental cements, as disclosed by Higashi, et al.,¹⁵ It was prepared by reacting ZnO with H₃PO₄ in an aqueous slurry with pH adjusted to 2.0. The compound sets by hydration (30 minutes) to a high compressive strength (400 kg/cm²).

A strong, hard mass for temporary fillings was prepared from ZnO and poly (acrylic acid) by National Research Development Corp.¹⁷ M. Gerner, et al.,¹⁴ were granted a patent covering a dental filling material composed of 88% ZnO in polystyrene in guaiacol.

Very strong, highly adhesive, and sterile, antibacterial cements were prepared by reacting a mixture of ZnO 88, MgO 10, and Bi₂O₃ 2 weight % with CaF₂ and a solution of H₃PO₄, Inoue¹⁶ disclosed.

American Cyanamid⁸ developed a therapeutic dental cement that relieves pain and combats infection of teeth. It consists of a ZnO-eugenol base to which is added tetracycline antibiotic and triamcinolone acetonide.

To accelerate the healing process in periodontal tissues, the dental filling for root canals consist of 20-50% ZnO₂ and 50-80% CaO₂, as patented by Odessa Science Research Institute¹⁸.

Plastic dentures and methods for their improvement were covered in the following patents: Durable and adherent dental plastics were prepared by the Central Scientific Research Institute of Stomatology¹⁰. They comprised an acrylate polymer 80-100, ZnO 20-30, and dibutyl phthalate 25-70 weight %.

The U.S. Dept. of Health, Education & Welfare²¹ patented a method of improving the adhesion between teeth and polymers in dentures. It consisted of the addition of 2-methacryloxyethyl p-hydroxybenzoate as the gallate. The filler was ZnO with benzoyl peroxide. It hardened in less than four minutes and had 2200 psi tensile strength and 16,800 psi compressive strength. These properties, they noted, were higher than those of ZnO-eugenol cements.

A dental impression material containing 30-70% ZnO in a polysulfide polymer was developed by Teledyne Dental¹⁹.

Mouth hygiene is the subject of the following patents: Colgate-Palmolive¹¹ patented the incorporation of 1% ZnO in tooth pastes at 6.5pH. Unilever Ltd.²⁰ prepared an anti-plaque and anticalculus mouth wash consisting of Zn 3,4,5-tribromosalicylanilide and other zinc salts (citrate, preferred). Only slowly soluble in saliva, they release their chemical action gradually. They penetrate between the teeth as well as into the dental plaque.

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DYES

In the specialty field of metal-containing dyes, zinc compounds contribute to the development of bright, lightfast shades, as illustrated in the following patents.

Patents

Azine heavy-metal pigments for addition to cellulose acetate and alkyd resins can be produced in brick-red shades, American Cyanamid¹ disclosed, by incorporation of the Zn ion into the formulation.

BASF²⁻⁶ covered the incorporation of the Zn ion into monoazo, cationic, and metal-complex dyes in a series of patents. Yellow to green shades of good fastness for use on wool or polyamides can be prepared by addition of Zn or other selected metal ions to monoazo dyes. Bordeaux shades on wool are produced by Zn-complex azo dyes. ZnCl_2 with diazo dyes gives a bright-red double salt. It is water-soluble and produces scarlet-red shades on polyacrylonitrile. A yellow pigment suitable for use in varnishes or as a dye (pure-yellow shades) for wool, silk, and leather is prepared as the Zn complex compound of chromium-containing organic dyes.

Ciba^{7,8} prepared a bright-red dye by the addition of ZnCl_2 to an azo compound. Furthermore, zinc cyanide reacted with substantive azo dyes was a useful compound for discharge printing, they discovered.

A diazo dye precipitated with ZnCl_2 gives a greenish-blue shade on acrylic fibers, Compagnie Francaise⁹ reported. Blue shades of superior lightfastness on cotton were developed by Daito Chemical¹⁰ by reacting an azo compound with ZnCl_2 . The product is an insoluble, complex salt.

DuPont¹¹ prepared dyes of better lightfastness for PVA resins by use of chelates of Zn, Co, Mn, Cr and Ni. Ineffective were chelates of Cd, Fe, and Pb.

A vivid orange shade for dyeing and printing polyacrylonitriles was patented by Geigy^{12,13}. It was produced by reacting triazine dyes with ZnCl_2 . However, heterocyclic azo basic dyes treated with ZnCl_2 gave a violet dye.

Hoechst A.G.^{14,15} covered orange-to-red Zn salts of pyrazolones, pointing out that they are lacquer-soluble and even faster to light than dicyclohexylamine types which are metal-free. They also reported the formation of solid, stable diazonium compounds as intermediates for production of azo dyes. The diazonium compound produced by reaction with ZnCl_2 was a yellow-brown precipitate.

Flame-resistance of dyes for glass-fiber yarn or fabrics can be improved, Nishikawa¹⁶ revealed, by treating the fabric first with ZnCl_2 , followed by application of sulfur dyes.

A thermal indicator dye was developed by the Chemical-Technical Institute, Moscow¹⁷. It consisted of PVC, ZnO and metal salts of Groups 1,2,7 and 8 of furancarboxylic acid.

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FERRITES

Zinc oxide continues as an essential ingredient in the "soft" type of ferromagnetic materials for television, radio, and tele-communication applications. In these fields ferrites based on magnetite, nickel oxide and zinc oxide are used as elements in many types of electronic devices, (Fig. 6-1).

Numerous electronic instruments for the consumer market utilize ferrites to impart specific functions. In portable and car radios, the antenna cores are ferrites designed to provide highly selective tuning. Television picture tubes (black and white, as well as color) constitute a major market for ferrites, particularly for use in flyback transformers and deflection yokes. These units are fitted tightly around the neck of the picture tube. The transformers pull the electron scanning beam back quickly to the starting line on the picture tube after each horizontal sweep. The deflection yokes, by contrast, deflect the beam both vertically and horizontally, thus projecting a picture. In the communications area, ferrites are extensively used in the filter inductors of telephone circuits to permit precise inductance adjustment for the purpose of separating channels.

Some of the varieties of composition of zinc oxide-containing ferrites that have been developed are indicated in the following patents.

Patents

Manganese-zinc ferrites consisting of Fe_2O_3 51-60, ZnO 18-25, and MnO 18-30 mole % were developed by Compag-

nie generale de telegraphic¹. These compositions are intermediate in analysis between the "soft," ZnO-containing type and the "hard," MnO-containing type. The types are not competitive as they exhibit different characteristics. The hard type is preferred for high-frequency microwave applications.

Magnetic tape for recorders is improved by use of a magnetite precipitated in the presence of ZnO, Fuji Photo Film² disclosed. The magnetite is precipitated on needle-shaped seeds of ferric oxide hydrate or ZnO, they point out.

Higher permeability and lower losses are obtained in Zn-Mn ferrites by pre-sintering the mixed oxides (including Fe₂O₃) at 1050°C, followed by grinding, washing with boiling water, molding, and sintering at 1300°C, International Standard Electric discovered³.

Use of boric acid as mineralizing agent instead of sodium chloride is a means of producing a ferrite of high magnetic strength, according to Licentia Patent-Verwaltung⁴. The composition consists of NiO 0.15, ZnO 0.35, Fe₂O₃ 0.5 mole plus 2 weight % boric acid. The mixture is annealed 6 hours at 1300°C in an oxygen stream. Property: Initial permeability is 3,000 gauss/Oersted, as compared with 1700 when NaCl is the mineralizer.

Lignes Telegraphiques & Telephoniques^{5,6} was granted patents on two ferrite compositions: (a) Addition of 1% SiO₂ increased the permittivity and thus reduced dielectric losses in ferrite composition consisting of Fe₂O₃ 56, NiO 20, ZnO 23 and CoO 1 mole %. (b) Composition having a rectangular hysteresis cycle: Fe₂O₃ 30-52, MnO + NiO + CuO 33-70, and ZnO or CdO 0-15 mole %. This ferromagnetic material is suitable for magnetic switches, recorders and similar devices.

Material for magnetic recorders consists of a mixture of Fe₂O₃ 40-50, MgO 10-40, CoO 10-40 and ZnO up to 15 mole %, reported Medvedieff⁷. One advantage of this composition: its magnetic properties can be varied over wide limits, he observed.

National Cash Register⁸ patented ferrites with the composition: Fe₂O₃ 39-43, MnO 38-50, MgO 9½-21 and up to 13 mole % ZnO.

Philips Electric N.V.^{9,10} developed these two compositions for soft-type ferrites: (a) Polycrystalline ferrites for magnetic recording heads are prepared by doping a Zn-ferrite composition to increase the average particle size from 10-20 micron to more than 50 micron. Example: Fe₂O₃ 50, ZnO 32, Ni 18, B₂O₃ + SiO₂ 0.1 weight %; (b) Soft magnetic ferrites for yoke rings and antenna rods have the composition: Fe₂O₃ 50, CuO 10, CoO 2 mole % with the balance consisting of ZnO, Li₂O and FeO.

RCA¹¹⁻¹³ was granted patents on a series of zinc ferrites: (1) Addition of carbon black to a ZnO-NiO-CoO-Fe₂O₃-MoO₃ ferrite makes possible selective partial reduction of the oxides during sintering, which could

modify the semiconductor properties of the oxides. Partial reduction of ZnO could introduce interstitial Zn⁺ ions into the crystals, for example, and thus modify their sintering and other electronic properties.

(2) Elongated particles of ferrites for use in coatings for magnetic recording medium have the molar composition aMnO·bZnO·cFe₂O₃. They are produced in elongated form by diffusion of ZnO and/or MnO into acicular Fe₂O₃.

(3) Method of diffusion of cations to form elongated ferrites: Example is as follows: Heat ZnCO₃ 19 grams and acicular, hydrated alpha Fe₂O₃ 81 grams in a H₂ atmosphere. Final product: Zn²⁺_{1.57} Fe²⁺_{7.44} Fe³⁺_{2.066} O₄ having a moment of 4.63 Bohr magnetons.

Ferrites with lowered electromagnetic losses and improved reproducibility were developed by Titenko, et al.,¹⁴ by addition of a minor amount of CoS and CuS. Composition of the mixture ZnO 13-24, NiO 10-13, SiO₂ 0.02-2.0, CoS 0.05-0.2, CuS 0.01-0.1 weight %, the balance being Fe₂O₃. The CuS, they pointed out, was principally responsible for the lower hysteresis losses and better uniformity.

Ferrites of the composition FeO 40-60, ZnO 15-40 mole %, balance NiO are improved in electronic properties by addition of 0.01-1.0 weight % MoO₃ and/or WO₃, Tokyo Electrochemical Ind.¹⁵, reported.

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FIBERS—SURFACE TREATMENTS

Zinc oxide and its derivatives contribute distinctive properties to the operations of spinning and processing of mineral fibers, as well as to resin treatments for consumer fabrics.

Patents

The use of zinc acetate in a lubricant for drawing glass fiber made from alkaline glass was patented by Mirer, et al.¹

Montecatini² reported that zinc oxide is an essential ingredient in their viscous aqueous system for the spinning of glass fibers. Example of composition of the system: H₂O 60, Na₂O 9, silicate 28, B₂O₃ 1.5, Al₂O₃ 0.9 and ZnO 0.56 weight %.

Cotton and cotton-polyester fabrics resistant to bacteria were prepared by treatment with a finishing solution consisting of mercaptopyridine-ZnO salts, Olin Corp.⁴ disclosed.

Adhesion of rubber to glass fibers was improved by addition of ZnSO₄ to the coating/sizing medium, PPG Industries⁵ disclosed in a 30-page patent. Composition of the medium: SBR latex 20-70 containing ZnSO₄ up to 5, 28% NH₄OH up to 10, H₂O 60-85 volumes. Omission of ZnSO₄ dropped tear strength of test film from 80 units to 70.

The use of zinc compounds to improve the fire resistance of mineral wool is the subject of the following three patents: (a) E. Nystrom³ prepared "Fireboard" by treating mineral wool mats with zinc stearate in a potato starch binder. Composition: mineral wool 1500 kg, zinc stearate 1500 kg, and potato starch 120 kg., (b) Ruetgerswerke A.G.⁶ bonded glass wool or mineral wool with a mixture of phenolic or urea resins and ZnCO₃-Zn₃(BO₃)₂ or ZnCO₃-Al₂O₃·9H₂O or MgCO₃ + Zn₃(BO₃)₂. The product, they reported, is a "practically nonflammable insulating material," and (c) Wood Conversion Co.⁷ treated mineral wool fibers with ZnCl₂ and NaOH, and then formed a mat which they treated with sodium aluminate to prepare "fireproof building panels."

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FIRE RETARDANTS

Zinc oxide and its derivatives were used extensively in fire retardants for the military in World War II and those zinc compounds have since been the subject of extensive research and development for preparation of fire-retardant compositions for a variety of substances. A review of the technical papers and patents in this field is presented in this section.

Papers

Draganov, et al.,¹ conducted a comparative evaluation of a

hydrated zinc borate and antimony oxide, using various fire-testing methods. The borate used was "Firebrake ZB", developed by U.S. Borax:³⁴ 2ZnO·3B₂O₃·5H₂O. They found that up to 75 per cent of Sb₂O₃ could be replaced by the borate without reduction in fire-retardant properties. Furthermore, a mixture of Firebrake ZB and Al(OH)₃ was more effective than Sb₂O₃.

Zinc chloride reduced flammability and heat-index values in Douglas fir plywood, Eickner, et al.,² found, but increased smoke-index values when retentions were above two pounds per cubic foot.

Zinc borate not only improved flame resistance of cotton fillers for plastics, Furgason, et al.,³ noted; it also reduced after-glow in that material.

Best fire-retardant properties were obtained with zinc borate compared with many pigments and chemicals evaluated by Murray, et al.,⁴ in a development program on fire-retardant paints. Alkyd resins proved to be the best binders.

Patents

The use of ZnO:

Bayer A.G.⁹⁻¹¹ developed fire-resistant polyamides based on the composition: nylon granules 700, glass fibers 300, terphenyl 100, ZnO and Fe₃O₄ 20 grams. Self-extinguishing polyamides for molding were the basis for two patents by that company. The additives in both consisted of halogenated polymers or chemicals and mixtures of ZnO and iron oxides. They pointed out that combinations of those oxides provided synergistic effects.

Domtar, Ltd.¹³ prepared noncombustible fiberboard by molding cellulose fibers with ZnO and alum in substantial quantities. Flame-retardant, flexible polyurethane foams were developed by General Tire & Rubber¹⁶ by addition of French-process ZnO (3 phr) and antimony oxide (7 phr), to obtain a synergistic combination which was superior to antimony oxide alone at 14 phr.

I.C.I.²¹ disclosed that a mixture of ZnO and a pentadiene performed in a synergistic manner in imparting flame-resistant properties to nylon.

Solutions for fireproofing textiles, Humphrey Chemical¹⁹ reported, contain ZnO, boric acid, and ammonia in various proportions. It deposits water-insoluble Zn borate on the fibers.

Rolls-Royce²⁶ developed flame-resisting coatings for high-temperature applications, such as on vital surfaces within a jet engine. The paints to form that type of coating were based on ZnO, epoxide resin and melamine hydrobromide.

Self-extinguishing nylon, patented by Teijin, Ltd.²⁹ contained 20-100% ZnO (based on weight of polymer) and 5-20% triphenylphosphine oxide. However, Toray Industries³⁰ imparted fire resistance to nylon by the addition of ZnO, Mg stannate and tetrabromodiphenylamine.

U.S. Dept. Army³³ was granted a patent on the following

composition for application to fabrics to impart fire resistance; ZnO 6-10, chloramide 65-85, C1-paraffin 6-10, and sorbitan monolaurate 0.5-5 weight %.

The use of zinc borate:

GAF Corp.¹⁵ found that mixtures of dibromobutenediol and Firebrake ZB increased the fire resistance of polystyrene, SBR, polyurethanes, and urethane rubber.

A fire-retardant composition for paper and paperboard, Humphrey Chemical²⁰ disclosed, comprises Zn borate, Sb₂O₃ and PVC plastisol or a chlorinated paraffin.

A composition for fireproofing rubber was patented by Struzik²⁷. It consisted of Zn borate 20, PVC 100, and metal oxides 20-100 parts by weight. Zn borate was the reactive agent in fire-resistant phenolic resin compositions developed by Sumimoto Bakelite²⁸. Uemura³², however, found a barium zinc borate effective in the preparation of fireproof synthetic resins.

U.S. Borax³⁴⁻³⁶ found that the addition of 0.5-30% hydrated Zn borate imparted flame-retardant properties to PVC resins. A mixture of Zn borate and ZnO contributed to exterior house paints' intumescent as well as fire-retardant properties, Vita Var Paint³⁷ revealed.

The use of zinc chloride:

A fire-resistant treatment for both wood and fabrics consists of a two-step process using ZnCl₂ and Zn(NO₃)₂ to form a water-insoluble basic zinc chloride on the walls of the wood pores and on the fibers of the fabrics, according to American Zinc^{5,6}.

Fire-extinguishing foaming agents consisting of ZnCl₂, NH₄Cl, NH₄OH, protein solution and caprylic acid were developed by Etablissements Phillips¹⁴. Henkel und Cie.¹⁷ found that cellulose textiles could be flame-proofed simply by treating with ZnCl₂.

The use of other zinc compounds:

Fire-resistant treatments for wood and fabrics based on ZnSO₄ and zinc borofluoride were disclosed by American Zinc^{7,8}, and a stock mixture for producing a fire-resistant coating was revealed by the Central Science Research Institute, Moscow¹². The coating mixture consisted of zinc aluminophosphate 40-60, perlite filler 10-20, potassium fluoride 10-20, Al(OH)₃ 13-14 and CuO 10-14. Flame-retardant, insoluble coatings developed by Krema²² consisted of sodium silicate solutions insolubilized by the addition of complex ammonia compounds of Zn, Cu, Al or Fe.

Hoechst A.G.¹⁸ prepared foaming agents for fire extinguishers from mixtures of protein-decomposition products, protective colloids, and dissolved metal amine complexes containing zinc. The mixtures, they pointed out, must contain at least 1.8% Zn.

A fire-resistant coating for fabrics, prepared by Leatheram^{23,24} was composed of PVC, acrylic acid ester,

and ZnCO₃. On heating, the PVC and ZnCO₃ decomposed, liberating products which smothered combustion. Toray Industries³¹, however, fireproofed polyester fabric by treating it with ZnBr₂, the add-on being 2.5%.

Rexall Chemical²⁵ utilized still a different zinc compound to contribute to the development of flame-retardant polypropylene. That compound was ZnNH₄ fluoborate, which was used in conjunction with antimony oxide.

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FOODS AND FOOD-PACKAGING MATERIALS

Zinc oxide and its derivatives contribute special fungistatic and chemical properties to the processing and packaging of various animal and vegetable products.

In the packaging of meat, fish, corn and peas, for example, zinc oxide has long been incorporated into the varnish linings of those metal containers to prevent formation of black sulfides which discolor the food.

Interesting applications of zinc compounds in the processing of beer, milk, and other edible products are illustrated in the following patents.

Patents

To absorb the H_2S evolved during sterilization of meat, fish and other albumin-containing food products in aluminum-foil packages, Aluminium Suisse¹ developed a method of incorporating zinc oxide as filler in a polyolefin lining. Zinc oxide neutralizes the odorous H_2S .

Armour² found that a quick-drying film for coating foods, such as sausage, could be formed by addition of $ZnSO_4$ to gelatin solutions. The zinc compound reacts with the gelatin to form zinc gelatinate films.

The head on beer can be increased and maintained for a longer time by addition of a zinc salt and gum arabic or an alginate, Baxter Laboratories^{3,4} disclosed. The effect of the foaming agent, they observed, is markedly improved by addition of 5-25 ppm Zn content.

Zinc caseinate, containing 7% Zn, can be prepared by an electrolytic-cell process using a zinc anode and an electrolyte composed of casein, $NaHCO_3$, and $Zn(NO_3)_2 \cdot 6H_2O$, Tanaka, et al.⁵, revealed.

Starch treated with $Zn(OH)_2$ is useful for the sizing of paper, Neumann reported⁶. As an example, a mixture of potato starch, $ZnSO_4$ and $Ca(OH)_2$ is heated to $58^\circ C$. The agglomerate which forms consists of steeped starch coated with $Zn(OH)_2$.

The typical, objectionable protein odor in laundry compositions based on bacterial protease and amylase enzymes can be minimized, Pabst Brewing⁷ found, by addition of zinc oxide.

The U.S. Dept. Agriculture⁸ has patented a process for preparation of sterilized concentrated milk products. It includes the addition of ZnO and ferrous salts to improve the storage properties of the milk products.

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FUELS

Addition of zinc compounds to fuels is an effective method of reducing high-temperature corrosion by the combustion gases.

Corrosion of furnaces and gas turbines by combustion gases continues to be a serious problem. The presence of vanadium compounds in fuel oils is considered particularly detrimental, and research on this problem has focused in large part on means for inhibition of the effects of that metallic element. Zinc oxide and its derivatives are prominent in such research.

Formation of deposits on sparkplugs and on walls of the combustion chambers in gasoline engines is another problem area. A new class of gasoline additives, designed to minimize the formation of such deposits, has been developed. Composed of metallic organophosphates, zinc compounds have proven beneficial in this application.

Papers

Sinclair Research Laboratory¹, Harvey, Illinois, (now part of Atlantic Richfield) has developed a new class of gasoline additives which improves engine performance and durability. During the research program, they discovered that trace metals added to gasoline can control combustion chamber deposits. Zinc was the first metallic element, added as a gasoline-soluble organophosphate, to show this favorable activity. Early test runs in a high-compression V-8 engine showed that the zinc salts surprisingly reduced the fuel octane requirement for antiknock by 20% and also reduced engine "rumble" from 70 to 40 units. These findings led to an extensive research program in which other metals were evaluated. Certain of those metals, such as titanium, manganese, and chromium had a detrimental effect on the octane or the "rumble" factors; nickel proved the only exception. Combinations of zinc and nickel additives also appear to have merit.

Another type of problem that may respond to fuel additives takes place inside oil-burning furnaces: corrosion caused by SO_2 from sulfur in the fuel oil. In investigating this problem, Murray² found that it could be minimized by addition of ZnO , MgO or NH_3 to the oil.

Sulfuric, paraffin-base crudes, however, present more operating difficulties. Their combustion causes corrosion and slagging of turbine blades as well as furnace interiors, due to vanadium compounds in the fuel oil, Svrsek³ explained. In testing the merits of various additives, he found that colloidal $Zn(OH)_2$ was an effective inhibitor at furnace temperatures in the $810-950^\circ C$ range, when added in a ratio of 6 parts zinc to 1 part vanadium.

Patents

The corrosive attack of combustion gases on metal can be reduced, Amber Chemical, Ltd.⁴ disclosed, by direct

addition of inhibitor mixtures to the combustion gas. Such mixtures consist of the oxides, hydroxides or carbonates of Zn or other selected metallic element, together with carbon black and special metal powders, they pointed out.

Antistatic additives for hydrocarbon fuels were patented by Cities Service⁵. They consisted of synergistic mixtures of barium and zinc salts of C₁₆₋₂₄ naphthenic acids and 2-ethylhexanoic acid, together with specified organic compounds. These mixtures, they noted, are effective in fuel oil, diesel fuel and turbine fuel.

Cities Service⁶ in another patent reveals smoke-suppressant compositions for petroleum fuels. Zn 2-ethylhexanoate is an effective smoke-suppressant for diesel fuel, they reported.

High SO₂ content of combustion gases can be substantially lowered, according to Dasic Chemical⁷ by the addition to the fuel oil of a colloidal emulsion of ZnO, MgO or PbO, separately or mixed.

Several methods of offsetting the effects of vanadium in fuels are the basis of the following five patents:

(a) Esso⁸ covered the addition of oxides of Zn, Al, Ca, Mg or Sn reacted with a mixture of phosphorus and sulfur. (b) Gulf Oil⁹ specifies the addition of ZnO with alkali-metal compounds. As an example, the addition of 0.12% ZnO and 0.02% Na₂CO₃ to residual fuel oil containing 203 ppm vanadium and 11 ppm Na reduced the corrosion of a stainless-steel probe from 1430 mg/in² to only 9 mg/in² at 1450°F in a 100-hour test period. (c) Power Jets, Ltd.¹¹ reported that vanadium corrosion in gas turbines was decreased by the addition of Zn, ZnO, Mg and MgO.

(d) Perolin Co.¹⁰ developed a method of preparing dispersions of metal oxides, such as ZnO, in water-in-oil emulsions. These are useful, they noted, as fuel-oil additives. (e) Shell Oil¹² likewise covered a method of incorporating oxides, hydroxides and carbonates of Zn and other selected metals into fuel oil, specifically oils of high ash content for use in gas turbines. The method consists of preparing aqueous suspensions of the compounds and incorporating them into the oil with aid of alkylamines as emulsifying agents.

Mobil Oil^{13,14} developed a method for stabilization of distillate fuel oils and lube oils against sludge formation, screen clogging, rusting and emulsification. It is based on the addition of metal salts, Zn and others, of itaconamic acid and of maleic anhydride.

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FUNGICIDES

Zinc oxide and its derivatives contribute effectively to the control of fungi in many different types of applications. Zinc oxide per se is not a fungicide; rather it is a fungistat, that is, it inhibits the growth of fungi, such as mildew on the surface of exterior house paints. This property is also used to particular advantage in the fortifying of fungicides; zinc oxide is added to fungicides to increase their effectiveness in specific applications.

Many zinc oxide derivatives are fungicides; generally they consist of zinc salts with organic anions, such as the following, chosen at random from the technical papers and patents in this section:

- Benzimidazolone
- Dimercaptoquinoxaline
- Diethylcarbamodithioic acid
- Dodecylguanidine
- Ethylenebisdithiocarbamic acid
- Morpholine
- Nitroso diphenylamine
- Polyalkoxycarbonylimine
- 8-Quinololinol

How zinc oxide inhibits the growth of fungi was discovered some years ago by Salvin¹⁵, who also established the effect of zinc oxide content and types of zinc oxide on growth of fungi. These studies were conducted under controlled laboratory conditions at Harvard University. Rate of growth was determined by measuring at periodic intervals the diame-

TABLE 6-1
CHARACTERISTICS OF ZINC OXIDES

Zinc Oxide Particle size, Microns Range	A	B	C	D	E	F	G	H	I
	0.4-2.0	<0.6	<0.2	<0.1	<1.0	<1.0	0.2-3.0 (Long) Acicular	<1.0	<1.0
Average	0.8	0.3	0.14	0.03	0.4	0.5		0.5	0.55
Total S (as SO ₂), %	0.2	0.01	0.01	0.01	0.25	0.1	0.1	1.0	8.0
Total Pb as (PbO), %	0.2	0.001	0.04	0.06	0.08	0.08	0.08	3.0	28.0

A = American process paint oxide.

B = French-process oxide of high purity (U.S.P. grade).

C = Colloidal French-process oxide.

D = Specially prepared oxide of fine particle size.

E = American-process rubber-grade oxide.

F = American-process oxide treated with phosphoric acid to lower reactivity.

G = Acicular American-process oxide.

H = 5% leaded oxide.

I = 35% leaded oxide.

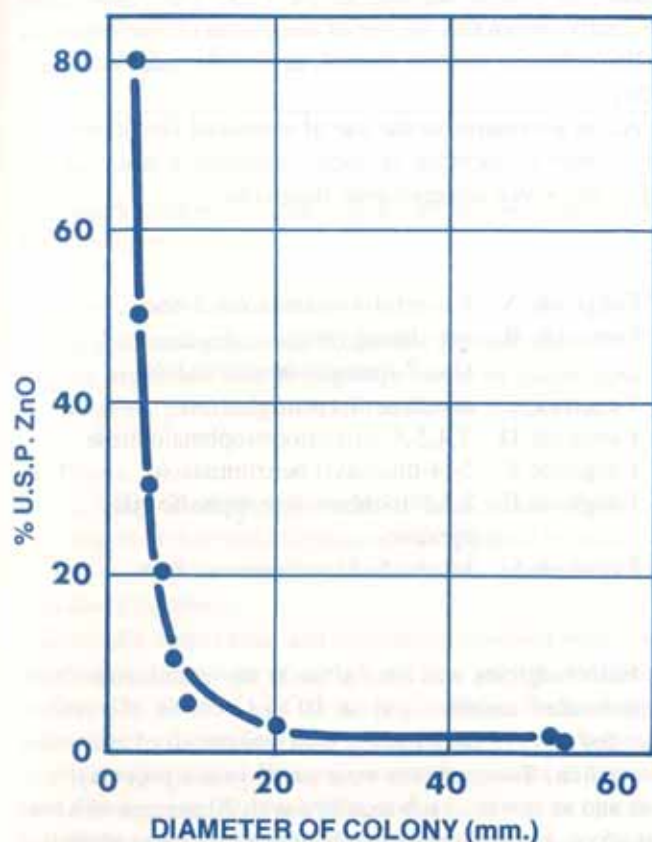


Fig. 6-2. Effect of nutrient's zinc oxide content on mycelium growth.

ter of the fungi colonies in a standard nutrient agar (in a Petri dish), with and without zinc oxide additions.

To determine the most suitable concentration of zinc oxide, a uniform quantity of *Aspergillus niger* mycelium was added to a series of the agar plates in which the U.S.P. grade of zinc oxide varied from 0.025 to 80.0%. The plates were incubated at 25°C for 220 hours, during which time the

TABLE 6-2
DIAMETERS OF COLONIES 280 HOURS AFTER
INOCULATION, in mm³

Zinc Oxide ^b	<i>Clado- sporium</i>	<i>Peni- cillium</i>	<i>Dema- tium</i>	<i>Asper- gillus sp.</i>	<i>A. niger</i> ^d	Aver- age ^c
A	c	c	17.8	35.7	65.7	39.7
B	35	23.7	16.1	43.2	52.0	32.2
C	27.7	21.0	12.0	38.8	51.6	29.0
D	13.3	16.1	11.3	25.5	40.9	21.4
E	32.0	17.2	19.0	30.6	56.6	31.1
F	11.7	18.3	22.2	30.9	54.9	27.6
G	33.1	18.0	15.6	27.5	57.0	30.2
H	33.9	25.8	21.1	30.8	69.1	36.1
I	32.3	22.0	20.8	26.7	68.5	33.0

a Each figure is the average of nine experiments.

b See Table 6-1 footnotes.

c The colonies were scattered throughout the plate; hence, exact figures were unobtainable.

d 200 hours after inoculation.

e Since this average was calculated from only three species, it represents only the approximate value.

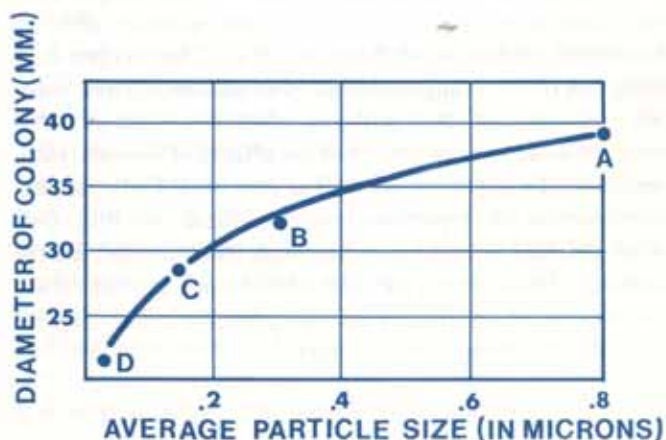


Fig. 6-3. How ZnO particle size relates to fungistatic power.

diameters of the developing mycelia were measured. The results (Fig. 6-2) indicate that the zinc oxide contents in the range 5-80% by weight of the culture medium were strikingly inhibitory.

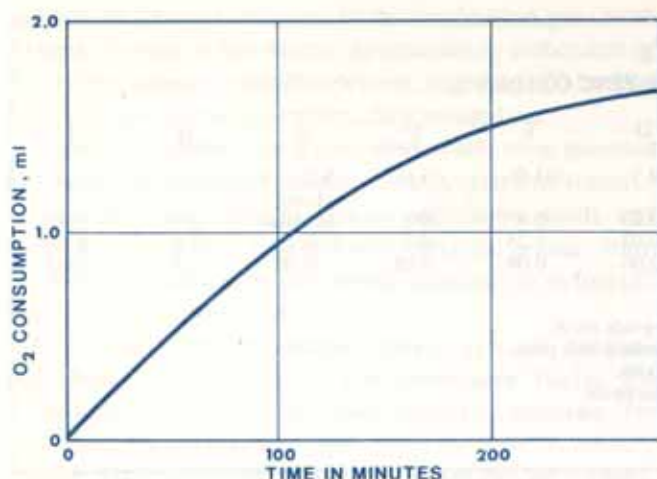


Fig. 6-4. Zinc ions (Zn^{++}) in many products containing ZnO restrict the use of oxygen by fungi. (After Salvin).

The effects of different types of zinc oxide were evaluated in a similar manner using nine specimens of oxide (Table 6-1) at 0.5% by weight of the medium and five types of fungi. From the growth measurements in Table 6-2 it is evident that the type of zinc oxide has a marked effect on the inhibition of fungi. Particle size is of major importance; the finer the average particle size the more pronounced is the fungistatic effect, as shown in Fig. 6-3.

Many workers prior to Salvin had illustrated that heavy-metal ions inhibit respiration of fungi, but the exact method of this inhibition remained in doubt. To continue such studies, Salvin proceeded to measure the oxygen consumption of *A. niger* in a 3% sucrose solution after an incubation period of 48 hours at 25°C. The oxygen consumption of the young mycelium was measured, first, without zinc ions and then with the addition of zinc or other ions. In these tests he observed the effects of sodium, magnesium and manganese, as well as zinc ions. Only the zinc ions lowered the respiratory level, and these ions (Fig. 6-4) were provided in the form of zinc oxide, the chloride, and the sulfate. Thus, the zinc ion affects the carbohydrate metabolism of the fungus and this property is basically responsible for the fungistatic effect.

Special Report

NON-MERCURIAL FUNGICIDES IN EXTERIOR LATEX PAINTS

Producers of oil-based house paints have long known how much the fungistatic properties of zinc oxide contribute

to the appearance of those coatings. They knew from years of experience that such paints for most areas of the U.S. should carry 2 - 2½ pounds of zinc oxide per gallon to keep the mildew problem under control, as well as to contribute to the control of film chalking and durability. For hot, humid climates, however, they found it necessary to bolster the mildew-resistance of their products by use of higher loadings of zinc oxide and/or the addition of mercurial fungicides.

With the advent of exterior latex house paints, producers formulated away from zinc oxide and relied mainly on mercurial fungicides for mold and mildew control. To establish the shelf-aging and weathering properties of such latex coatings with moderate loadings of zinc oxide, the Zinc Institute has been conducting for many years exterior panel exposure studies in several sections of the U.S. The results have generally shown that the use of one pound of zinc oxide per gallon enhances mildew control, decorative value and durability.

As an alternative to the use of mercurial fungicides, the Zinc Institute included in their exposures a study of the following seven nonmercurial fungicides:

Fungicide A	2-n-octyl-4-isothiazolin-3-one
Fungicide B	zinc dimethyldithiocarbamate zinc 2-mercaptobenzothiazole
Fungicide C	diiodomethyl p-tolylsulfone
Fungicide D	2,4,5,6-tetrachloroisophthalonitrile
Fungicide E	2-(4-thiazolyl)-benzimidazole
Fungicide F	2,3,5-trichloro-4(propylsulfonyl) pyridine
Fungicide G	bromo-5-chlorobenzoxazolone

Each fungicide was used alone at the manufacturer's recommended amount, and at 10 per cent of the recommended level in combination with one pound of zinc oxide per gallon. Two vehicles were employed, a polyvinyl acetate and an acrylic, each modified with 20 per cent of a long oil alkyd. Each of the 46 paints in this series was applied as a two-coat system to yellow pine panels. The panels were exposed north vertical at sites in New Orleans, Louisiana, and Ashtabula, Ohio, in May 1973. The mildew results of the first nine months' exposure at New Orleans, recently reported by Madson⁹, are given in Table 6-3.

These tests show that the use of zinc oxide in acrylic and PVA latex paints is necessary to provide acceptable decorative value to the consumer during early weathering. Many of the nonmercurial fungicides in these tests failed to provide protection against mildew in the absence of zinc oxide.

A review of the technical papers and patents collected on this subject for the years 1965-74 is presented below; the

TABLE 6-3

NEW ORLEANS PAINT EXPOSURES AFTER NINE MONTHS

	Mildew Ratings (1-10; 10 = no mildew)			
	Acrylic Vehicle		PVA Vehicle	
	No ZnO	With ZnO	No ZnO	With ZnO
Fungicide A	6	10	3	9
Fungicide B	0	10	5	9
Fungicide C	4	10	4	9
Fungicide D	5	10	5	10
Fungicide E	2	9	2	10
Fungicide F	5	10	5	10
Fungicide G	8	10	8	10

references obtained for the period 1955-64 are listed in the Further References.

Papers

The technical papers on fungicides for the years 1965-74 may be organized into three groups based on major types of applications: paints, agriculture, and other applications.

(1) Paints

In a study of shelf-preservation of latex paints, Carter, et al.,¹ reported that mold formation was inhibited by mixtures of ZnO with 1,2-benzisothiazolin-3-one; tributyltin oxide was also effective.

ZnO, Ba metaborate, and mercury compounds were compared in a three-year study of mildew growth on coated surfaces by the C-D-I-C Society for Paint Technology². They observed that ZnO provided long-term protection.

In a comparison of 18 nonmercurial fungicides in exterior latex house paints, Erdman⁶ found that none was as satisfactory as the control standard, ZnO with phenylmercuric propionate. But the effectiveness of each of the 18 nonmercurials was improved by the addition of ZnO.

The method of production of ZnO may influence its fungistatic properties. Hoffman, et al.,⁷ of Melbourne, Australia, reported that ZnO produced from metal was superior to ZnO made from ore, when tested for mildew inhibition in exterior latex paints. In that climate, high ZnO loadings are necessary to provide fungistatic properties sufficient to inhibit mildew. ZnO produced from metal, for example, was incorporated in these paints at 57% by weight of the pigment portion. In tests on linseed oil paints in tropical areas, Rischbieth, et al.,¹² noted that mold resistance was markedly

improved by use of more than 15% ZnO (by weight of total pigment) in the formulations and that a chalking type of ZnO was superior to nonchalking type.

(2) Agriculture

Laboratory and field tests on Zineb and other fungicides against downy mildew on lettuce showed that Zineb was highly effective, according to Channon, et al.,³ (Zineb is Zn ethylenebisdithiocarbamate.)

In an evaluation of fungicides for control of Curvularia leaf blight on corn, Davide⁴ found the following to be the most effective: "Omadine" (50% Zn salt of 2-pyridine) and "Orthocide"-50W (50% Captan thiol oxide).

Zn diethylcarbamodithioate controlled the pathogenic agent of root rot on cotton seed, without adversely affecting germination, Maksudov, et al.,¹⁰ observed.

Zincop, a copper-zinc fungicide, was found effective as a protective treatment on potatoes, Trzecki, et al.

The properties of Zineb and Ziram (Zn alkylidithiocarbamates) were reviewed by Zawadzka¹⁷.

(3) Other Applications

The antibacterial activity of Zn pyridinethiol oxide, El-khouly⁵ observed, was more effective than thiocarbanilide against *Staph. aureus*.

Psoriasis vulgaris was treated effectively by use of a mixture consisting of ZnO paste, Amylum paste, Lactacyd-pH 2, and anthralin, Hulsebosch, et al.,⁸ reported.

ZnCl₂, Money¹¹ noted, is an alternative to sodium chlorite for short-term preservation of hides and skins. The use of ZnCl₂ with a fungicide was the least expensive and safest of several alternatives, but the fungicide could cause an effluent problem.

An ammoniacal-ZnO treatment developed by Shields, et al.,¹⁴ controlled fungi and molds in pine lumber. The composition of the solution: 5% ZnO, 6% (NH₄)₂CO₃ in 6% NH₄OH. This treatment reduced the incidence of stain fungi and molds despite warm, humid conditions; the treatment was effective in prevention of development of chemical brown-stain during kiln-drying; and it imparted hydrophobicity to the lumber, enabling the wood to shed water during exterior storage.

Fungus-resistant XM205 nonmetallic cartridge case was developed by Teitell and Ross¹⁵ of Frankford Arsenal. It is based on kraft fiber containing 0.3% Zn pyrithione.

Patents

Salts of Zn with p-nitrosodiphenylamine are new fungicides¹⁸. The addition of 0.5-3 weight % ZnO to Maneb lowered its phytotoxicity and increased fungicidal activity¹⁹. (Maneb is a dithiocarbamate of manganese.) Coprecipitates of Zineb and Zn N-morpholinodithiocarbamate showed greater fungicidal properties than mechanical mixtures of these compounds²⁰.

Dow Chemical^{21,22} patented Zn alkylenebisdithiocarbamate complex compounds as antifungal agents and growth promoters for plants. Complexes of zinc salts and 8-quinolinol, GAF²³ disclosed, are useful as algicides in swimming pools, and as fungicides in greenhouse soils. Kawaguchi Chemical²⁴ developed a bactericide by means of the following procedure: ZnO was heated 2 hours with a solution of 2-mercaptobenzothiazole in PhNH₂. Addition of methanol to the cooled mixture precipitated the Zn salt; m.p. 302-4°C.

Minnesota Mining²⁵ prepared zinc algicides for roofing granules by treating 2,000 parts by weight of granules with 20 parts ZnO and 15 parts of a 10% solution of AlCl₃. Shingles showed no algal growth after 25 months' exposure; whereas, untreated shingles were covered with algae.

Monsanto²⁶ patented a fungicide for control of apple scab based on organocomplexes of Zn and Ni (2:1 ratio). Nippon Kayaku^{27,28} found that a double salt of Zineb and n-dodecylguanidine is a very effective fungicide for use on apple and pear trees.

Zinc borate with antibacterial properties was developed by Nippon Oils & Fats, et al.,²⁹. The properties can be modified by adjusting, within limits, the ratio of ZnO, B₂O₃ and H₂O in the formula. ZnO/B₂O₃ ratio limits are 1:3 to 3:1; whereas, those for B₂O₃/H₂O are 3:1 to 1:12. The borate protects cellulose derivatives and resins of vinyl acetate or acrylate ester copolymers. In paints and adhesives they are as effective as mercury phenylacetate, and of particular interest, the borate has no toxic effects on humans or domestic animals.

Zn and antimony salts of N,N-dibutyl dithiocarbamate are mildewcides³⁰ effective against powdery mildew of the Erysiphaceae and Podosphaceae families. Some Zn salts with algicidal properties show a synergistic effect with Hg salts³². Cu, Cd, and Zn salts of dihydroxydiphenyl sulfides and sulfoxides are useful as antibacterial, antifungal, and anticoccidial agents³³. The addition of 10% ZnO to Maneb stabilizes that compound in water³⁴.

A wood preservative, having insecticidal and fungicidal properties, consists of the Zn salt of hexachloro-5 norbornene-2,3-dicarboxylic acid³¹.

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LUBRICANTS

In the research and development of improved lubricants over the past two decades, zinc oxide and its derivatives have been intently studied, their properties assessed in various types of lubricants, and many of the results have appeared in technical papers and patents. The publications reveal two major areas of interest:

(1) Zinc dithiophosphates in lubricant additives.

Prepared by reacting zinc oxide with organic phosphates, these zinc salts are used in substantial quantities as additives to lubricating oils for automotive engines, to reduce oxidation, corrosion and wear.

The merits of zinc dithiophosphates as additives has stimulated research into the means by which they function and has initiated many development programs to produce modifications of these salts. Both of these approaches are apparent in the papers and patents reviewed in these pages.

(2) Zinc oxide in miscellaneous lubricants

Zinc oxide has been found to contribute special properties in many types of lubricants, such as cutting fluids, extreme-pressure lubricants, seizure-resistant lubricants, and greases. U.S. Air Force patent U.S. 3,525,691 (8/25/70), for example, covers the composition of a solid lubricant consisting of 7% ZnO, 68% MoS₂ + Sb₂O₃ and 25% powdered polybenzothiazole. For application, a layer of this mixture is applied to a surface and heated at 600°F in nitrogen for the ZnO to react with the resin. The resulting solid lubricant film resists wear at 500°F 3-fold better than a similar composition without zinc oxide. Improved adhesion is another feature which zinc oxide contributes.

Papers 1960-74

Basic research on the lubrication process of zinc dialkyldithio-phosphate (ZDTP) is producing a variety of hypotheses to account for the mechanism of action of that zinc compound. Barton, et al.,¹ found that ZDTP is preferentially adsorbed by ferrous surfaces under service conditions to such a degree that formation of a metal-phosphate surface is a distinct possibility. Baumgarten² studied the adsorption of ZDTP by radiochemical techniques and concluded that its effectiveness in lubricating oils is due to the properties of the adsorbed film. Francis and Ellison⁶, using reflection infrared methods, found that fresh films of ZDTP adsorbed on ferrous surfaces showed five different zinc compounds: ZnO, ZnSO₄, ZDTP, and two organo-zinc complexes. Sanin, et al.,¹² detected the presence of micellar structures in mixtures of ZDTP and detergent additives of various structures in hydrocarbon media, and proposed a mechanism of action of motor oil additives based on the micellar structures.

The effects of zinc additives on the lubrication process is also being investigated by testing various zinc compounds,

as well as modifications in the alkyl radicals in the ZDTP structure. Shimizu¹³, for example, prepared and identified 14 different ZDTP structures. Kalmutchi, et al.,⁹ evaluated ZDTP with C₈, C₄ & C₈, and C₈ & C₁₁ alkyls and noted a direct correlation between ease of thermal decomposition and lubrication efficiency of these modifications. Short alkyl chains, they found, are desirable since thermal stability increases with alkyl chain length.

Thermal decomposition of zinc dialkylphosphorodithioate and its relation to boundary lubrication has also been the subject of investigations. Feng⁵ observed that pyrolysis of the dithioate proceeds in two steps at 176°C: (a) release of an olefin and (b) formation of a waxy, solid thioanhydride with anticorrosion and wear-reduction properties. Rowe and Dickert¹¹ found that the effectiveness of metal dithioates for mitigating wear under sliding conditions is directly related to their thermal stability. Gansheimer⁷, in an investigation of other phosphates, reported that mixtures of Zn₂P₂O₇ (pyrophosphate) and Ca(OH)₂ were highly effective additives for improving the lubricating properties of mineral oil.

The functions of zinc compounds, particularly zinc oxide, in solid lubricants have been reported in several papers. Devine and Sander³, in a study of the interatomic-spacing concept for solid lubricant-metal systems, found that lattice constants of zinc oxide and other solid lubricants closely match those of the bearing metal. Dunker, et al.,⁴ developed highly effective solid lubricants based on ZnO and other compounds. Holinski and Gansheimer⁸ noted that a mixture of ZnP₂O₇ and MoS₂, added to a lithium-soap grease, formed a solid lubricant film on metal surfaces under boundary friction conditions. McConnell and Benzinger¹⁰ markedly improved the properties of a solid-film lubricant based on polybenzothiazole as binder by the addition of 10% zinc oxide, followed by a heat treatment.

Patents, Lubricant Additives (1965-74)

The 27 patents in this group¹⁴⁻⁴⁰ cover the preparation and/or use of a wide array of organozinc compounds as lubricant additives. Modifications of ZDTP are prominent, as would be expected, but many other organic radicals are of interest, such as: alkenylsuccinic acid, dialkyl-naphthalenesulfonates, diphenylthioethanethiolates, haloalkanoic compounds, phenylphosphinates, phosphorodithioates, and succinimide.

Patents, Miscellaneous Lubricants (1965-74)

Zinc oxide and its derivatives contribute to the performance of a variety of types of lubricants, as illustrated by the patent references for this section. ZDTP is useful in metal-forming lubricants⁴¹, such as the rolling of billets, and also in gear-cutting⁵² and grinding⁵³ compositions. Toyo Kogyo⁶⁴

developed a process for forming an antiwear film of ZDTP on metal surfaces by a baking operation. Lubrizol⁵⁵ patented compositions of ZDTP, ZnO and propylene oxide as extreme pressure lubricants.

Zinc phosphorodithioates were components of lubricant compositions developed by Ethyl Corp.⁴⁸ and Lubrizol⁵⁶⁻⁵⁸.

Zinc oxide imparts special properties to greases and a variety of other types of lubricants. Amalgamated Oxides, Ltd.⁴² prepared gelled greases based on a special type of zinc oxide, i.e., an ultra-fine particle size ZnO (58 m²/g surface area) coated with stearic acid. Chevron Oil⁴³ found that greases thickened by use of aluminum soaps are stabilized against heat by addition of ZnO and carboxylates. Such greases, they noted, are useful in the lubrication of food-processing equipment. Entin, et al.,⁴⁵ developed a bearing grease consisting of ZnO and PbO in mineral and castor oils thickened with lithium and potassium soaps of C₁₇₋₂₀ fatty acids. Esso⁴⁶ disclosed that a mixture of solid thickening agents in an extreme-pressure grease is more effective than the use of only one or two such agents. The patent covered lubricant fluids thickened with colloidal asbestos, 1-15, fluorocarbam powder 1-15, and talc or ZnO 1-25 weight %.

Miscellaneous applications of zinc oxide in lubricants are these:

- Oils for knitting machines, to prevent staining of textiles. A composition patented by Esso⁴⁷ consists of lubricating oil 95, ZDTP 0.5, oleic acid 0.5, sperm oil 3 and ZnO dispersion 1 weight%. The ZnO dispersion comprises mineral oil 94, Zn naphthenate 5, and fine particle size ZnO (0.11 micron) 1 weight %.

- A lubricant for molds⁵⁴ consists of mineral oil 20, ZnO 15, talc 5, Al stearate 40, Na stearate 10 and Ca stearate 10 weight %.

- A terrazo-resin, self-lubricating composite, patented by Dow Corning⁴⁴, is useful as bearing-forming material. For such application, large, rigid, lubricating granules (ZnO, ZnS, MoS₂, MgO) are dispersed in the resinous matrix.

- A cutting fluid⁶¹ for control of temperature and tool wear comprises a 5 per cent dispersion of ZnO in water.

- Silicone lubricant compositions containing ZnO or Zn naphthenate were patented by General Electric⁴⁹⁻⁵¹

- A seizure-resistant lubricant⁶² contains a mixture of soap 80-87, ZnO 14½-16, and graphite 5½-7 weight % in water.

- Lubricant for a press form⁵⁹ consists of graphite 4-6, ZnO 6-7, talc 19-21 and lubricating fluid 67½-69½ weight %.

- A lubricant developed by Texaco⁶³ is based on a sodium silicate solution containing a mixture of poly-p-phenylene 55, ZnO 10, and graphite powder 60 parts by

weight. The dry film has a decomposition point of 350°C.

- Films of solid lubricants are improved in wear resistance by coating with a sodium silicate solution containing metal oxides such as ZnO and PbO⁶⁴.

- A solid lubricant developed by the U. S. Dept. Defense, Air Force,⁶⁵ consists of polybenzothiazole resin 25, ZnO 7 and a mixture of MoS₂ and Sb₂O₃ 68 weight %. A film of this lubricant is applied to a metal surface and heated at 600°F in nitrogen to hasten the reaction of ZnO with the resin. This application of ZnO, they pointed out, improved adhesion and imparted more wear resistance than any other materials tested. At 500°F the film with ZnO showed three-fold more wear resistance than without ZnO.

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METALLURGY

Zinc oxide contributes special properties in such areas of metallurgy as metal extraction, metal additives, and metal treatments.

Addition of zinc oxide to silver powder used for production of electrical contacts improves the welding properties of such contacts, Kleinle¹ reported.

The dispersion hardening of metals by introduction of a hard second phase can be effective with metallic zinc. Pops and Libsch³ found that the addition of 5 per cent zinc oxide to zinc powder strengthened the resulting alloy. In a similar investigation, McCarthy, et al.,² studied the effects imparted by three types of zinc oxide on dispersoid morphology. The spheroidal type, they noted, was the most effective, particularly in its improvement of the ductility of zinc-base alloys.

Patents

Each of the following ten patent references describes a different application of zinc oxide in the metallurgical field.

Du Pont⁴ developed strong thin bodies of pure Al_2O_3 by compacting and burning at 850-1000°C an intimate mixture of granular aluminum and zinc oxide. As the ZnO oxidized the Al, the resulting Zn vaporized, leaving pure Al_2O_3 .

Carburizing, sherardizing, and similar methods for heat-treating alloy articles can be conducted in fluidized beds of fine solids, according to an Esso⁵ patent. The fine solids consist of sand, Zn-ZnO mixtures, charcoal, and others.

General Motors⁶ found that the soldering of aluminum is improved by first immersing the aluminum parts in a solution of ZnO in NaOH.

Silver-powder electrical contacts containing 3-20% ZnO (weight) provide improved wear, arc resistance, and resistance to welding, Kornienko, et al.,⁷ revealed in their patent.

Meehanite Metal Corp.⁸ found that the addition of ZnO to foundry sand molds increases their chilling effect. They reasoned that this result is due to the heat absorbed in the endothermic reaction between ZnO and the sand.

Desulfurization of steel in open-hearth furnaces is accomplished by a method patented by Skhodtsev⁹. It consists of covering the slag with ore containing zinc oxide. The sulfur in the charge reacts with the ore to form volatile ZnS.

Swiss Aluminium, Ltd.¹⁰ developed improved anodes for aluminum fusion electrolysis consisting of a mixture of oxide semiconductors. Composition: SnO_2 80-98, ZnO 0.2-7, and Fe_2O_3 0.3-6 weight %. Such anodes provide good resistance against oxygen and the corrosive effects of the aluminum fluoride melt.

Zinc and its alloys can be colored by use of a novel, two-step process developed by Toyonari Nakabayashi, Inc.¹¹. First, a porous zinc chromate film is formed on the metal parts by dipping them in a solution of chromic anhydride 10-150, potassium alum 5-50, and ZnO 2-15 g/liter.

Time of immersion is 10-60 seconds at 10-30°C in the solution of pH 1.0 - 4.0. Second, the chromated parts are dipped in a dye bath at 30-60°C for several minutes. The dye is absorbed by the porous film.

A heat-insulating packing for electrode liquid baths was patented by Vinintsa Apparatus Plant¹². The baths are used for tempering metals. The packing composition consists of a mixture of quartzite 60-68, ZnO 25-30 weight % and boric acid.

Wegematic Corp.¹³ reported that zinc oxide in gun barrels is effective in wear reduction.

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NUTRITION

The element zinc is a common constituent of all living matter. It is an essential nutrient for man, animals, and plants. (See also Agriculture.) Though our knowledge of the biological roles of the element is still in its infancy, zinc has been identified as a constituent of several metalloenzymes which catalyze various vital biological processes, including metabolism and respiration¹.

Zinc-deficiency symptoms, similar to those found in plants and animals, have been observed in humans in many parts of the world. Studies reported on this subject in recent years have indicated a favorable response of the individuals to zinc therapy. In the United States, two zinc-responsive disorders have been reported: a) poor growth of children with malabsorption of the element due to disease of the gastrointestinal tract; and b) improved wound healing². A recent

study from Denver suggests that zinc-responsive growth failure of children in this country may also reflect inadequate zinc intake due to poor eating habits. Their consumption of meat generally is small, and milk is their major source of animal protein.

Inadequate zinc intake also appears to bear a close relationship to impaired wound healing in many instances, as indicated by some of the technical papers in this section. Increasing the zinc level, readily accomplished by addition of zinc oxide to the diet, has resulted in dramatic improvement in the healing of cuts and burns.

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PAINTS

House Paints

Zinc oxide in organic coatings provides a broad spectrum of properties, optical, chemical, biochemical and physical. Over the past century the paint industry, in its constant development of improved products, has utilized various aspects of those properties to a high degree. A few examples will illustrate some of the many roles played by zinc oxide in the kaleidoscopic development of the paint industry.

Shortly after the start of zinc oxide production in the United States in the middle of the 19th century, paste-paint manufacturers discovered that they could produce coatings of brushing consistency and good suspension properties by incorporation of zinc oxide into their pastes. Such paints, they soon found, could be sold through retail outlets, thus markedly expanding the market. The improved quality of these ready-mixed coatings became apparent as their use developed. Painters noted that they furnished better hiding power, whiteness, cleaner tints, tint retention, and durability, as well as nondarkening in the presence of sulfur fumes.

In the early interior enamels based on natural-gum varnishes or cold-cut dammar, zinc oxide as the sole white pigment imparted new standards for color, brightness, and hiding power. With the passing of the years, zinc oxide enamels based on special kettle-bodied oils became popular. Although slow in drying properties, they provided excellent film integrity and notable resistance to yellowing on interior surfaces. Later, the hiding power of those enamels was increased by incorporation of new white pigments based on zinc sulfide or titanium dioxide. A major market for those

enamels in the 1920-40 period was the interior of mills and factories to improve illumination levels and facilitate maintenance conditions. In those "mill white" coatings, zinc oxide was retained as a substantial portion of the pigment content to aid gloss retention and minimize yellowing.

The incorporation of zinc sulfide- or anatase titanium-based pigments into white and tinted exterior linseed oil house paints in the mid-1920's represented a major change in film properties compared with those of the prevailing white lead-zinc oxide coatings. The test formulations, low in zinc oxide, furnished a more loosely knit film which developed heavier chalking during weathering. Repaint properties were superior to those of the lead-zinc films, but tint retention suffered due to the chalking. These characteristics of the formulations reflected the nonreactivity of the hiding pigments with the oil binder and their low protection of the binder against the destructive rays of the sun. Additions of hardening varnish failed to correct the deficiencies, but they were minimized by raising the zinc oxide-content to approximately 2 pounds per gallon. Lead-zinc paints, by way of contrast, carried 3 pounds or more of the oxide per gallon. Several years later, the apparent dirt collection on the new formulations in certain climatic areas was found to be due largely to formation of mildew. The addition of mildew additives to supplement the fungistatic effects of zinc oxide became a general practice.

In recent years the studies on the properties of zinc oxide in retail coatings have centered largely on its use in exterior latex house paints, as indicated by the following references.

Papers

In an extensive series of studies on the formulation of zinc oxide-containing latex paints, Hoffmann, et al.,¹⁻⁴ of Melbourne, Australia, reported that zinc oxide can be used with "any exterior latex vehicle if the content of unreacted monomer and of low molecular weight polymer is minimal and if proper additives are used." French-process zinc oxide proved superior, in their tests, to American-process types in fungus resistance and in less sulfide staining. They observed considerable chalking of zinc oxide-containing latex coatings in their climate and investigated that subject. The chalk, on analysis, was found to consist mainly of zinc basic carbonate. Zinc oxide, they reported, chalks more than rutile TiO_2 in latex vehicles under conditions of high humidity in their area. Addition of even small quantities (1 lb/100 gal.) of zinc oxide to exterior latex paint containing a phenyl mercuric compound for mildew control furnished several important advantages, Engelhardt⁵ observed. It minimized or eliminated sulfide discoloration, improved mildew resistance, and imparted a noticeable improvement in general appearance. These benefits, he reported, were produced by the zinc oxide additions without inducing any unfavorable change in package stability or paint-film properties.

Various other properties of zinc oxide in latex coatings were investigated. Sawyer⁸ reported on the effectiveness of zinc oxide in color retention . . . Krus, et al.,⁶ in a study of the effect of pigment concentration on internal stresses in polymer coatings, concluded that loadings of ZnO or TiO_2 should not exceed 50% of the film weight . . . Zorll¹⁰ found that acicular zinc oxide, when properly oriented by shearing stresses in the film, provides superior physical properties in solid polymer films as compared with randomly oriented particles. Water permeability was decreased 25%, tensile strength was increased 5%, and elongation at break was 60% higher. . . Tolstaya, et al.,⁹ in an investigation of the adsorption of PVC polymer by zinc oxide from PhMe solutions, observed that the quantity of PVC of 37,000 molecular weight adsorbed was influenced by the heat treatment of the zinc oxide and also by surface treatments. Treatment in a muffle furnace, followed by application of a stearic acid surface treatment, increased the quantity of such PVC adsorbed compared with unmodified zinc oxide.

Over many years the Zinc Institute has been studying the optimum use and performance characteristics of zinc oxide in exterior paints, and the results have been reported at various intervals. The results of the latest investigation in this series were recently presented by Madson⁷. They covered a four-year exposure study to evaluate various rutile/anatase titanium dioxide pigment ratios at three levels of zinc oxide in four types of latex emulsions. The following conclusions were drawn:

(1) White latex house paints containing 1.0 to 2.0 pounds of zinc oxide per gallon have excellent mold resistance and general appearance, distinctly superior to zinc oxide-free formulations containing mercurial fungicide. These findings apply to each of the four vehicles studied: vinyl acrylic, acrylic, vinyl acetate/ethylene and vinyl chloride/acrylic.

(2) A higher level of anatase titanium dioxide (20-30% of total TiO_2) is desirable for improved appearance in white latex house paints based on zinc oxide, compared with 15% anatase TiO_2 in zinc oxide-free formulations. The chalking characteristic of higher levels of anatase TiO_2 during weathering provides a self-cleaning action.

(3) The can-stability data on the paints used in this program cover a period of nearly five years' shelf storage; they show very stable consistency. These results add confirmation to the growing amount of information that latex paints of excellent stability, durability, and paint properties can be made containing 1.0 to 2.0 pounds of zinc oxide per gallon.

Complementing these studies, the Zinc Institute developed exterior exposure data showing that the use of zinc oxide pigments in exterior colored latex house paints improve the quality of the products.

A colored photograph of representative panels exposed 34 months south vertical in New Orleans, La., reproduced in black and white in Fig. 6.5, shows the fungistatic effectiveness of zinc oxide in this application.

Patents

Several companies have developed for paints fungus-resistant materials based on zinc compounds. Du Pont^{12,13} developed two such mildewcides: One is a mixture of a Zn-dithiocarbamate with a new complex organic compound; the other consists of a mixture of Zn dithiocarbamate, Zn mercaptopyridine salts, and (thiazolyl) benzimidazole . . . Napko Corp.¹⁴ patented a fungus-resistant composition comprising 100 parts ZnO and one part pyrogenic Al_2O_3 . Added to paint, it checked fungus growth effectively over a four-year exposure period in Houston, Texas . . . Olin Corp.¹⁵ developed an antimicrobial agent for latex paints consisting of 20% Zn-2-mercaptopyridine-1-oxide and 80% of a mixture of bromosalicylanilides.

Dust-repelling alkyd paints were prepared by addition of a mixture of ZnO 70, MgO 5, and TiO_2 25%, as disclosed by All-Union Science & Research Institute (Russia)¹¹. Dust particles, they commented, are generally positively charged and, therefore, can be repelled by surfaces with a like charge. A polished-marble surface, they noted, is highly repellent to dust, probably because it is a basic carbonate. Zinc oxide in the above mixture is effective, they reason, due to its amphoteric properties.

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10. Zorll, U. (Forschunginst. Pigm. Lacke, Stuttgart) "Distribution and orientation of fillers in solid polymer films." *Adhesion* **2**, 46-8, 1970 (Ger.).

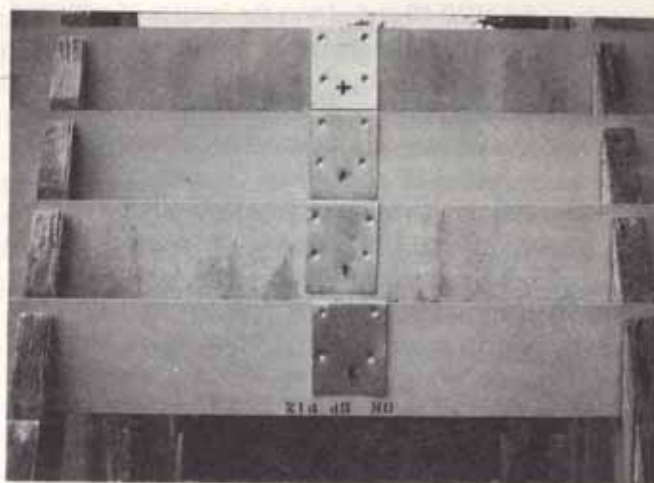


Fig. 6-5. Zinc oxide pigment improves performance of tinted exterior latex paints. Primed red cedar panels show differences after 34 months of south vertical exposure in Louisiana when primed with solvent-thinned alkyd paint and topcoated with ZnO-tinted alkyd modified latex. From top down: acrylic latex without ZnO; with 1/4 lb./gal ZnO; polyvinyl acetate latex without ZnO; with 1/4 lb./gal ZnO.

Patents

11. All-Union Sci.-Res. Inst. (Russia), Fr. 1,499,013 (10/20/67)
12. Du Pont, U.S. 3,817,762 (6/18/74)
13. Du Pont, U.S. 3,817,760 (6/18/74)
14. Napko Corp., U.S. 3,826,825 (7/30/74)
15. Olin Corp., Ger. Offen. 2,052,235 (4/27/72)

Metal-Protective Coatings

Zinc metal powder (zinc dust) and zinc compounds have long been utilized for their anticorrosive properties in metal-protective coatings, and today they are the basis of such important specialty metal primers as zinc dust-zinc oxide paints, zinc-rich coatings, and zinc chromate primers.

Zinc dust-zinc oxide paints, which came into use in the United States in the 1920's, are especially useful as primers for new or weathered galvanized iron. Such surfaces are difficult to protect because their reactivity with organic coatings leads to brittleness and lack of adhesion. Zinc dust-zinc oxide paints, however, retain their flexibility and adherence on such surfaces for many years.

Zinc dust-zinc oxide paints also provide excellent protection to steel structures under normal atmospheric conditions, as well as to steel surfaces in such under-water conditions as dam faces and the interior of fresh-water tanks.

A more recent application for zinc dust is in the preparation of zinc-rich paints, based on both organic and silicate vehicles. In these coatings, the zinc dust content is so high (about 95% by weight) that it behaves electrically like a zinc

panel and provides protection by galvanic action. These primers, available in several types of binders, are finding increasing use in various problem areas such as petrochemical and heavy-industry plants, underbodies of automobiles, and interior and top-side maintenance of freighters and oil tankers.

Zinc chromate primers (e.g., TT-P-666B and TT-P-1757) for metal surfaces is another important application for zinc compounds. Still others are described in the following references.

Papers

In a study of the potentiometric evaluation of anticorrosive pigments, Rao, et al.,⁵ found that zinc oxide improves many types of rust-inhibitive paints by imparting inhibition to bare metal near an edge.

Reviews of recent developments in zinc dust and zinc-rich primers were presented by Dahlke¹ and Van Oeteren³.

Zinc chromate primers were the subject of study by Fragnerova² and Ruf⁸. The former developed a quick-drying paint based on zinc tetroxychromate and a catalyst containing phosphoric acid. He found it useful on zinc, galvanized steel, glass, ceramics, and phenolics, among others. Ruf investigated the thermal behavior of zinc chromate paints and also their swelling in various vehicles. He found that corrosion protection is optimum at 40% by volume of zinc chromate in the dried film.

Zinc phosphate as an anticorrosion pigment was studied by Pepin⁴. In paints formulated to contain 25-32% of that pigment in an alkyd resin vehicle, the best anticorrosive properties developed at 36% pigment volume, he reported.

Addition of zinc oxide to aluminum-powder primer with an alkyd vehicle has promising possibilities, according to two reports from India. Samban, et al.,⁹ observed that, after five years' exposure on structural steel panels, the Al-ZnO primer was superior to Al-red lead, or red lead. Singh, et al.,¹⁰ obtained comparable results, but added that the primers were suitably top-coated. They reported that the Al-ZnO primer was better than either red lead or zinc chromate coatings.

In a series of studies on the antifouling properties of shipbottom paints, Rascio, et al.,^{6,7} of Argentina found that the most effective toxicant mixture consisted of Cu_2O -ZnO-HgO, followed by Cu_2O -ZnO- Cu_3AsO_3 , and Cu_2O -ZnO-Hg₃AsO₃. Vehicles tested comprised rosin-phenolic resin, and vinyl vehicles. The vinyls were superior to the resin types, they commented. Although ZnO is a constituent of each of the above effective toxicants, its action is not synergistic, they found.

Patents

Zinc-rich and zinc dust paints were the subject of several patents. Celanese Coatings¹⁴ developed a zinc-rich primer, based on a silicate vehicle, with a pot life of up to 16 hours

and a cure time of less than 24 hours. Its distinctive ingredient is a carboxylic acid amide having a solubility of less than 1% in water. Examples are: oxamide, adipamide, and succinamide . . . Diamond Shamrock¹⁵ obtained protection of five compositions of zinc dust primers with improved corrosion resistance, shear, and other properties . . . Mitsui Mining²⁰ oxidized the surface of zinc dust prior to using it in a zinc-rich epoxy paint.

Du Pont^{16,17} patented two anticorrosive primers for steel. The first consists of zinc phosphate dispersed in a benzoguanamine-formaldehyde copolymer and suitable solvents. The coating is baked on steel ten minutes. The second primer contains hydrated zinc borate in alkyd or other suitable binders. It is said to provide excellent corrosion resistance for automobiles, trucks, and appliances.

A mixture of B_2O_3 and ZnO in water was found by Borax Francais¹³ to afford protection to iron and steel when sprayed on their surfaces.

Addition of ZnO to a shipbottom paint improves its antifouling action by promoting leaching of Cu from the film, Japan National Railways¹⁸ disclosed. Example of composition: Rosin varnish 43, Fe_2O_3 8, pigment 12, Cu_2O 21, ZnO 11 and solvent 5%.

Zinc molybdate pigments or their paints were patented by two companies. American Metal Climax¹¹ prepared a corrosion-inhibiting molybdate pigment from a mixture of ZnO 36, MoO_3 64, and CaCO_3 400 parts. This combination is stirred in water at 70°C, then calcined 8 hours at 550°C . . . Oakite Products²¹ patented a wash-primer coating consisting of the conventional polyvinyl butyral-zinc-tetroxychromate composition in which the chromate pigment is replaced by zinc molybdate.

Zinc oxide aids in the electrostatic deposition of coatings. Aquitaine-Organico¹² revealed that the addition of only 0.3% ZnO to polyundecanamide coatings eliminated the nonuniformity of the deposition and the poor adhesion to the metal sheet. After deposition, the coating is heated in an oven 4-5 minutes at 220°C.

Rolls-Royce²² included zinc oxide as a fluxing agent in an intumescent paint for the interior of jet engines. The composition: ZnO 60, melamine hydrobromide 180, Araldite resin 88, diaminodiphenyl sulfone 32, and methylcyclohexanone (solvent) 203 parts.

Matsushita Electric, et al.,¹⁹ prepared an inorganic coating composition consisting of a ZnO- TiO_2 (ratio 1 : 1) mixture calcined 2 hours at 900°C, phosphates of Al, Ca, and Mg, and ammonium silicate. The coating, sprayed on steel, is baked 20 minutes at 150°C to produce a film resistant to water, weather and impact.

A coating containing a dispersion of Al powder and ZnO was patented by Teleflex²³. Composition: Al 1300, ZnO 250, CrO_3 12 grams, H_2O 650cc and 3000cc sodium silicate (43% solids). Applied to steel, it is dried at temperatures up to 150°F, then heated to 600°F over 6 hours.

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8. Ruf, J., "Properties of active chromate pigments in primers. Thermal behavior in finished paints. Swelling in various vehicles." *Korrosion* **25**, 65-70, 1974.
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11. American Metal Climax, Ger. Offen. 2,334,542 (1/24/74)
12. Aquitaine-Organico S.A., Ger. Offen. 2,134,127 (5/25/72)
13. Borax Francais S.A., Fr. 2,029,285 (10/16/70)
14. Celanese Coatings, Brit. Amended 1,103,832 (3/25/70)
15. Diamond Shamrock, U.S. 3,819,425 (6/25/74)
Diamond Shamrock, Ger. Offen. 2,352,150 (4/25/74)
Diamond Shamrock, Ger. Offen. 2,352,143 (4/25/74)
Diamond Shamrock, Ger. Offen. 2,352,130 (4/25/74)
Diamond Shamrock, Ger. Offen. 2,352,104 (5/2/74)
16. Du Pont, U.S. 3,829,395 (8/13/74)
17. Du Pont, Ger. Offen. 2,317,104 (11/22/73)
18. Japan National Railways, Japan. 72 40,452 (10/13/72)
19. Matsushita Electric & Kansai Paint, Japan. Kokai. 74 26,335 (3/8/74)
20. Mitsui Mining & Smelting, Japan. 72 08,700 (3/13/72)
21. Oakite Products, U.S. 3,272,663 (9/13/66)
22. Rolls-Royce, Brit. 1,215,286 (12/9/70)
23. Teleflex, U.S. 3,656,975 (4/18/72)

PHOSPHORS

Some of the unique electronic properties of zinc oxide are utilized in the preparation of phosphors based on that oxide. By selection of suitable dopants and heat treatments, zinc oxide phosphors can be produced in a range of colors, speed

of decay, and activation properties. The methods of preparation of such phosphors covered by patents in the period 1965-74 are presented below.

Several patents covered the preparation of zinc oxide phosphors for television picture tubes and other cathode ray devices. Glinka, et al.,^{2,3} disclosed the composition of two ZnO phosphors for cathode-ray-tube coatings: (1) ZnO:Zn + 20% 2CaO·Al₂O₃·SiO₂·Ce₂O₃ and 60% ZnSe:Ag, Ni; and (2) ZnO:Zn + 20% Sr₃(PO₄)₂:Eu and 60% ZnSe:Ag, Ni. These phosphors provide almost instantaneous decay, a primary requirement of coatings for the face of television picture tubes. Tokyo Shibawa Electric⁹ developed blue-emitting phosphors by the addition of up to 35% ZnO to ZnS:Ag, followed by a two-hour heat treatment at 900°C. These phosphors were developed for use in television picture tubes. Westinghouse^{10,11} patented high-speed phosphors based on ZnO doped with aluminum, gallium or indium. They observed that each atom of dopant adds one free electron to the conductivity of the phosphor, resulting in very rapid decay characteristics, e.g., 10⁻¹⁰ sec.

Luminous substances based on zinc oxide-containing phosphors were the subject of a number of patents. Owens-Illinois⁵⁻⁷ developed photoluminescent glass systems possessing high output emission levels and high stability. One consisted of SiO₂ and Al₂O₃ with a synergistic zinc oxide phosphor, e.g., SiO₂ 30-80, Al₂O₃ 1-20, and ZnO:Cu 10-25 weight %. A second patent disclosed the formation of Zn₂SiO₄ crystals to produce a bi-colored luminescent glass. At low-voltage electron bombardment, it luminesced green; at high voltage the luminescence was blue. In a third patent, Owens-Illinois covered the preparation of surface-crystallized glass for cathode luminescent glass, cathode ray tubes, and light bulbs. Containing a high content of ZnO, they were prepared in both red and blue luminescence types. Philips Electric⁸ developed zinc-lithium-gallate phosphors which furnished 60% light yield and 8.5% conversion under ultraviolet or electron excitation. Westinghouse¹² patented ZnMgSiO₂GeO₂ as a luminous substance, noting that the use of Bi₂O₃ as additive increased the light output 8%.

Paper luminescent under x-rays was prepared by incorporation of ZnO into the paper pulp, Arjomari-Prioux S.A.¹ disclosed. Minnesota Mining⁴ patented a method of preparing ZnO crystals with high fluorescence efficiency. The method included doping ZnO with Zn, ZnS, CdS, S, In₂O₃, Ga or hydrogen to obtain an active donor level of up to 20 ppm.

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1. Arjomari-Prioux S.A., Fr. Demande 2,029,427 (11/27/70)
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3. Glinka, A., et al., U.S.S.R. 238,020 (2/20/69)
4. Minnesota Mining, Ger. Offen. 2,347,881 (3/28/74)
5. Owens-Illinois, Inc., U.S. 3,440,172 (4/22/69)
6. Owens-Illinois, Inc., Fr. 1,498,646 (10/20/67)
7. Owens-Illinois, Inc., Fr. 1,498,645 (10/20/67)
8. Philips Electric, N.V., Ger. Offen. 1,961,332 (7/2/70)
9. Tokyo Shibawa Electric, Japan. 73 31,477 (9/29/73)
10. Westinghouse Electric, U.S. 3,583,929 (6/8/71)
11. Westinghouse Electric, U.S. 3,534,211 (10/13/70)
12. Westinghouse Electric, Ger. Offen. 2,039,526 (3/9/71)

PHOTOCOPYING

Some of the unique electronic properties of zinc oxide are distinctively utilized in the photocopying process described in the pages on Photoconductivity in Chapter Four. For use in that process, zinc oxide is increased in photoconductivity and semiconductor properties by special heat- and/or doping treatments (addition of foreign elements). Also, zinc oxide is greatly modified in optical properties to increase its absorption of light rays in the visible region. This process, known as sensitization, is generally carried out by addition of certain dyes, which are absorbed on the surface of the zinc oxide. The dyes may be added to the dry oxide, to the liquid coating mixture, or to the coating after application to the paper base (known as the zinc oxide layer). Finally, the layer may be modified by additives to further improve sensitivity or other properties.

The multiplicity of variables evident in the maze of treatments and additives for zinc oxide has resulted in a large number of patents, many of which are described below.

Zinc Oxide Preparation

Commercial zinc oxide for photocopying is generally produced from metallic zinc, rather than ore, to obtain a product of higher purity. Some companies^{1-3,6,7} in the photographic field have been issued patents on modifications of that French process to develop products of high photosensitivity.

Zinc oxide may also be prepared by decomposition of certain zinc salts. Fuji Photo Film³⁻⁵ disclosed two such processes: thermal decomposition of zinc oxalate, for example, at 500°C; aqueous decomposition of $\text{Zn}(\text{OH})_2$ or basic ZnCO_3 by heating in an autoclave.

Zinc Oxide Sensitization, by Doping and Heat Treatments

Most of the patents reviewed indicated that doping accompanied the heat treatments, only two exceptions being noted. One⁹ of these was developed to produce a photoconductive zinc oxide with uniform water-dispersion proper-

ties, through reduction in the degree of aggregate formation. The treatment consisted of heating French-process zinc oxide in a stream of air and water vapor for 5 minutes at 700°C. The other exception¹⁷ stressed the importance of semiconductor properties to impart the required electrostatic effects in the charging of the zinc oxide layer during the photocopying operation. The color of luminescence of the oxide under irradiation at 3650 Angstrom units is indicative, it noted, of the suitability of the zinc oxide. A lavender or orange luminescence is desirable; green or yellow is objectionable, and can be converted to the favorable colors by reducing the zinc oxide in H_2 for 10 minutes at 1000°C.

In the dopant processes, a majority introduced metals of 2+ or 3+ valence, particularly Al^{3+} and In^{3+} . Ricoh Co.¹⁸ disclosed that their process utilizes 0.5% indium oxide as the dopant since it reduces electrical resistance of zinc oxide, thus increasing electrosensitivity. In this process the zinc oxide and dopant mixture is degassed (an important step to remove oxygen from the ZnO surface) by heating in nitrogen to 800°C. It is then heated 10 minutes at 850°C in a reducing atmosphere, 70% N_2 -30% H_2 , to form Zn^+ ions in the mixture. Such ions further increase the electrosensitivity.

Three of the patents in this category specified the use of monovalent metallic elements as dopants. One¹⁰ covered the addition of sodium, potassium or lithium in the form of cyanide or carbonate. Their mixtures with zinc oxide are heated above 650°C and below the sintering temperature of zinc oxide in a mildly reducing atmosphere. A second patent¹¹ on monovalent dopants disclosed the use of silver and lithium compounds as additives to improve the photoconductivity of zinc oxide, while another¹² specified only the use of lithium.

The use of quadrivalent elements germanium and tin as additives was the subject of two patents. The first²¹ incorporated their oxides into zinc oxide by heating to 600-900°C in a nonoxidizing atmosphere consisting of a mixture of nitrogen and hydrogen. The second²⁵ specified a temperature range of 750-850°C and the addition of zinc or magnesium vapor to the furnace atmosphere.

Sulfur and its compounds were found effective as additives for production of photoconducting zinc oxide by two companies. One¹⁶ disclosed the addition of ZnS to the oxide and heating the mixture at 250 - 450°C in a nitrogen atmosphere. This heat treatment, they noted, forms a ZnO-ZnS complex on the surface of the oxide particles, materially increasing the speed of development of zinc oxide layers. The other company³¹ covered the addition of sulfur powder, ZnSO_4 , H_2SO_4 or SO_2 . Example: 0.02 grams of sulfur powder was added to 200 grams ZnO and heated three hours at 500°C, resulting in a three-fold increase in the photosensitivity of the zinc oxide.

Four patents were granted covering the use of silanes (e.g., $\text{Me}_3\text{SiO-Et}$ and variations) as additives. One⁸ of

these pointed out that treatment of zinc oxide with suitable silanes in vapor form produced an oxide of highest light-sensitivity and lowest dark conductivity. The other patents^{23, 24, 26} disclosed that organic silicon compounds cover a wide range of compositions and, accordingly, their selection is important in the treatment of zinc oxide. A range of hydrophobic and hydrophilic surfaces may be formed on the surface of the oxide by heating mixtures of siloxane and zinc oxide at 300 - 650°C in a nonoxidizing atmosphere. Hydrophobic zinc oxide, they observed, imparts antistatic and delustering effects in plastics; whereas, hydrophilic zinc oxide provides high photoconductivity in photocopy paper.

Antistatic and photoconductive properties may also be developed²⁰ in zinc oxide by the addition of such bivalent metallic elements as iron, cobalt, nickel or copper. The process consists of heating the mixtures at 600-900°C in a nonoxidizing atmosphere.

In the conventional photocopying process based on zinc oxide layers, a negative corona discharge is utilized and the patents cited above covered zinc oxide for use with a negative discharge. Under some conditions the use of a positive discharge may be desirable, in which case a zinc oxide capable of accepting such a charge would be necessary. Brubaker, et al.,¹⁰⁹ discussed this subject, and a process for production of a bi-chargeable (negative or positive) photoconductive zinc oxide has recently been patented¹⁹. It consists of heating zinc oxide with 0.1 - 1.0% powdered selenium at 400-500°C for 10-30 minutes.

The other patents^{13-15, 22, 27-30} describing processes for zinc oxide sensitization by doping and heat treatments illustrate other modifications of properties by addition of bivalent and trivalent metallic elements.

Zinc Oxide Sensitization, by Dyes

Patents in this area cover the application of a wide variety of types and formulations of dyes, since they differ in wavelength range of sensitization, the point of maximum sensitization, and efficiency. Since the process consists essentially of adsorption of the dye on the surface of the oxide, methods of application do not appear to represent the subject of many patents. One⁴¹, however, discloses the use of a dye solution with a solvent having a dielectric constant of more than 5 units. The zinc oxide is immersed in the solution at 20°C and allowed to stand 3 hours at temperatures below 200°C. On removal of the oxide from the solution, the excess dye is removed by washing, leaving a monolayer adsorbed. This process is suggested for use with-acridine, thiazine, cyanine and triphenylmethane dyes.

The dyes covered in other patents are these:

Azo⁴⁶—Sensitizing range: 5000-7600 Angstrom units (Å)

Azomethine⁴⁴: Range: 4000-5000 Å; maximum at 5000 Å

Cyanine^{33, 50, 51}

Eosine, phloxine and others³⁷

Merocyanine^{35, 36, 42}

Phthalocyanine⁵²—76% spectral absorption at 6800 Å.

Bis (p-aminophenyl) methane³⁴—Increased speed 37%.

Methine³²—Maximum sensitivity at 6700 Å.

Rose Bengal^{45, 49}

Phenol blue³⁸

Thione blue⁴⁰—Range: 4000-5000 Å.

Chrome black or green⁴³

Xanthene³⁹

Miscellaneous⁴⁸

Zinc Oxide Sensitization, by Chemicals

Zinc oxide or its coatings may be improved for photocopying applications by addition of various chemicals, such as the following:

Acrylamide-acrylic acid copolymer dispersant⁶⁰

Amines⁵⁸

Aniline compounds⁶⁶

Carboxylic acids, aliphatic⁶¹

Cuprous chloride⁶²

Chelating agents⁶⁷

Fluorine compounds⁶⁸

Lewis acids⁶⁵

Mercaptans^{55, 56}

Mercuric sulfide⁷¹

Naphthenates, cobalt or manganese⁷⁰

Organosilicon compounds⁵⁴

Phthalic anhydride⁵⁹

Propane sulfonates⁶³

Silver emulsion⁶⁴

Thioacetic acids⁵³

Various inorganic chemicals⁵⁷

A treatment of a nonchemical character was the subject of another patent⁶⁹. It covered the high-frequency irradiation of zinc oxide for removal of moisture from its surface.

Development of an Image on Zinc Oxide Layers

Development of an image depends on distinguishing, on a corona-charged sheet, those areas which were subsequently exposed to light from those not exposed. The areas differ in the amount of negative charge, the unexposed areas having a much higher potential. Thus, development can be carried out with a mixture of iron filings and a suitable electroscopic powder, since such a mixture carries a positive charge.

In the development process, the developer mixture is brushed across the zinc oxide-coated sheet and a potential is applied between the mixture and the ground plate on which the sheet rests. In the areas unexposed to light, the mixture is bound to the layer by the attraction between its positively charged particles and the negative charge on the sheet. In the exposed areas, on the other hand, such attraction does not exist and the mixture is readily removed by brushing, leaving

an electrostatic image on the sheet. It is made permanent by subjecting it to heat, to fuse the resinous mixture to the sheet in the unexposed areas.

Developer powders, composed of a variety of ingredients, are the basis of many patents such as the following:

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PLASTICS

The chemical and physical properties of zinc oxide and its derivatives have been the subject of an increasing number of studies in the plastics field over the past two decades and the trend is continuing. Of the 436 such papers and patents reviewed in this survey, the number published in the 1965-74 period was more than triple that of the preceding decade, and the interest in zinc compounds was expressed mainly in the form of patents rather than technical papers, as is evident in Table 6-4.

The interest in zinc oxide and its derivatives is not confined to a few types of plastics but, as shown above, covers a broad assortment. The increasing breadth of interest is also apparent. In the 1955-64 period, three plastics types (acrylics, polyethylene, and PVC) accounted for 75 per cent of the number of patents involving zinc compounds. In the more recent decade those three types were responsible for a smaller

TABLE 6-4

PUBLICATIONS ON ZINC OXIDE AND ITS DERIVATIVES IN PLASTICS 1955-1974

Type of Plastic	Number of Papers		Number of Patents	
	1965-74	1955-64	1965-74	1955-64
Acrylics	11	1	33	16
Epoxides	5	3	23	4
Nylons	1	1	19	1
Polyesters	3	0	41	7
Polyethylene & polypropylene	11	5	63	18
Polyvinyl chloride (PVC)	14	11	56	27
Styrenes	3		7	1
Urethanes	2	1	22	7
Other	8	1	12	0
Total	58	23	276	81

portion (55 per cent) of the patents, as polyesters, epoxides, nylon, and urethanes moved ahead. The technical papers and patents indicate that zinc compounds can provide a variety of properties in the plastics field, whether added in the polymerization process or incorporated into the compositions. In the polymerization step, zinc salts are useful as catalysts for some types of polymers. Examples: zinc chloride for acrylics, ethyl zinc for epoxides, and zinc acetate for polyesters.

However, the incorporation of zinc oxide and its derivatives into plastics compositions permits more flexibility in use of the properties of the zinc compounds. This conclusion is illustrated in Table 6-5 which lists 15 properties of plastics compositions improved by zinc compounds. The digits in this table represent the number of mentions of each property in the patents for three classes of plastics compositions.

Classes of plastics compositions differ markedly in the properties they derive from zinc compounds, as shown in Table 6-5. This selectivity reflects the properties in need of improvement to better meet the end-use or market requirements. Examples: heat- and ultraviolet-light resistance of polyethylene, stability (clarity) of PVC, and fire resistance and antistatic properties of polyesters.

To focus-in on this complex field, the following review of papers and patents is restricted to those in which a single zinc compound, zinc oxide, was studied in the period 1965-74. This review deals with each type of plastic shown in Table 6-4; references to all other papers and patents involving zinc compounds and located in this survey are listed in Further References.

TABLE 6-5

NUMBER OF MENTIONS OF PROPERTIES OF PLASTICS COMPOSITIONS IMPROVED BY ZINC OXIDE AND ITS DERIVATIVES IN PATENTS

Properties	Classes of Compositions		
	Polyethylene & Polypropylene	PVC	Polyesters
Antistatic		3	7
Crosslinking	2		1
Curing	1	1	
Dyeability	3		3
Electrical conductivity	1	1	
Fire Resistance	1	1	5
Foam quality	2	2	
Fungistatic		2	
Heat resistance	4	9	1
Mechanical properties	2		
Pilling resistance			3
Spinning-bath additive		3	
Stability	4	14	
UV resistance	7	1	
Other	6	2	
Total	33	39	20

Acrylics

Heat resistance and mechanical strength were imparted to acrylic composites by zinc oxide. Kao Soap Co.² thermally stabilized acrylonitrile/butadiene/styrene (ABS) resin compositions by adding zinc oxide and zinc stearate. This mixture, they observed, prevented discoloration of the compositions when molded at 260°C and 10 minutes' dwell time. . . . M. Shinpo⁷ improved the heat resistance and mechanical strength of an acrylic acid-ethylene copolymer (8.3 mole per cent acrylic acid) by addition of zinc oxide. Example: 60 grams zinc oxide in 100 grams copolymer gave a tensile strength of 260 kg/cm² and no fluidity point, compared with 99 kg/cm² and 69° fluidity point for the copolymer without zinc oxide. . . . Monsanto³ prepared tough, heat-resistant, shaped items by compression-molding a mixture of 5.3 parts zinc oxide, 13.5 parts mica and 10 parts acrylic polymer at 200-300°C and 10,000 psi. . . . Nitto Chemical⁴ formed hard, thermoplastic-resin foams with a density of 0.4-0.7 grams/cm³ from mixtures of ABS copolymer, PVC resin, and resin-azodicarbonamide compounded with conventional fillers but a special vulcanizing system. The vulcanization is conducted at 160-180°C, using a system composed of 50 parts copolymer, 0.7 sulfur, 1.5 ZnO, 0.5 mercaptobenzothiazole, 0.3 D.T.G., stearic acid, and an organotin stabilizer.

Zinc oxide also provides improved properties to other

acrylic compositions. Toho Rayon⁸ prepared acrylonitrile copolymer composite fibers with self-crimping properties and a wool-like feel by heating with zinc oxide . . . Nitto Electric⁵ developed an adhesive of higher peel strength for bonding PVC to steel plate. The composition: chloroprene-acrylonitrile copolymer 90, reactive alkylphenyl resin 95, xylene resin 25, ZnO 4, toluene 230, and ethyl acetate 230 parts. Peel strength at 180°C was 8.6 kg/25 minutes . . . Ivanovo Institute¹ disclosed that partially reduced zinc oxide is an effective catalyst for vapor-phase hydration of acetylene . . . Pennwalt Corp.⁶ developed denture compositions of improved impact resistance by addition of zinc oxide to an acrylic acid-itaconic acid copolymer.

Epoxides

Zinc oxide contributes to the formation and cure of epoxide resins. Schreiner, et al.¹⁰, in a study on the influence of the photocatalytic activity of ZnO on internal stresses in coatings based on an epoxy resin, found that the increase in hardness of an epoxy coating at 200°C with a 10 volume per cent loading of zinc oxide correlated with the increase in photochemical activity of the coating . . . Epoxy-resin adhesives filled with 50 volume per cent loadings of ZnO, or finely divided talc or quartz had lower strain and higher tensile strength than unfilled test samples, Andreeva, et al.,⁹ reported . . . Hercules, Inc.¹² was granted a patent on use of zinc oxide for crosslinking of an epihalohydrin . . . Blyakhman, et al.,¹¹ found that the addition of zinc oxide to epoxy resins cured with aliphatic polyamines imparted higher tensile strength and water resistance.

Nylons

Zinc oxide imparts fire-resistant properties to nylon fibers and moldings. Bayer A.G.¹⁴ developed self-extinguishing polyamides for injection moldings by addition of synergistic mixtures of ZnO, Fe₂O₃ and Fe₃O₄ . . . Imperial Chemical Ind. (I.C.I.)¹⁶ disclosed that zinc oxide forms a synergistic mixture with hexachlorocyclopentadiene-1,4 cyclohexadiene 2:1 adduct in production of flame-resistant polyamide compositions. The mixture consists of equal weights of ZnO and the adduct. Self-extinguishing nylon-6 or -66 were prepared by addition of a mixture of ZnO and triphenylphosphine, Teijin, Ltd.¹⁷ found. Toray Industries¹⁸ developed fire-resistant polyamide fibers by addition of 7 per cent ZnO and 15 per cent polybromobiphenyl to poly(caprolactam) . . . Nylon-66 self-extinguishing moldings for the electrical industry were prepared from mixtures of nylon, glass spheres, Dechlorane, ZnO and antimony oxide, Wellman Inc.²⁰ reported.

Zinc oxide is also useful in the preparation of nylon polymers and in increasing their heat resistance. Yakhnin¹³, in an electron microscope study of nylon loaded with various

fillers, observed that ZnO, TiO₂, carbon black, among others, serve as nucleating agents for growth of polymer crystals. Hydrophilic fillers, such as ZnO, have higher nucleating power and are more effective in promoting crystallization and crosslinking than are hydrophobic fillers. . . . Toyo Rayon¹⁹ found that ZnO is superior to CaO, MgO, or CuO as a neutralizing agent for H₂SO₄ in the preparation of lactams from cycloalkanone oximes by Beckmann rearrangement, which involves the use of H₂SO₄ . . . Du Pont¹⁵ disclosed that the addition of 1-6 per cent ZnO to various polyamides increased their heat resistance in contact with copper or iron as in electrical insulation.

Polyesters

The formation of polyesters in the presence of zinc oxide imparts higher viscosity and other improvements. Voo, et al.,²² observed that ZnO reacted with unsaturated polyesters to form higher viscosity and a thixotropic body. MgO, however, proved too reactive and introduced no thixotropy . . . Vapor phase catalytic esterification of terephthalic acid with methanol was improved by addition of 50 per cent ZnO to the silica gel catalyst, according to Bhatia, et al.,²¹ . . . The addition of a mixture of styrene, ZnO and water to ethylene glycol-maleic anhydride-phthalic anhydride copolymer of acid number 20 - 100 to increase the viscosity was patented²⁷. The improved body resulted from crosslinking of COOH groups induced by the zinc oxide. This method, it was reported, produces a resin of high molecular weight when conducted at 85-95°C . . . The preparation of marblelike plates and objects of unsaturated polyester was patented²⁸, based on polyester resins increased in viscosity by addition of up to 15 per cent zinc oxide.

Fire resistance and formation of granular polyesters are aided by zinc oxide. Chemische Werke Witten²⁵ found that unsaturated polyesters which can be granulated could be prepared by condensation of fumaric acid and ethylene glycol in the presence of zinc oxide as a crystallization accelerator . . . Allied Chemical²³ developed granular, unsaturated polyester molding compositions containing zinc oxide. Example: resin 24, clay 30, asbestos 23, wood cellulose 10, ZnO 5, Zn stearate 2 and FeO (yellow) 2 parts. BASF A.G.²⁴ developed fire-resistant molding compositions based on poly (butylene terephthalate) by addition of octabromobiphenyl 10, ZnO 5, and silica fume 4 parts.

The dyeability of polyester fibers is improved by zinc oxide. Kurashiki Rayon²⁶ reported improved dyeability of poly(ethylene terephthalate) fiber by addition of up to 5 per cent zinc oxide before spinning . . . Sandoz, Ltd.²⁹ developed improved prill resistance, dyeability, and dimensional stability in copolyesters from aromatic dicarboxylic acids and diols by precipitation in the presence of zinc oxide and Ph₃P.

Polyethylene and Polypropylene

Zinc oxide mixtures stabilize polyethylene against aging and ultraviolet radiation. Eastman Kodak³⁴ disclosed that a mixture of 10 parts ZnO and 0.01 part Zn dithiocarbamate imparts a synergistic effect in stabilization of 100 parts poly alpha olefin resins against UV radiation . . . Zinc oxide doubled the transparency of poly(chlorofluoroethylene) molding resin, Daikin Kogyo³³ reported. The addition of 25 ppm ZnO raised the transparency of sheets of 2 mm thickness from 15 per cent (without ZnO) to 32 per cent . . . Phillips Petroleum⁴³ stabilized ethylene-1-butene copolymers with a mixture of ZnO and 2-hydroxy-4-(n-octyloxy) benzophenone . . . Polyethylene for electric cable insulation was improved in aging by addition of a mixture of ZnO, mercaptobenzothiazole, a trimethylquinoline and kaolin³⁹ and also by a mixture of 15-50 parts ZnO, 0.5-3 parts metal soap, and 0.5-5 parts carbon black per 100 parts polymer⁴³.

Polyolefins are improved in color, tensile strength, and vulcanization properties by addition of zinc oxide. Mitsubishi Chemical⁴⁰ disclosed that discoloration of injection-molding polyethylene and polystyrene foams by decomposition residues of azodicarbonamide is prevented by foaming them in the presence of 40 - 50 per cent ZnO by weight of the amide . . . BASF A.G.³² increased the tensile strength of open-cell ethylene-copolymer foams by incorporating (under pressure) zinc oxide and a blowing agent. The zinc oxide serves as a crosslinking agent to improve physical strength . . . Zinc oxide was effective as a temperature-control agent in the preparation of polyolefin foams, Phillips Petroleum⁴⁴ reported. Example: polymer 100, ZnO 0.4, azodicarbonamide (blowing agent) 0.2 parts . . . A suitable polyolefin stabilizer, according to Kresta, et al.,³⁸ consists of 0.8% ZnO, 0.5% Zn stearate, and 0.3% dilauryl thiodipropionate . . . Monsanto⁴² developed vulcanizable olefin copolymers (ethylene-propylene type) which cured at 160°C in 40 minutes. The curing mixture for 100 parts copolymer consisted of organic accelerator 5, ZnO 2 and sulfur 1 part . . . Porous polyethylene or polypropylene fibers were prepared by incorporation of 3 per cent zinc oxide, which is dissolved out in a HCl bath later in the process, Toyo Rayon⁴⁷ disclosed . . . Mitsubishi Chemical⁴⁰ developed antistatic polyolefins through addition of zinc oxide. Example: 0.05% ZnO is added to polyethylene containing a butyl cresol . . . Low-density polyethylene³¹ was increased in thermal resistance by ZnO, carbon black and plasticizer.

Polypropylene is improved in uv stabilization and mechanical properties by zinc oxide. Deanin, et al.,³⁰ in a study of ultraviolet light stabilization of polypropylene by zinc oxide, observed that ZnO of fine average particle size (0.11 micron) provided optimum results . . . Hoechst A.G.³⁷ developed polypropylene compositions more amenable to electrodeposition of metal by incorporating 10-50 per cent zinc oxide. Such compositions

can be economically and uniformly coated with metals.

Polyolefinic compositions with improved mechanical properties were reported by Hercules, Inc.³⁵. Examples: (a) ZnO 80 to polyethylene 100 parts and (b) ZnO 100 to polypropylene 100 parts. Shaped objects from filled crystallizable olefin polymers also benefitted from additions of zinc oxide, Hercules³⁶ found. Example: polypropylene 211, ZnO 192, kerosine 31 parts.

Polyvinyl Chloride (PVC)

Zinc oxide in the preparation of PVC was reported in several papers and patents. Dow Chemical⁴⁹ produced styrene-type bead polymerization by reacting the vinyl compounds in the presence of 3 per cent zinc oxide plus 0.003-0.012% Na₂HPO₄. Particle size of the beads was 18 - 40 U.S. screens . . . Granular PVC of 10-micron size was prepared⁵² by suspension of vinyl monomers in the presence of zinc oxide and methylstyrene. They were also transparent and uniform. The same company, Fuji Photo⁵³, also prepared granular vinyl polymers by kneading a mixture of ZnO 150, styrene 1, acrylates 80 parts and, after addition of 500 parts water, heating 5 hours at 90°C. The ZnO is dissolved out with HCl. The polymer particles are in the 5 - 70 micron range . . . Pearl polymerization of N-vinylcarbazole was effected by Ricoh Co.⁵⁷ with the use of less than 5 per cent zinc oxide by weight of the carbazole. The polymer is useful for electrical apparatus and electrophotography.

Stereoregular PVC was prepared by irradiation of vinyl chloride at 0°C or less in the presence of ZnO by Sekisui Chemical⁵⁸. Example: A mixture of 2 parts vinyl chloride and 1 part ZnO irradiated by gamma rays from ⁶⁰Co at -78° for 20 hours produced a resin with 45 percent conversion . . . The crosslinking of PVC with a reaction product of castor oil, 2-mercaptoimidazoline and a diisocyanate in the presence of 15-20 parts ZnO in 10 minutes at 180°, with no apparent degradation of the product⁵⁹ . . . In a study of mineral additives on radiation polymerization of vinyl monomers, Kornienko, et al.,⁴⁸ reported that zinc oxide and silica gel were effective and comparable at 40 per cent loadings under gamma irradiation from ⁶⁰Co.

Thermal stabilization of PVC was effected by zinc oxide. Pechiney-St. Gobain⁵⁵ discovered that the use of zinc oxide with cyano-acetamide imparts a synergistic improvement in stabilization of PVC and copolymers to heat . . . Pennsalt Chemical⁵⁶ developed a heat-stabilized poly(vinylidene fluoride) consisting of polymer 79, ZnO 6 and carbon black 15 parts. It showed a weight loss of only 6 per cent in one hour at 455°C compared with 33 per cent loss for the control.

Antistatic, fungistatic, and emulsion stability are additional properties imparted to vinyl polymers by zinc oxide. Poly (vinyl alcohol) fibers with antistatic properties were developed⁶⁰ by addition of ZnCl₂ which was converted to Zn(OH)₂ on the fibers . . . A mixture for protection of

plastic materials against organisms growing under water consists of ZnO 4.5, CuO 4.5, HgO 0.5 and perchloroethylene 80 parts⁵⁴ . . . Du Pont⁵¹ controlled the gelation of aqueous poly(vinyl alcohol) solutions by adjusting the pH in the presence of zinc oxide or other selected chemicals . . . They⁵⁰ also stabilized vinyl ester polymer emulsions on long storage by addition of zinc oxide, the emulsions being free of reactive groups.

Styrenes

Zinc oxide contributes to the formation of styrene beads, granules, and foam, as well as providing improved mechanical properties as a filler in moldings. In a method for preparation of polystyrene beads, developed by Dow Chemical⁶⁴, 100 grams of styrene monomer is stirred in an aqueous suspension containing 0.3 grams benzoyl peroxide, 3 grams ZnO and 150 grams water in a sealed glass vessel at 90-115°C for 5-7 hours. The suspension was adjusted to 9 pH with NH₄OH . . . That company⁶³ also developed a diffusion process for preparation of foamable styrene polymer granules in which zinc oxide contributed to the blowing operation . . . In the preparation of foam styrene polymers with a fine cellular structure by the reaction of barium azodicarboxylate and azodicarbonamide, Asahi, Ltd.⁶² found that the addition of 5 parts zinc oxide to 100 parts azodicarbonamide improved the process by lowering the decomposition temperature of that amide . . . In a study of the properties imparted to polystyrene compositions by fillers, Pone, et al.,⁶¹ reported that zinc oxide imparted better shearing strength than the others included in the tests . . . General Electric⁶⁵ developed a method for copper-plating sheets of polystyrene-blend elastomer. It comprised the preparation of such sheets containing zinc oxide, and reduction of the surface particles to metallic zinc. Reduction is accomplished in 7 minutes in a KOH electrolyte.

Urethanes

Zinc oxide aids in the preparation of urethane foam and to that product it imparts flame-resistance, stabilization, and corrosion protection. General Tire & Rubber⁶⁷ developed a catalyst system for preparation of urethane foam of improved heat discoloration stability. The catalyst for polymerization of a polyol-diisocyanate-PVC mixture consisted of tin dioctoate, Sb or Bi carboxylates, ZnO or Sb₂O₃, and N-methyldicyclohexylamine . . . A flexible, flame-resistant urethane foam was developed by that company⁶⁶ based on the following additives: 0.1 phr ZnO, 0.15-15 phr Sb₂O₃ and a chlorinated paraffin. They commented that, in the absence of zinc oxide, the foam was not self-extinguishing . . . Rhone-Poulenc Chemical⁶⁸ found zinc oxide highly effective in stabilization of polyurea urethanes to ultraviolet light (120 hours' exposure). Tensile strength of test specimens after such exposure: no filler, 505, 5% TiO₂ 409, 5% ZnO 580, 5% ZnO plus 1.8 betaine citrate 626

. . . Westinghouse Electric⁶⁹ disclosed a method for prevention of corrosion of metal by urethane refrigeration insulation. It consisted of the addition of 0.1-1% antacid to the urethane liquid composition. Zinc oxide was found effective as antacid in that composition.

Other Plastics

To assorted types of plastics, zinc oxide contributes to their formation and mechanical properties. Tanabe, et al.,⁷⁰ discovered a new mixed-oxide catalyst for isomerization of butenes. It consists of several combinations of ZnO and SiO₂ which showed very high activity with some selectivity. Neither oxide alone displayed any appreciable activity . . . Reichhold-Albert-Chemie⁷⁴ developed modified hydrocarbon resins by reaction of zinc oxide to form salts with semiesters of maleic anhydride and isobutanol . . . Matsushita Electric⁷² developed inorganic blowing agents for plastic foam based on phenolic molding compositions. Example: ZnO 45, Al(OH)₃ 50, and H₃PO₄ (89% strength) 100 parts . . . ABS and similar resins can be extended with mixtures of ZnO and CaCO₃ without detrimental effect on impact strength⁷¹ . . . Addition of up to 30% ZnO improves the impact strength and Rockwell hardness of Hycar 1072, Epikote 828 or Unox 201 molding materials⁷³.

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Special Report

ZINC OXIDE AS A STABILIZER FOR POLY- PROPYLENE AND POLYETHYLENE IN OUTDOOR WEATHERING

This study was sponsored by ILZRO to determine the effectiveness of zinc oxide in improvement of the ultraviolet resistance of selected polyolefins.

Organic materials are activated by UV-light energy, which initiates free-radical chain reactions, particularly oxidation in the presence of oxygen. The strength of a carbon-carbon bond is approximately 80 k-cal; UV wavelengths 2800-4000 Å correspond to energies of 100-70 k-cal. Those wavelengths, representing the UV range of the sun's rays, are, therefore, of sufficient strength to produce such oxidation reactions¹.

Most organic plastics absorb strongly in these wavelengths and are highly activated by the energy they absorb², resulting in degradation reactions, especially during outdoor weathering. Such degradation is reflected in changes in color, gloss and the development of embrittlement. Plastics for extended outdoor service thus require protection by addition of UV stabilizers. These may either reflect those rays or absorb them. Absorption should convert them to less-harmful, longer wavelengths.

Most light-stabilized plastics depend upon the use of organic UV absorbers which transform the UV rays, emitting their energy as longer wavelengths. When these are in the visible region, they cause discoloration; when even longer, they produce infrared heat. These organic UV absor-

bers, because of their cost, are not used as often or in as high concentration as desirable to provide effective protection.

Some pigments offer a degree of protection simply by reflecting or absorbing the UV rays before they penetrate the polymer to any significant depth. Carbon black, for example, is a highly effective pigment for UV stabilization as it absorbs essentially all the radiant energy, converting it to harmless longer wavelengths; but its use is limited to opaque black applications. Many pigments and extenders of high reflectivity in the visible region, such as antimony oxide, blanc fixe, china clay and anatase titanium dioxide, are not effective absorbers of UV rays. Zinc oxide is an exception, and it has long been used as a UV absorber in such outdoor products as house paints and white-rubber articles.

Method of Test

The test program, conducted by DeBell & Richardson, Inc., Enfield, Conn., consisted of the preparation and exposure of polypropylene and polyethylene plaques containing selected pigments and extenders. The investigation extended over several years and included both accelerated indoor aging and outdoor exposures.

Results of Tests

A. Accelerated Aging

Among the pigments and extenders incorporated into polypropylene at 3 parts per 100 parts polymer (3 phr), zinc oxide was the only white filler (Table 6-6) that stabilized (no flex-break) the plastic for more than 2000 hours under sunlamp* aging. The most effective type of zinc oxide was French process oxide of finest (0.11-0.25 micron) average particle size. *General Electric Co. RS-4 sunlamp.

A number of synergists were tested with zinc oxide and several imparted high improvement. Ethyl zimate (zinc diethyldithiocarbamate) proved especially effective. Optimum combinations of zinc oxide and ethyl zimate in polypropylene provided lifetimes more than 60-fold longer than the polymer alone. (Table 6-7).

Comparison of the zinc oxide-synergist and organic-absorber systems in the stabilization of polypropylene (Table 6-7) showed a 66 improvement factor for the former system compared with 13 for the latter. The results of these and other accelerated aging studies are being confirmed.

B. Outdoor Weathering Tests

Tables 6-8,-9 and -10 compare various zinc oxide/synergist systems with standard organic UV stabilizers at reportedly typical use levels in low- and high-density polyethylene and polypropylene plaques weathered 4 years outdoors at Enfield, Conn. With each of the three types of polymers the zinc oxide/synergist systems provide distinctly superior performance. Physical measurements at the end of the 4-year period showed tensile strengths in the range 1250-4430 psi and elongations of 14-130% for the plaques with the zinc oxide/synergist systems. In high-density polyethylene and polypropylene with organic UV stabilizer,

however, the plaques were brittle and registered 0% elongation.

C. Commercial Aspects

Physicals on unaged plaques show no adverse effect of loading up to 10-phr zinc oxide in film or sheet of these polymers. Zinc oxide also has no adverse effect on water absorption and, since it is insoluble in water, neutral oils, and solvents, it cannot bleed or leach out. The material can be compounded by conventional techniques and is not abrasive to processing equipment. Zinc oxide also provides the added side benefit of conferring increased mildew resistance.

Zinc oxide/synergist systems, for the formulations used in these tests, cost approximately the same as organic UV stabilizers per cubic inch of stabilized compound. However,

TABLE 6-6
UV STABILIZATION OF POLYPROPYLENE BY
SELECTED PIGMENTS AND EXTENDERS AT 3
PHR*- UNDER SUNLAMP AGING

Pigment or Extender	Initial Color	Time to Flex-break, hr	Length of Test, hr	Color at End of Test
None	White	159	423	Yellow
Clay	Off-white	161	425	Yellow
Silica	White	93	457	Yellow
TiO ₂	White	1992	1992	Yellow
Zinc Oxide	White	No break	2184	Off-white
Carbon black	Black	No break	2184	Black

*= parts per 100 parts of resin (polymer)

TABLE 6-7
UV STABILIZATION OF POLYPROPYLENE BY
ZINC OXIDE AND SELECTED SYNERGIST UNDER
SUNLAMP AGING

ZnO (phr)	Ethyl Zimate (phr)	Time to Flex-break, hr	Improvement Factor
0	0	168	1
3	0	2,184	13
10	0	3,768	22
0	1	912	5
2	1	11,100	66
Comparison Standard*		2,184	13

*Commercial organic UV absorber (0.3 phr)

given their greater effectiveness, zinc oxide enjoys a cost-performance advantage 8 to 14 times over the organic stabilizers.

Applications in development for zinc oxide-stabilized polypropylene and high-density polyethylene include safety

TABLE 6-8
ZINC OXIDE IN HDPE WEATHERED 4 YEARS OUTDOORS^a

UV Stabilizer	Phr	Tensile Strength (psi)	Elongation (%)
None	—	Brittle	0
Zinc Oxide	2	3800	130
Polygard ^b	1		
Cyasorb UV 531 ^c	0.3	Brittle	0

^a1/16-in. plaques exposed at Enfield, Conn. ^bUniroyal, Inc. ^cAmerican Cyanamid Co.

helmets, stadium seating, insulation, pallets, bags, fiber and filament, agricultural and recreational equipment.

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Note

This special report was prepared from information in the three papers listed under Cited Reference No. 30 and in the following paper:

"Low-cost UV Protection Proves Effective for Polyolefins." *Plastics Technology*, Sept. 1975, p. 11.

Additional information may be obtained from the International Lead Zinc Research Organization, Inc., 292 Madison Ave., New York, N.Y., 10017.

Special Report

ORGANOZINC COMPOUNDS AS POLYMERIZATION CATALYSTS

In a recent exploration of the chemistry of organozinc compounds, J.G. Noltes, et al., of the Organisch Chemisch Instituut, Utrecht, discovered several catalyst systems that are highly effective in the conversion of acetaldehyde butadiene, isocyanates and propylene oxide into new products of special interest: (a) Stereoregular poly-acetaldehyde in high yield, (b) butadiene cyclic trimer, the starting material for Nylon-12, (c) the trimerization of isocyanates to form isocyanurates, and (d) the formation of poly(propylene oxide) rubber.

1. Acetaldehyde

Many efforts have been made in the past to obtain polymers from acetaldehyde, which is relatively low in cost and abundantly available. With the known catalysts, however, low molecular weight products with poor mechanical properties had been obtained. The reason: The relative positions of the methyl groups in the polymer formed an irregular (atactic) structure:

TABLE 6-9
ZINC OXIDE IN PP WEATHERED 4 YEARS OUTDOORS^a

UV Stabilizer	Phr	Tensile Strength (psi)	Elongation (%)
None	—	Crumbled in 2 nd yr	0
Zinc Oxide	2	3970	14
Polygard ^b	1		
Zinc Oxide	2	4430	14
Ethyl Zimate ^c	1		
Cyasorb UV 531 ^d	0.3	Brittle	0

^a1/16-in. plaques exposed at Enfield, Conn. ^b Uniroyal, Inc.

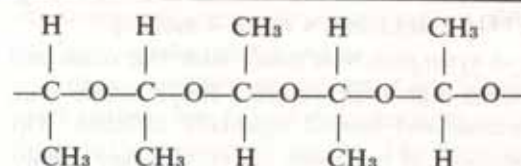
^c R.T. Vanderbilt Co. ^d American Cyanamid Co.

TABLE 6-10
ZINC OXIDE IN LDPE WEATHERED 4 YEARS OUTDOORS^a

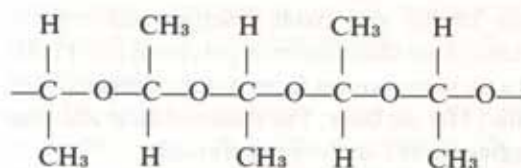
UV Stabilizer	Phr	Tensile Strength (psi)	Elongation (%)
None	—	Brittle	0
Zinc Oxide	3	Brittle	0
Zinc Oxide	2	1250	117
Polygard ^b	1		
Cyasorb UV 531 ^c	0.3	970	30

^a1/16-in. plaques exposed at Enfield, Conn. ^b Uniroyal, Inc.

^c American Cyanamid Co.



Atactic poly-acetaldehyde



Isotactic poly-acetaldehyde

Structure has a marked influence on polymer properties. The more isotactic the structure, the more crystalline is the polymer and the better its mechanical properties.

In their investigation of organozinc compounds as potential catalysts for aldehyde polymerization, Noltes, et al., reported the discovery of catalyst systems that convert acetaldehyde in high yield into almost completely stereoregular poly-acetaldehyde. Two different catalytic systems must be distinguished:

A. A mixture of a diarylzinc (e.g., diphenylzinc) and an N-arylamide (e.g., acetanilide).

Diphenylzinc alone displays a degree of catalytic activity, but it is strongly enhanced by the addition of a cocatalyst (organic amide) in the proper ratio (preferably 1:1). The presence of water, on the other hand, has a strong deactivating effect.

U.S. Patent 3,535,283, Oct. 20, 1970.

(corresponding foreign applications were also filed).

B. A ternary mixture of a dialkylzinc (e.g., Et_2Zn), water (or an alcohol, a phosphine), and an organic amide (or various other compounds containing the $\text{N}-\text{C}=\text{O}$ group).

This is a particularly effective and conveniently prepared catalyst. Whereas Et_2Zn alone is inactive (contrary to Ph_2Zn), the system $\text{Et}_2\text{Zn} - \text{H}_2\text{O}$ has some activity, but only if a very special mixing procedure is used. However, an extremely active system is obtained in a few minutes of mixing by inclusion of the amide derivative in the catalyst package.

U.S. Patent 3,579,481, May 18, 1971.

(and corresponding foreign applications).

Some practical problems, of course, must be overcome before commercialization of acetaldehyde polymer is feasible. Examples: End-group stabilization is required even as in polymerization of formaldehyde. A more serious problem is the susceptibility of poly-acetaldehyde to oxidative attack due to the presence of tertiary hydrogen atoms in the polymer chain. However, the start has been made; catalyst systems for preparing the stereoregular polymer in high yield are now available.

2. Cyclotrimerization of Butadiene

The stereospecific polymerization of dienes (butadiene and isoprene) leading to synthetic rubbers can be effected by various catalyst systems and this process is now widely used. In view of the relative abundance of butadiene, interest has arisen in finding new outlets for this monomer. An important development in this respect is the growing interest in Nylon-12, a recently developed thermoplastic with very attractive properties. The starting material for this polymer is cis, trans, trans-cyclododecatriene, which may be obtained by cyclotrimerization of butadiene.

Organozinc compounds as such and binary mixtures of organozincs and transition- or main-group metal halides were screened for catalytic activity in butadiene trimerization. Only combinations of diorganozinc compounds with titanium chloride were found to be catalytically active. The molar ratio of R_2Zn and TiCl_4 must lie, it was found, within narrow limits. Diarylzincs proved more catalytically active than dialkylzincs. The addition of alcohols, ethers, or amines (some of which had a favorable co-catalytic effect in the aldehyde polymerization) had a negative influence.

The cyclotrimerization of butadiene is best performed in

benzene solution with a catalyst consisting of a 2:1 molar mixture of diphenylzinc and TiCl_4 . A better than 95% conversion of butadiene is realized with only very little polymer-forming taking place. The catalyst is stereospecific in that among the various possible isomers only the cis, trans, trans-product is formed.

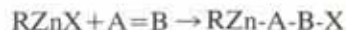
The availability of this organozinc-titanium chloride catalyst for the selective conversion of butadiene into butadiene cyclic trimer will be of interest to the petrochemical industry and, accordingly, a patent has been obtained.

U.S. Patent 3,458,585, July 29, 1969.

(and foreign applications).

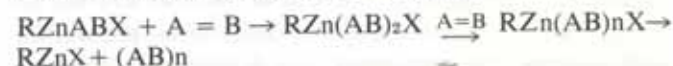
3. Cyclotrimerization of Organic Isocyanates

In a study of mono-organozinc compounds of the type RZnX (X is a group bound to zinc via hetero atom O, N, S, P, etc.), Noltes, et al., discovered that organic molecules containing carbon-hetero atom unsaturated bonds readily insert into the zinc-hetero atom bond of compounds RZnX :

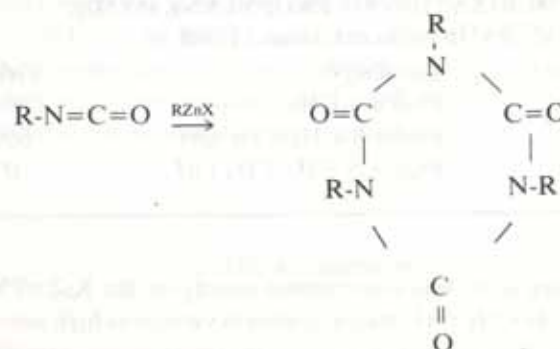


Examples of $\text{A}=\text{B}$ are isocyanates ($\text{R}-\text{N}=\text{C}=\text{O}$), isothiocyanates ($\text{RN}=\text{C}=\text{S}$), and carbon disulfide ($\text{S}=\text{C}=\text{S}$).

Since the product of the reaction again contains a zinc-hetero atom bond, reaction of a catalytic amount of RZnX with a large excess of $\text{A}=\text{B}$ might be expected to result in polymerization of $\text{A}=\text{B}$ by repeated insertion of $\text{A}=\text{B}$ into the zinc-hetero atom bond, followed by elimination of the polymer with regeneration of the catalyst.



However, tests in which $\text{A}=\text{B}$ was organic isocyanates failed to confirm the expectation that the reaction might involve an insertion-elimination mechanism and result in polymerization of the isocyanates. Instead, the product of the reaction was a cyclotrimer of the isocyanates:



Only certain representatives of compounds RZnX cause cyclotrimerization of isocyanates (formation of isocyanurates), investigation revealed. Only trimeric species

($RZnX$)₃, or compounds that give rise to trimeric species upon 1:1 reaction with organic isocyanates, are catalytically active. Dimeric or tetrameric compounds are inactive. Closer investigation showed that a coordination-template mechanism is involved, i.e., the trimetallic organozinc species forces three-coordinated isocyanate into a configuration that is favorable for trimerization to occur. Intermediates containing an isocyanate molecule coordinated to each of the three zinc atoms of the catalyst have been isolated (so-called "pre-trimer" complex). Displacement of the "pre-trimer" by excess of isocyanate followed by bond rearrangement affords the isocyanurate. In this process the "pre-trimer" complex is regenerated and the reaction can repeat itself.

This mode of trimerization catalysis has not previously been demonstrated. It is of special interest as the trimerization of isocyanates may also be catalyzed by other types of organometallic compounds; furthermore, this concept may have wider ramifications in other areas.

4. Polymerization of alkylene oxides

In introductory experiments, organometallic compounds of the IVth group containing a metal-sulfur bond as well as a free hydroxyl group in combination with dialkyl- or diaryl-zinc proved to be extremely useful cocatalysts. The combination of $Ph_3Pb-S-CH_2-CH_2-OH$ with Ph_2Zn was particularly effective: propylene oxide dissolved in benzene was polymerized within 3 hours at room temperature to give a 100% yield of an elastomeric product.

The catalyst was prepared by heating 1 mol per cent $Ph_3M-S-CH_2-CH_2OH$ and 1 mol per cent Et_2Zn in benzene during one hour at 80°C. With both the lead and the tin compound a precipitate formed which was filtered and washed with benzene. No precipitate was formed with the germanium compound; therefore, the solvent was removed by distillation in vacuum. The activity of the catalysts is shown in Table 6-11.

TABLE 6-11

POLYMERIZATION OF PROPYLENE OXIDE (at 20°C in bulk; cat. conc.: 1 mol %)

Catalyst	Cocatalyst	Yield
Et_2Zn	$Ph_3Pb-S-CH_2-CH_2-OH$	100%
Et_2Zn	$Ph_3Sn-S-CH_2-CH_2-OH$	60%
Et_2Zn	$Ph_3Ge-S-CH_2-CH_2-OH$	0%

Further work was concentrated mainly on the $R_2Zn/Ph_3Pb-S-CH_2-CH_2-OH$ catalyst system in view of its high activity. Variables studied in solution polymerizations: catalyst concentrations, catalyst preparation methods, and solvents useful as polymerization media. A selection of the most interesting results is shown in Table 6-12.

TABLE 6-12

SOLUTION POLYMERIZATION OF PROPYLENE OXIDE USING CATALYST

(room temp.; time: 1 day; volume ratio of solvent to propylene oxides 1:1)

Solvent	Catalyst		
	Conc., mol%	Yield, wt%	Molecular weight*
Benzene	0.5	99	1.8×10^6
	0.25	86	2.9×10^6
	0.125	65	2.2×10^6
Hexane	0.5	93	2.2×10^6
	0.25	96	3.5×10^6
	0.125	48**	3.5×10^6
Carbon tetrachloride	0.5	98	
	0.25	93	
	0.125	80	

*Calculated from viscosity measurements of a 0.05% sol. in benzene at 25°C.

**Some PO had escaped during the experiment.

As Table 6-12 shows, the yields are excellent and the molecular weights are high. Films pressed at 120°C from these polymers show interesting properties. They can be stretched several times mono- or bi-axially and thereby become extremely strong, pliable, and elastic. These properties, which are quite unusual for this type of polymer, are probably connected with the high amount of microcrystalline domains in the polymer. These regions act as physical "cross links," rendering the polymer a micro-molecular, three-dimensional, network structure. These films, thus, are an example of a reversible thermoplastic elastomer.

This type of rubber should be of considerable economic importance since it can be processed as a thermoplastic at elevated temperatures yet reverts to its elastomeric nature on cooling to ambient temperature. These properties would enable processors to materially reduce costs connected with incorporation, building up, and vulcanization.

ILZRO'S patents based on the above research studies:

U.S. 3,458,585 (7/29/69) Cyclotrimerization of butadiene.

U.S. 3,535,283 (10/20/70), U.S. 3,579,480 (5/18/71); and U.S. 3,579,481 (5/18/71) Polymerization of aldehydes.

U.S. 3,641,080 (2/8/72) & U.S. 3,641,081 (2/8/72) Preparation of dialkyl-zinc compounds.

U.S. 3,798,249 (3/19/74) Polymerization of epoxides.

U.S. 3,641,178 (2/8/72) Codimerization of aromatic compounds.

PLATING

Zinc oxide additions to zinc electroplating baths enhance the rate of dissolution of components and contribute to formation of a bright plate.

Du Pont² disclosed that, in the preparation of aqueous alkaline cyanidic zinc baths, the dissolution rate of components was sharply increased by adding the ZnO, NaCN and NaOH as a solid mixture. Example: ZnO 0.89, NaCN 0.69 and NaOH 1.09 grams was added to 378 ml of a prepared bath. The solid mixture dissolved in 8 minutes as compared with 32 minutes for successive addition of the components.

Philips Electric⁴, found that a bright zinc surface is formed in electrolytic galvanizing if the bath contains an excess of $\text{Zn}(\text{OH})_2$ or ZnCO_3 . Example: ZnO, NaCN and NaOH is a bath which develops a bright surface on addition of ZnCO_3 .

A Russian method of plating zinc, according to A. Brenner¹, comprised a bath containing ZnO 12-15, NH_4Cl 240, H_3BO_3 20-25, and a colloidal agent 1-2 g/l. Such a bath is operated at 30-35°C and 0.5 -1.0 amp/sq.dm.

Enthone, Inc.³ reported that ferrous metals may be cleaned for plating by immersion in a strongly alkaline solution (pH more than 10) containing ZnO. Heat the solution to 70-150°F. An example in the patent showed the use of 19 grams ZnO/liter.

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PREPAINT PHOSPHATE COATINGS

Zinc phosphate coatings applied to metal surfaces prior to painting have proven so effective in corrosion resistance and paint-holding properties that they are widely used on new automobiles, both domestic and foreign, and on major interior appliances such as refrigerators and dishwashers. Generally prepared by dissolving zinc oxide in solutions of phosphoric acid with suitable modifiers, and applied by dip or spray, they form crystalline coatings chemically bonded to the iron or steel surface. Technical papers and patents in this field in recent years reveal continuing progress in understanding the reactions involved, the types of crystals formed, and means of modifying the process to broaden still further its applications.

Papers

A review of the status of phosphate coatings and their applications was presented in several technical papers^{1,3,7,8} and others proposed various modifications in the process. Machu^{5,6} developed a zinc phosphate solution with high ZnF_2 content for use not only on steel but also on zinc and aluminum surfaces. Addition of ZnF_2 to zinc oxalate coatings, he noted, broadened their usefulness to include Mo and Cr-Ni steels. . . . Zubarev, et al.,⁹ improved the quality and density of phosphate coatings for drawing of steel wire by increasing the $\text{Zn}(\text{H}_2\text{PO}_4)_2$ content of the parkerizing solutions. . . . Gebhardt² discussed the kinetics of phosphating processes on both steel and zinc surfaces. . . . Kozarev⁴ reported that x-ray examination of depositions from zinc phosphate solutions showed that they consist of $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeZn}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ in various ratios, depending on conditions.

Patents

Modifications of the composition of zinc phosphate solutions were reported by a number of companies^{10-12, 15, 23, 25, 27} and detailed descriptions of the chemical mechanisms involved in the process of phosphatization were presented^{24,26}. Heatbath Corp.¹⁷ disclosed a bath composition which deposited coating weights of 2000-3000 mg/ft² on steel in 2-30 minutes at 160-200°F. The preferred composition: Zn 3.8, PO_4 9.9, NO_3 3.3, Ni or Co 0.06 g/l (all as ions), and a beta-oxo ester (e.g., methyl or ethyl acetoacetate) 5g/l. . . . ICI¹⁸ reported that the addition of pastes containing 20-50% ZnO to coating baths maintains constant simultaneously the pH and the Zn content. . . . Lubrizol¹⁹⁻²² developed a suspension-agent for phosphate baths, and disclosed modifications of the solution composition designed to prevent formation of scale and to provide higher corrosion resistance. Preparation of the metal surface prior to application of phosphate solutions was the basis of some patents. Collardin, Gerhard¹³⁻¹⁴ found that more uniform layers of zinc phosphate were deposited on galvanized surfaces if the latter were first treated with a mixture of TiOSO_4 and Na_2HPO_4 in gelatin. . . . Du Pont¹⁶ disclosed the composition of a pretreatment solution: tri- or perchloroethylene, an alcohol, 0.2-0.8% H_3PO_4 and 0.005-0.5% bivalent zinc from a phosphate salt.

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PYROTECHNIC COMPOSITIONS

Progress continues in the development of improved pyrotechnic white smoke compositions, and zinc oxide continues to contribute to the performance of these products.

Jarvis¹ discussed the combustion reactions of a pyrotechnic white smoke composition, pointing out that British smoke generators consist of ZnO 29-47, Ca silicide 7-25%, and a Cl₂-donating material such as Cl₃CCCCl₃.

Patents

Several new compositions were the basis of patents. Jack De Ment⁴ reported more than 370 formulations . . . Catalyst Research³ developed a pyrotechnic primer consisting of fuel and oxidizer. Compositions: Fuel: red P 50, Sb₂S₃ 45, and binder 5%. Oxidizer: KClO₃ 86, S 5, ZnO 3, K₂Cr₂O₇ 1 and

binder 5% . . . Hooker Chemical⁵ patented a composition consisting of ZnO, perchloropentacyclodecane, and powdered aluminum.

Mixtures for the preparation of permanently colored inorganic smokes, patented by Stoltzenberg⁷, were based on three classes of constituents: (a) color-forming metal powders (Al, Fe, Mg & Zn); (b) organic halides (hexachloroethane, for example); and (c) light metals (Al, Mg) to form very high combustion temperature. An example in the patent contained both zinc powder and zinc oxide.

Spasmodic consumption of pyrotechnic mixtures, Buck K-G² found, was prevented by use of a highly dispersed SiO₂ in the following composition: hexachloroethane 40-60, Zn 20-30, Al 1-10, ZnO 2-10, SiO₂ 0.1-1 part . . . Olin⁶, in two patents, disclosed compositions to form brilliant flame and white smoke, based on the use of ZnO and MgCl₂, or ZnO with Mg metal and C₂Cl₆. Example: ZnO, C₂Cl₆ and NH₄ClO₄.

Rubber-based compositions were developed by the United Kingdom Defence Dept.⁸. Example: Thiokol 10, Zn 31, ZnO 12, KClO₄ 16 and hexachloroethane 31%. The United States Dept. of the Navy⁹ disclosed the composition of a long-burning mixture: Mg 12, ZnO 45, organic Cl compounds 25, and non-acid binders 14-22 parts.

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RUBBER

The rubber industry, in its development over the past one hundred years, has utilized an increasing number of the many optical, physical, and chemical properties of zinc oxide.

Shortly after the turn of the century, in the days of horse-drawn street cars, rubber makers called upon zinc oxide to provide new properties: reinforcement together with high heat conductivity, in a new type of product, solid rubber tires for trucks and buses. Unlike pneumatic tires for bicycles and

the early automobiles, the cushioning effect of solid tires was provided by compression of rubber rather than compression of air, resulting in the development of heat in the thick, solid-rubber tires. Excessive heat buildup, producers soon found, caused "blow-outs" due to devulcanization and melting. This problem was overcome by use of high (typically, 150 phr) loadings of zinc oxide, which also furnished the required degree of reinforcement.

A few years later the industry called on zinc oxide to assist in a major change in formulations of most types of stocks, the development and adoption of vulcanization by organic acceleration. Zinc oxide proved the most effective activator to speed up the rate of cure with the new accelerators. This innovative method of curing was also applied to the many new products being developed by the industry, including pneumatic tires for trucks and buses. Those heavy-duty tires likewise carried high loadings of zinc oxide for heat conductivity as well as reinforcement since heat-buildup was critical at their higher operating speeds compared with their solid-rubber counterparts.

Thus, by the start of World War I the industry was using several properties of zinc oxide: whiteness and tinting strength for white and light-colored articles, chemical reactivity for activation of accelerators, reinforcement and heat conductivity in solid and pneumatic tires for trucks and buses, and an increasing number of passenger car tires were carrying zinc oxide for its reinforcement properties.

With the diversification of the industry's products in more recent years and the adoption of various types of synthetic elastomers and other compounding ingredients, many other properties and applications of zinc oxide have developed. Numerous references to them were found among the technical papers and patents collected in this survey, and they are discussed below or are listed in Further References.

Highlights of the properties and applications of zinc oxide in rubber are these:

Activation

In the curing process for natural rubber and most types of synthetic rubbers, the chemical reactivity of zinc oxide is utilized to activate the organic accelerator. The mechanisms involved are not completely understood, but there is general agreement that a portion of the zinc oxide reacts with fatty acid, forming a rubber-soluble zinc soap. This soap reacts with the accelerator to form a salt which combines with the sulfur, converting it to a form that reacts with the unsaturation in the rubber molecule to form sulfur crosslinks between molecules. Free zinc oxide is essential, it is important to note, since the use of either a zinc soap or the zinc salt of the accelerator alone does not result in vulcanization.

The unreacted portion of the zinc oxide remains available as a basic reserve to neutralize the sulfur-bearing acidic decomposition products formed during vulcanization. Thus,

if the level of zinc oxide is too low and no free zinc oxide is available, reversion of cure may set in prematurely when the rubber product is in service. Adequate levels of zinc oxide contribute markedly to chemical reinforcement, scorch control, and resistance to heat-aging and compression fatigue.

Acceleration

Zinc oxide serves as the accelerator with some types of elastomers, and the crosslinking which it induces takes several forms, depending upon the presence of sulfur. With polysulfides (e.g., Thiokols), chloroprenes (e.g., neoprene), and chlorobutyl, zinc oxide is the customary accelerator for curing of these elastomers which require no addition of sulfur. The mechanisms involved represent two types of crosslinking, sulfur atoms and chlorine atoms. In the curing of chloro-type polymers, zinc oxide is considered to react with the chlorine atoms, forming zinc chloride which induces the formation of chlorine crosslinks.

With some systems, zinc oxide is an effective co-accelerator in the vulcanization process. With hexachloro-p-xylene, for example, it cures butyl acrylate compositions without the addition of sulfur. In phenolic resin vulcanization systems for butyl rubber, mixtures of Hypalon and zinc oxide accelerate the cure.

Biochemical Activity

Zinc oxide is useful in the preservation of plantation latex as it reacts with the enzyme responsible for the decomposition. The oxide is also a fungistat, inhibiting the growth of such fungi as mold and mildew.

Dielectric Strength

In high-voltage wire and cable insulation, zinc oxide improves the resistance to corona effects by its dielectric strength, and at elevated operating temperatures it contributes to maintenance of the physical properties of the rubber compound by neutralization of acidic decomposition products.

Heat Stabilization

Zinc oxide similarly retards devulcanization of many types of rubber compounds operating at elevated temperatures.

Latex Gelation

In the production of latex foam rubber products, zinc oxide is particularly effective in gelation of the foam with sufficient stability of body to withstand vulcanization. Gelation is effected by a slight lowering of the alkalinity of the compounded latex from the region where zinc oxide is not ionized (approximately 10.5pH) to a point where positive zinc ions, $Zn(NH_3)_4^{++}$, appear. Such ions destabilize the latex, resulting in a firm stable gel.

Light Stabilization

Zinc oxide is outstanding among white pigments and extenders for its absorption of ultraviolet rays. Thus, it serves as an effective stabilizer of white and tinted rubber compounds under prolonged exposure to the destructive rays of the sun.

Pigmentation

Through its high brightness, refractive index, and optimum particle size (approximately 0.25 micron), zinc oxide provides a high degree of whiteness and tinting strength for such rubber products as tire white sidewalls, sheeting and surgical gloves.

Reinforcement

Zinc oxide provides reinforcement in natural rubber, as noted above, and in some synthetic elastomers such as polysulfides and chloroprenes. The degree of reinforcement appears to depend upon a combination of the particle size of the oxide, the finest size being the most effective, and the reactivity of the oxide with the rubber. For example, the reaction of zinc oxide with carboxyl groups in the rubber molecule has been indicated as a possible means for the development of structure.

The type of reinforcement imparted by zinc oxide is characterized by its low degree of heat buildup under rapid flexing or compression. Accordingly, reinforcing loadings of the oxide are used in the carcass stocks of some tires for passenger cars, as well as for heavier-duty service in bus and truck tires. For rapid-compression service, high loadings of zinc oxide have proven highly effective in automotive engine mountings and calender rolls for the paper industry.

Under such service conditions involving rapid flexing or compression, zinc oxide also provides heat conduction to more rapidly dissipate the heat and thereby provide lower operating temperatures. In addition, it imparts heat stabilization by reacting with acidic decomposition products.

Rubber-Metal Bonding

In the bonding of rubber to brass, zinc oxide reacts with copper oxide on the brass surface to form a tightly adhering zinc-copper sulfide salt.

Tack Retention

One of the unique properties of zinc oxide is its ability to retain over many months of shelf-storage the tack of uncured rubber compounds for adhesive tapes.

Zinc Compound Formation

In many applications in the rubber industry, zinc oxide contributes important properties through the compounds which it forms with other constituents of a compound. Examples are these: (a) the zinc salt formed with the organic accelerator in the vulcanization process; (b) the formation of zinc resins which improve the bonding of adhesives; (c) in

vulcanization of chloroprene rubber, zinc oxide reacts with the chlorine to form zinc chloride which participates in crosslink formation; (d) and in bonding SBR rubber to nylon by use of a resorcinol adhesive, the reaction product of zinc oxide and resorcinol is a precursor to resin-bond formation.

Papers

The influence of zinc oxide on crosslink formation during vulcanization was studied by several researchers. Dimov, et al.,⁴ evaluated the activating properties of various compounds on the basis of the concentration of crosslinks formed, using natural rubber nitrated in solid phase. The highest concentration, they reported, was formed when zinc oxide was the activator. . . . Frenkel⁸ attributed the advantages of zinc oxide as an activator to its greater electron affinity and to a narrower forbidden zone in the zinc oxide crystals. . . . Preheating zinc oxide at 100°C for one hour, Ebich, et al.,⁶ reported, increased the vulcanization rate (at 50-80°C) 2-3 fold. This increase was due to more rapid reactivity of the oxide with the COOH groups, they reasoned, since the per cent of vulcanizable COOH groups remained the same (65%) as customary. . . . Pavlov, et al.,¹⁸ found that zinc oxide imparts a stiffening effect in rubber through reaction with COOH groups.

Zinc oxide serves as both accelerator and filler in chloroprene rubbers. Zhovner, et al.,^{27,28} in investigations on that subject, found that zinc oxide reacts with the chlorine atoms in the rubber to form $ZnCl_2$ which participates in crosslink formation at vulcanization temperature. . . . In the compounding of chloroprene rubbers for resistance to silicate-ester fluids, Novy & Clark,¹⁷ reported that zinc oxide ranks high both as accelerator and as filler. . . . Ivanov, et al.,¹² studied the effect of zinc oxide additions on the rheological properties of adhesive compositions based on chloroprene rubber. Composition: rubber 100, resin 10, thiuram 1.5, DPG 0.15, Captax 0.2, and $FeCl_3$ 1 part (dissolved in benzene-ethyl acetate). Additions of zinc oxide lowered the limiting Newtonian viscosity linearly over the range of 10-20 parts. . . . Aleksandrova et al.,¹ investigated a different chloro rubber, chlorobutyl, which also can be vulcanized without sulfur. They tested several chelates as vulcanization agents for that rubber and reported that they ranked in this order without ZnO: Zn (best), Fe, Cu and Ni. Joint use of chelates, sulfur and ZnO did not produce satisfactory vulcanizates, due to lack of tensile. Best results were obtained with ZnO and Zn chelate together: 90-120 kg/cm² modulus at 400% elongation as compared with 60 kg/cm² for ZnO vulcanizates.

The role of zinc oxide in vulcanization of other rubbers was also explored. Tarasova, et al.,²⁴ in the vulcanization of an aqueous dispersion of cis-isoprene with several systems, compared the effects of a number of zinc compounds as activators, e.g., ZnO, Zn mercaptobenzothiazole and Zn

dithiocarbamate, among others . . . Glazolev, et al.,¹⁰ developed a butyl acrylate composition of good technical properties and possessing a distinctive feature: it did not corrode the processing equipment. The composition: 88:12 butyl acrylate-acrylonitrile copolymer 100 parts, phenol-formaldehyde resin 5 parts, and carbon black 50 parts. The accelerator consisted of a mixture of 5 parts ZnO and 2 parts hexachloro-p-xylene. . . Acrylonitrile-butyl acrylate copolymers could be crosslinked with various chlorinated polymers in the presence of ZnO, Zakirova, et al.,²⁶ found. The stocks, compounded with stearic acid and carbon black, had excellent resistance to aging in both oil and air, they noted . . . A curing system developed by Kastorskii, et al.,¹⁵ consisted of mixtures of ZnO and vinylidene chloride for vulcanization of ternary butadiene-acrylonitrile-vinylidene chloride copolymers without the use of sulfur. The ZnO was incorporated in sufficient amount (3-10 phr) to completely ban all formation of HCl and permit normal vulcanization. Jones & Hall¹³ presented a comprehensive report on the fundamentals of zinc oxide as an activator in the vulcanization of carbon black - pigmented NR-butadiene rubber . . . Romanova, et al.,²¹ reported on the vulcanization of liquid thiokols (polysulfide rubbers) by use of H₂O₂ with zinc oxide, the customary accelerator. A suitable composition consisted of Thiokol 100, H₂O₂ 6, and ZnO 30 parts.

In phenolic resin vulcanizing systems, zinc oxide is also effective. Giller⁹ found that mixtures of Hypalon and zinc oxide imparted an acceleration effect when used with phenolic resin vulcanization systems for butyl rubber. The effect was more pronounced by hot milling, or by heat treatment of the Hypalon and ZnO prior to addition of the resin. Good physical properties were developed in the butyl vulcanizates, especially after aging. . . In the ambient curing of unsaturated elastomers with halomethyl phenolic resins, Petersen¹⁹ reported that zinc oxide proved highly effective as a co-catalyst.

The properties of zinc oxide and other zinc compounds were investigated for preservation of natural latex and for controlled gelation of carboxylated latexes. Angove, et al.,² of Malaya evaluated ZnO and various organozinc compounds as secondary and tertiary preservatives of natural-rubber latex concentrates. (The best primary preservatives, they commented, consist of Pb-Hg salts.) Their results showed that ZnO should be classed as a secondary preservative and used with ammonia, the quantities being 0.05% ZnO and 0.2% NH₃. Oxines and organozinc compounds in the range 0.005-0.025% were effective as tertiary preservatives and, they added, they are attractive at low economic cost. In this classification, Zn carbamates performed well, they reported, due to the CS₂ group connected to a nitrogen or oxygen atom . . . Savinkova, et al.,²³ developed for styrene-butadiene latexes suitable gelation mixtures consisting of ZnO, NH₄Cl, NH₃ solution, and Zn(NH₃)₄⁺⁺ complex.

The reactivity of zinc oxide is also useful in production of foam-rubber articles. Demishev, et al.,³ in an investigation of the influence of various components of rubber compositions on the decomposition of azodicarboxamide, a blowing agent, found that zinc oxide mixtures produced the largest amount of evolved gas per gram of decomposition of that blowing agent. Captax and thiuram were two of the other compounds included in the tests.

Natural-rubber compounds for high-temperature service were studied by Fletcher, et al.,⁷ of the British Rubber Producers' Research Association. Of 17 different types of oxides tested in the sulfurless gum stocks cured with 3 parts tetramethylthiuramdisulfide, they reported that only zinc oxide furnished good curing and aging (temperature range for aging tests: 100-125°C).

Zinc oxide improves the bonding of rubber compositions to selected substrates. Hewitt¹¹ studied the adhesion mechanism involved in bonding styrene-butadiene rubber to nylon by use of an adhesive consisting of resorcinol, hexamethylenetetramine, silica and zinc oxide. Precursors to resin-bond formation, he noted, were two steps: (a) solubilization of ZnO and (b) reaction of that Zn compound with resorcinol . . . In bonding rubber to brass Saijo, et al.,²² found that the ZnO content of a conventional black compound was critical. Tests on a range of ZnO contents produced maximum bonding at 40% ZnO, and fine-particle-size types were the most effective. Their investigation of the mechanism involved indicated that ZnO reacts with acidic CuO on the brass surface, forming a firmly adhering Zn-CuS salt . . . Kvardashov, et al.,¹⁶ found that zinc compounds are also important in the bonding of rubber to steel. By the addition of up to 30 phr ZnCl₂ to unfilled SKN nitrile rubber containing Santocure, stearic acid and activating amounts of ZnO, the strength of the rubber-steel bond developed during vulcanization was 80 times higher than without ZnCl₂. The tear strength, elongation, and electrical conductivity of the stock also increased. Rubbers filled with channel black, silica, and TiO₂ likewise responded to the addition of ZnCl₂, making possible their direct bonding to steel during vulcanization.

Other properties of zinc oxide in rubbers were studied by Jones and Baldyga¹⁴ in tests on heat aging and light stability of ethylene propylene terpolymers (EPT). In heat aging, the EPT stocks (unfilled, whiting-filled and clay-filled) were maintained 5 days in an oven at 350°F, and the effect of such aging was indicated by the change in retention of elongation after aging. The zinc oxide parameters investigated included the type of oxide, average particle size, and phr loading. The data obtained showed conclusively that French-process zinc oxides impart heat-aging resistance superior to that of American-process zinc oxides. The former type, being sulfur-free, has a higher pH and, thus, can neutralize more effectively the acidic decomposition pro-

ducts formed during aging. Moreover, the finer French process zinc oxides proved superior to coarser grades in heat-aging resistance. With regard to phr loading, 3, 5, 10 and 20 phr of zinc oxide were included in these tests; over that range the compounds showed superior aging performance for the higher concentrations of zinc oxide.

Patents

Vulcanizates are improved in numerous properties by addition of zinc oxide. Yurovskii, et al.,⁴⁷ improved the physico-mechanical and technical properties of an acrylate rubber composition by addition of 3-5 phr ZnO and 3-10 phr of an organic compound with Cl bound to an aliphatic group. . . . Firestone³⁶ improved the stability of unvulcanized, oil-extended, SiCl₄-interconnected styrene-butadiene rubber (SBR) by addition of up to 5 phr ZnO. . . . Velth-Pirelli A.G.⁴⁶ developed vulcanizates of SBR with ZnO-containing silicic acid. Example: SBR 100, dispersing agent 4, ZnO 40 (as ZnO-silicic acid; equivalent to 15 ZnO), halogenated butyl rubber is improved in cure by use of zinc compounds. Esso^{34,35} found that the addition of ZnO and ZnCl₂ overcame the inhibition of cure of such polymer caused by the presence of minor amounts of calcium soaps. And a combination of ZnO, ZnCl₂ and Zn butyl xanthate, they observed, cured the halogenated butyl rubber in 5 days at 75°F, a cure-time suitable for caulking compounds and cements.

Ethylene-propylene rubber compositions were developed without use of customary fillers. Dainichi-Nippon Cables³² disclosed that EPR compounded with ZnO, i.e., rahydrophthalic anhydride, and a curing agent produces vulcanizates with good electrical properties even under conditions of high humidity. . . . International Synthetic Rubber³⁹ used two additions of zinc oxide with EPR. Example: Mix EPR 650, ZnO 39 and N-bromosuccinimide 70 parts, then blend in a mixture of ZnO 32, stearic 6.5, mercaptoben-zothiazole 65, S 9.7 and tetramethylethylenediamine 6.5 parts.

With isoprene rubber, Shell N.V.⁴¹ compounded with double the usual zinc oxide content. Example: isoprene rubber 100, ZnO 10, HAF black 50, and Santoflex #13 1 part. Zinc oxide serves as the vulcanizing agent in polysulfide rubbers. Thiokol Chemical^{43,44} disclosed the use of 30 phr ZnO with LP-2 polymer to provide quick vulcanization. Also, they developed a combination of additives to stabilize a different polymer, poly (ethylene sulfide), against degradation, i.e., addition of KSeCN, KSCN and or NH₄SCN, together with an amine and zinc oxide. In foam production, zinc oxide can serve as accelerator, stabilizing agent, and crosslinking agent. Congoleum Ind.³¹ developed cellular foam laminates having a noncellular surface structure and using zinc oxide as accelerator. . . .

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Borg Warner Corp.³⁰ found that a mixture of 3 parts NaSiF₆ and 8 parts ZnO is an effective stabilizer for impact-absorbing cellular butadiene-styrene copolymer foams. . . . Uniroyal Ltd.⁴⁵ prepared crosslinked foam reactive latexes, ZnO being the crosslinking agent. Some of the other diverse applications of zinc oxide in the rubber industry are these: Borden²⁹ developed a resilient composition consisting of scrap rubber, polychloroprene latex binder, ZnO and emulsified Durex 998. . . . Deutsche Gold-und Silber⁴³ disclosed a composition for bonding metals (wire for treads) to natural or synthetic rubber. The composition: 6-8% ZnO, 2% PbO, 45% carbon black, 15% fine silica, 2.5% resorcinol, etc., in SBR. W.R. Grace Co.³⁷ prepared sealants for aerosol can caps based on 2-chloro-1,3-butadiene polymers compounded with ZnO, thiocarbamates and minor ingredients. The vulcanizates furnished improved resistance to oxidation, chemicals, oils and fuels. . . . In a rubber latex for carpet-backing surfaces, Reverex Ltd.⁴⁰ used ZnO as the gelation agent and Zn diethylidithiocarbamate as the accelerator. . . . Stamicarbon N.V.⁴² developed a catalyst of ZnO-CuO for purification of 1,3-butadiene. Operating temperature: 50-140°C. This process removed impurities which had interfered with polymerization by poisoning the catalyst.

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SILICATE COMPOSITIONS

Zinc oxide reacts with aqueous solutions of silicates, such as sodium silicate solutions (commonly known as water-glass), to form zinc silicate, a waterproof, fireproof, refractory material, which is useful as a binder in paints, as described previously, and in various other applications as indicated below:

Patents

Asahi Chemical¹ disclosed that zinc oxide heated at 400-800°C retards the hardening of waterglass adhesives and improves their resistance to water. Such refractory adhesives, they noted, are used in bonding asbestos-cement molded products to building structures. Example of the use of zinc oxide: Heat the oxide 30 minutes at 800°C and prepare a mixture of 5% zinc oxide in waterglass. As a binder this adhesive has a 6-hour hardening time.

Kukoku Chemical² formed a silicate foam of improved strength by reacting ZnSO₄ with Na silicate at 200°C, followed by heating it in a mold at 200°C for 30 minutes.

Matsushita Electric³ developed nonflammable building boards composed of: waterglass binder 100, waste pulp sludge 10-25, ZnO and phosphate or fluoride compounds 20-30 parts. The mixture is heated for a period of reactivity, then compression-molded.

NGK Insulators⁴ disclosed the preparation of a silicate paint for asbestos board, to provide a glossy film with good resistance to peeling, water, stains and chemicals. Mixture: ZnO 20, colloidal silica 80, 30° Bé potassium silicate (to give 11 pH). Stir 30 minutes to form a Zn silicate suspension. Add potassium silicate 330, TiO₂ 30, sand 3 parts. Apply to asbestos board and heat 30 minutes at 120°C.

Tao Gesei Chemical⁵ found that mixtures of Zn₃P₂O₇ and CaS accelerate the hardening of waterglass and improve the waterproofness and compressive strength of hardened waterglass products.

Toray Industries⁶ developed water-resistant, cellular products by addition of Zn(OH)₂ to waterglass, which is then foamed in the presence of water.

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SILICONES

Zinc oxide and its derivatives contribute a variety of special properties for both the preparation of silicones and the usefulness of their compositions.

Patents

Preparation

General Electric^{2,3} photopolymerized cyclotrisiloxanes to linear-form gums over a heat-activated zinc oxide catalyst. The latter in powder form is also useful as filler for elastomers in which hydrophilic properties are desired, they noted, and as charge carriers for electrostatic printing devices.

Khazanov, et al.,⁴ prepared dialkylpolysiloxanes by alcoholysis of selected silanes with a lower alcohol in vapor phase at 170-350°C in the presence of $ZnCl_2$.

Siemens-Schukertwerke⁶ prepared polysiloxanes of extremely high heat resistance by reaction of halosilanes with zinc oxide. The latter was refluxed with (O_2O' -biphenylenedioxy) dichlorosilane.

Applications

Dow Corning¹ described the properties of siloxane elastomers containing zinc oxide.

Produits Chimiques Protex⁵ disclosed that zinc octoate and an epoxyamine are hardening agents for polysiloxane waterproofing agents, and the resulting finish on textiles withstands repeated dry cleaning and laundering.

Rhone-Poulenc⁶ found that the addition of 0.5-10 parts zinc oxide to siloxane rubber imparted self-extinguishing properties. Example: With 4% zinc oxide content, the rubber self-extinguished in 4 seconds.

Rhone-Poulenc⁷ developed self-sealing properties in silicone elastomers by addition of organic zinc compounds, especially those of organic carboxylic acids.

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SULFUR REMOVAL

Numerous technical papers and patents in recent years have reported that zinc oxide is effective in removal of sulfur and sulfur compounds from a variety of fluids and gases, particularly industrial flue gases. In some processes the chemical, chemisorption, and catalytic properties of the zinc oxide are enhanced by special heat treatments and/or the addition of other metal oxides.

Papers

Removal of SO_2 from flue gas can be carried out by use of zinc oxide in either wet or dry processes. Peisakhov⁵ described a wet method consisting of bubbling the gases through zinc oxide pulp and decomposing the resulting $ZnSO_3$ at 300-350°C to recover the SO_2 . . . Graefe, et al.,³ developed a process based on the use of a dry, fluidized bed of zinc oxide as the absorbent. . . Sladek, et al.,⁷ in a study of the efficiency of various metal oxides for SO_2 removal from flue gas, reported that zinc oxide is one of the most promising.

Zinc is also effective in removal of H_2S from hydrocarbon gases and for desulfurization of H_2S and certain other sulfur-containing compounds. Silin, et al.,⁶ of Russia reported on the "industrial adoption of a zinc oxide absorber for thorough removal of H_2S from hydrocarbon gases." The zinc oxide was used in the form of dried pellets prepared as follows: 10 parts ZnO and 1 part kaolin are mixed with water and ammonia, pelleted, and dried. The pellets had sufficient strength for the process and furnished good operating efficiency in removal of H_2S . . . Cognium¹ improved the desulfurizing properties of zinc oxide by addition of CuO as promotor, followed by a heat treatment in H_2 to activate the mixture of 4 parts ZnO and 1 part of CuO . The resulting composition is an effective desulfurizer of H_2S , CS_2 , iso- $PrSH$, Me_2S , and thiophene, Cognion reported. . . Kakabadze, et al.,⁴ prepared a zinc oxide of higher desulfurization activity by thermal dissociation of $ZnCO_3$ at 400°C, resulting in a product of high surface area.

Patents

Various methods for improving the desulfurization activity of zinc oxide have been developed, as well as improved processes. Esso^{14,15} developed a series of catalysts for removing pollutants from fuel combustion. They were based on metal oxides classified into two groups: major constituents and modifiers. Zinc oxide was one of the major constituents. For higher operating temperatures, 750-1000°F, Esso found V_2O_3 or V_2O_4 effective alone or in combination with co-absorbents such as zinc oxide. . . Some laboratories^{17,19,20,25} enhanced the desulfurization activity of zinc oxide for flue gases by incorporating CuO as a promotor, or by increasing the surface area through formation of $ZnCO_3$, followed by calcination. . . Bleiberger Bergwerks Union¹¹ developed a different approach. They reacted ZnO with $CaSO_4$ in water and granulated the solid mass. Introduced into an absorption tower, it reduced the SO_2 content from 0.4% in the entrance gas to 0.0005% SO_2 in the exit gas.

For removal of H_2S in hydrosulfurization and reforming of hydrocarbons, zinc oxide may be used without modification in some processes but numerous patents indicate that the oxide is more effective after suitable chemical or heat treatments. BASF A.G.⁹ removed sulfur from hydrocarbon oils with boiling points below 300°C by passing over zinc oxide at 350-450°C. After saturation with ZnS, the oxide is regenerated by roasting in air at 600°C. . . Japan Gasoline Co.¹⁶ absorbed H_2S from the reforming process on ZnO at 280°C under a pressure of 2 atmospheres. . . Shell Oil²² found ZnO effective without modification. . . Russian researchers²¹ developed a hydrosulfurization process based on the use of ZnO as catalyst at above 530° and under a H_2 pressure of 1.1 kg/cm². . . B. P. Benzin-und Petroleum¹⁰ refined petroleum distillates by heating in an autoclave at 270°C and 20 atmospheres with ZnO and NaOH.

Methods proposed for modification of zinc oxide for desulfurization of liquids and gases are these: Azote & Products Chimiques⁸ developed two desulfurizing agents based on ZnO: (1) A mixture of ZnO and MgO (up to 20% of the latter) in hydroxymethylcellulose in 6-mm diameter particles removes S from natural gas or petroleum. (2) A mixture of 80 parts ZnO and 20 parts aluminum cement is kneaded with water; after 4 hours the hardened mass is granulated and used for desulfurizing gaseous mixtures. It retained 4.2% S compared with 0.11% retained by ZnO alone. . . Catalysts & Chemicals^{12,13} reported that ZnO for removal of sulfur compounds in steam-gas, shift-conversion processes should have a surface area of 30-60 m²/g, several fold larger than the 5-9 m²/g area of normal ZnO. . . Laporte Industries¹⁸ disclosed the preparation of pellets of $ZnO-Fe_2O_3$ (ratio 95:5) with bentonite binder; calcination temperature: 350°C. The pellets are effective absorbent compositions for desulfurizing liquids and gases, they noted. . . Topsoe, Haldor²³

activated ZnO by heating in H_2 at 400°C, followed by a steam treatment. This modified ZnO is useful as an adsorbent for H_2S from industrial gases. . . Universal Oil Products²⁴, for multiple-stage catalytic desulfurization of black oil, developed a catalyst consisting of ZnO and MoO_3 on an Al_2O_3 support.

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TOBACCO

Zinc oxide, as a constituent of cigaret filters, is effective in removal of selected ingredients from tobacco smoke.

Kuhn, et al.,¹ studied the removal of hydrogen cyanide from cigaret smoke by means of filters. They reported that "Myria" filters retained 7% of the HCN content of cigaret smoke, cellulose acetate retained 17%, and zinc oxide as a coating on the cellulose acetate increased the retention.

Patents

Zinc oxide can be incorporated into cigaret filters by various techniques to increase its absorption efficiency.

A two-part filter was developed² consisting of: (Part 1), silica gel and 5-15% active charcoal and (Part 2), an ion-exchange resin containing 1-15% zinc oxide.

Eastman Kodak^{3,4} disclosed the composition of two types of cellulose acetate filters containing zinc oxide for removal of HCN. The filter of one type containing 1% or more of zinc oxide was activated by treatment with triacetin, among others. The second type of cellulose acetate filter consisted of 12,000 fibers, each 20 mm in length, to which 21 mg zinc oxide was added.

Liggett & Myers⁵⁻⁷ found that a filter consisting of charcoal impregnated with zinc oxide and iron oxide removed significant amounts of HCN and H₂S from tobacco smoke without affecting its flavor. Also, they reported that the addition of 2% zinc oxide to tobacco reduced the content of polycyclic aromatics in cigaret smoke by 50 per cent or more. These results were determined by use of infrared absorption measurements at 11.9-14.0 microns.

McCarthy⁸ disclosed that the addition of ZnCl₂ or zinc acetate to toothpastes produced compositions for resisting the desire to smoke. Application to the teeth twice daily was suggested.

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ZINC CHEMICALS

Zinc oxide and its derivatives react with many different organic and inorganic compounds to form a variety of compounds with a broad spectrum of properties and applications.

Zinc Borate

U.S. Borax¹ prepared a crystalline zinc borate with a low content of water of hydration: 2.02 ZnO·3 B₂O₃·3.33 H₂O. It was formed by the reaction of ZnCl₂ with Na₂B₄O₇·10 H₂O, using as seed crystals 2 ZnO·3 B₂O₃·3.5 H₂O. The new product, they reported, is useful as a fire-retardant for halogenated polymer products.

Zinc Organics

Furukawa, et al.,² included a helpful list of 558 references in their 52-page review of the use of organozinc compounds in synthesis.

Eiwa Kasei Kogyo³ improved the properties of azodicarboxamide, a blowing agent useful in production of industrial foam products, by oxidizing it with Cl₂ or Br₂ in the presence of ZnO, to form a zinc complex with superior properties as a blowing agent.

Hercules⁴ developed zinc-rosin compounds for addition to rubber adhesives to improve their bonding properties. These compounds were prepared by reacting ZnO with a hydrogenated rosin in the presence of AcOH to obtain a product with 6-11% Zn content.

Mel'nikov, et al.,⁵ developed a one-step method for preparation of Zn ethylenebis (dithiocarbamate); yield, 92%. The method: To 200 ml H₂O and 16g ZnO, add 18g of 68% H₂NCH₂CH₂NH₂, 14g of 24% NH₃ and 30g CS₂ at 20°C; stir 3-4 hours as temperature rises to 30°C. Heat under reflux condenser to 45°C to evaporate the CS₂.

Phillips Petroleum⁶ disclosed methods for preparation of aromatic polycarboxylates, some involving the use of ZnO or its derivatives.

Sherwin-Williams⁷ reported that the addition of ½% ZnO to phthalic anhydride during distillation produced a marked improvement in color of the anhydride, substantially better than any other metal oxides tested.

Zinc Phosphates

Bitko, et al.,⁸ in a study of the reaction of potassium phosphate with various additives, found that ZnO converts that phosphate at 900°C to a vitreous form of di-, tri-, tetraphosphates and higher varieties.

Komrska, et al.,⁹ reported on the properties of zinc phosphates, particularly Zn₃(PO₄)₂·4H₂O, ZnHPO₄·3H₂O, ZnHPO₄·4H₂O and Zn(H₂PO₄)₂·2H₂O. They crystallized these compounds from supersaturated solutions and examined them by DTA and TGA methods.

Kovarskii, et al.,¹⁰ explored the physicochemical characteristics of zinc orthophosphates: $\text{Zn}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{ZnHPO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{ZnHPO}_4 \cdot \text{H}_2\text{O}$.

Liggett, et al.,¹¹ developed heat-resistant, cold-setting ceramic paints based on ZnO and organic phosphorus compounds. Example: ZnO 10, dimethyl phosphate 12, and colloidal silica 1 part. After curing under high humidity (essential), the coating resists wet abrasion and also thermal cycling from 1000°F.

Rogova, et al.,¹² investigated the synthesis of NH_4 polyphosphates with microadditives, and reported that ZnO serves as a catalyst in those reactions, increasing the rate of formation and the chain length of the polyphosphates.

Atlantic Richfield¹³ discovered that the addition of zinc alkyl orthophosphate to gasoline improved engine performance. They developed a process for production of the compound from ZnCO_3 or zinc acetate and P_2O_5 to provide higher stability of the phosphate.

Berner Osakeyhtio¹⁴ developed a liquid for removal of rust that simultaneously applies a coat of zinc to minimize further development of rust. An important component is a zinc chelate, e.g., ZnO 25, H_3PO_4 130, morpholine 75 and ethylene glycol 130 parts by weight. Composition of the rust-removal liquid: aqueous mixture of Zn chelate 5-20, H_3PO_4 30-50, surface-active agent 1-35, and a reducing organic acid 0.5-5% by weight.

Owens-Illinois¹⁵ disclosed the development of a new compound with piezoelectric properties. It is potassium zinc phosphate, prepared from ZnO and K_3PO_4 .

Union Carbide¹⁶ found that a solution containing ZnO, H_2O , H_3PO_4 and H_3BO_3 was highly effective as an impregnant in protecting graphite and carbon bodies against oxidation, permitting their use as furnace linings up to 950°C.

Zinc Silicates

Alekseeva, et al.,¹⁷ investigated the solubility of polysilicic compounds of zinc in ammonium solutions. Horikawa, et al.,¹⁸ in exploring the drying and water resistance of silicate films, observed that zinc oxide imparted a higher degree of water resistance than other additives tested.

Merkulov, et al.,¹⁹ studied the formation mechanism of zinc silicates through the reaction of ZnO, ZnCO_3 , ZnSO_4 , ZnCl_2 and zinc acetate with sodium silicate in selective solvents at 90-100°C.

Deutsche Gold-und Silver²⁰ developed a method of coating SiO_2 sols with zinc oxide and other metal oxides. . . . Diamond Shamrock²¹ found that the addition of 0.4-2.0% ZnO to sodium silicate solutions stabilized them against thermal decomposition. Such solutions are useful as impregnants to seal the pores in cast metal bodies.

Hoesch K-G²² developed an improved filler for rubber.

It was prepared by addition of ZnO to a fresh precipitate of silicic acid (pH 6.6); the mixture was then heated at 60-90°C. . . . Kurz²³ produced a bonding or impregnating agent based on ZnO and sodium silicate. Sheets were formed by addition of powders (e.g., FeSi or perlite) to the mixture.

Leningrad Optical-Mechanical Society²⁴ disclosed the composition of a thermally stable mastic for joining components with different coefficients of thermal expansion. The composition: waterglass 53-5, quartz powder 36-8 and ZnO 8-16% by weight.

Unilever²⁵ developed for bleaching powders a catalyst consisting of zinc silicate (100-mesh) 200 parts and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 38 parts. A bleaching powder containing the catalyst has the composition: Na dodecylbenzenesulfonate 9, SiO_2 72, borax 8, urea 3 and the above catalyst 4 parts.

Zinc Soaps

Fisel²⁶ presented the results of an investigation of complex soaps of higher fatty acids, including details on method of preparation of 72 complex soaps of palmitic & stearic acids with ZnO and other metal oxides. . . . Taranenko²⁷ studied the reactions of oleic and stearic acids with ZnO. Mixtures were heated one hour at 100, 150, and 180°C. At 100°C, 91% Zn oleate and 64% Zn stearate formed.

Th. Goldschmidt A.G.²⁸ prepared zinc soaps free of electrolytes by reacting at 80°C a suspension of ZnO in water, CO_2 and NH_3 with a fatty acid. . . . Shinagawa Kako²⁹ produced zinc stearate by heating at 55-65°C for 2 hours, with stirring, a mixture of ZnO, stearic acid, NH_4OH and NH_4Cl .

Zinc Thiocarbamates

Electro-Chemical Co.³⁰ was granted a series of 23 patents on the double zinc salts of dithiocarbamic acid.

Phillips Petroleum³¹ found that zinc alkyl trithiocarbamates and mercaptides are effective as bird repellents.

Zinc Chemicals, Miscellaneous

Rasjid, et al.,³² prepared active carbon by treating coconut-shell carbon with ZnCl_2 Zakharov, et al.,³³ found that the addition of 10% ZnO to lead azide (PbN_6) accelerated the evolution of N_2 under irradiation. This effect, they reported, was due to development of a positive charge on the azide by the ZnO addition.

Aerojet-General³⁴ disclosed that the addition of zinc nitrate to smokeless-propellant compositions containing a polyester resin serves effectively as a burning-rate catalyst. . . . Allibert³⁵ developed quick-setting gypsum by addition of 1% ZnSO_4 and 0.5% ZnO. These additions decreased the setting time by 6 minutes and increased the hardness 20%.

Dostal, et al.,³⁶ removed HCl from waste gases by passing the gas stream through a Venturi tube or foam scrubber containing an aqueous suspension of zinc oxide. . . . Garde³⁷ produced ZnCl₂ by passing Cl₂, activated by irradiation, through a ZnO-packed tower. Water, added at the top, dissolved and removed the ZnCl₂.

Nippon Soflan³⁸ prepared a zinc compound by reacting ZnO with excess urea 2-8 hours at 140-170°C, with or without a solvent. Suitable solvents were: DMF, Me₂SO, and AcNMe₂. The reaction can also be carried out in a nitrogen atmosphere. Example: ZnO 246 and urea 360 grams in DMF were heated 5 hours at 130-140°C under N₂ to yield 315 grams of compound.

Ogawa³⁹ developed a combustion-promoting additive for coal and heavy oil; it also inhibited the formation of alkali deposits and carbon flowers. Composition: NH₄Cl 40-50, NaHCO₃ 7-13, NiSO₄ 3-8, Cu naphthenate 12-18, ZnCl₂ 12-18, ZnO 7-13 and CaO 12-18 parts.

Siemens A.G.⁴⁰ prepared a carbon electrode through the use of ZnCl₂ and polyacrylonitrile. The method: The nitrile is dissolved in a solution of ZnCl₂ at 100°C; it is carbonized at 850-1000°C in a nitrogen atmosphere. The resulting powder is crushed to a fine particle size (32 micron diameter) and formed into electrodes.

A.E. Staley⁴¹ disclosed the preparation of acidic floor polishes with high resistance to detergents, but easy removal (for maintenance) with an aqueous solution of Na₃PO₄ at 11 pH. The floor polish is prepared from zinc acetate and a polymer emulsion.

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