Rare Earth Technology and Applications

CHEMICAL TECHNOLOGY REVIEW No. 154

ndc

RARE EARTH TECHNOLOGY AND APPLICATIONS

Edited by F. Villani

NOYES DATA CORPORATION
Park Ridge, New Jersey, U.S.A.
1980

Library of Congress Catalog Card Number: 80-42
ISBN: 0-8155-0795-X
Printed in the United States

Published in the United States of America by
Noyes Data Corporation
Noyes Building, Park Ridge, New Jersey 07656

Library of Congress Cataloging in Publication Data

Villani, F, 1926-
Rare earth technology and applications.

(Chemical technology review ; 154)
Includes indexes.
1. Rare earth metals--Patents. 2. Earths, Rare--
Patents. I. Title. II. Series.
TA480.R3V54 669'.29'0272 80-42
ISBN 0-8155-0795-X

RARE EARTH TECHNOLOGY AND APPLICATIONS

FOREWORD

The detailed, descriptive information in this book is found in U.S. patents issued since January 1973 that deal with rare earth technology and applications.

This book is a data-based publication, providing information retrieved and made available from the U.S. patent literature. It thus serves a double purpose in that it supplies detailed technical information and can be used as a guide to the patent literature in this field. By indicating all the information that is significant, and eliminating legal jargon and juristic phraseology, this book presents an advanced commercially oriented review of rare earth technology and applications.

The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure." These patents include practically all of those issued on the subject in the United States during the period under review; there has been no bias in the selection of patents for inclusion.

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially useful information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas of research and development. The information contained in this book will allow you to establish a sound background before launching into research in this field.

Advanced composition and production methods developed by Noyes Data are employed to bring these durably bound books to you in a minimum of time. Special techniques are used to close the gap between "manuscript" and "completed book." Industrial technology is progressing so rapidly that time-honored, conventional typesetting, binding and shipping methods are no longer suitable. We have bypassed the delays in the conventional book publishing cycle and provide the user with an effective and convenient means of reviewing up-to-date information in depth.

The table of contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor and patent number help in providing easy access to the information contained in this book.

15 Reasons Why the U.S. Patent Office Literature Is Important to You –

1. The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical commercial process information assembled here than is available from any other source.

2. The technical information obtained from the patent literature is extremely comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure."

3. The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature.

4. An important feature of the patent literature is that it can serve to avoid duplication of research and development.

5. Patents, unlike periodical literature, are bound by definition to contain new information, data and ideas.

6. It can serve as a source of new ideas in a different but related field, and may be outside the patent protection offered the original invention.

7. Since claims are narrowly defined, much valuable information is included that may be outside the legal protection afforded by the claims.

8. Patents discuss the difficulties associated with previous research, development or production techniques, and offer a specific method of overcoming problems. This gives clues to current process information that has not been published in periodicals or books.

9. Can aid in process design by providing a selection of alternate techniques. A powerful research and engineering tool.

10. Obtain licenses – many U.S. chemical patents have not been developed commercially.

11. Patents provide an excellent starting point for the next investigator.

12. Frequently, innovations derived from research are first disclosed in the patent literature, prior to coverage in the periodical literature.

13. Patents offer a most valuable method of keeping abreast of latest technologies, serving an individual's own "current awareness" program.

14. Copies of U.S. patents are easily obtained from the U.S. Patent Office at 50¢ a copy.

15. It is a creative source of ideas for those with imagination.

INORGANIC CHEMICAL INDUSTRY PROCESSES, TOXIC EFFLUENTS AND POLLUTION CONTROL 1978

by Marshall Sittig

Chemical Technology Review No. 118
Pollution Technology Review No. 52

While industrial inorganic chemistry may seem less glamorous than the complex chemistry of the life sciences, the progress in wonder drugs, miracle fibers and recombinant DNA is basically dependent on the uninterrupted flow of "heavy" chemicals, such as sulfuric acid, chlorine and sodium hydroxide.

The present book provides helpful directions for making these inorganic chemicals. The arrangement is encyclopedic starting with alumina and ending with various zinc compounds. The process details provide a wide choice of raw materials due to a changing economy and partial cutoff of the customary supplies, e.g., natural gas, which in inorganic processing is a most convenient source of hydrogen, carbon, carbon monoxide and carbon dioxide. Careful perusal of this book will reveal many alternate sources and energy-sparing processes.

Contaminated wastewater and air pollution problems are considerable, but new commercial processes are shown, as well as detailed technology from the U.S. patent literature. Because of the stable nature of this industry, established processes and obsolete equipment units remain sufficiently profitable to continue in use. Still, considerable progress in pollution control has been achieved during the past 5 or 6 years and is reflected in this book. The following chemicals have received detailed treatment:

Alumina
Aluminum Chloride
Aluminum Fluoride
Aluminum Sulfate
Ammonia
Ammonium Chloride
Ammonium Diuranate
Ammonium Hydroxide
Ammonium Nitrate
Ammonium Phosphate
Ammonium Sulfate
Antimony Oxide
Arsenic Acid
Arsenic Oxides
Barium Carbonate
Barium Sulfate
Beryllium Hydroxide
Beryllium Oxide
Borax
Boric Acid
Boron Trichloride
Bromine
Cadmium Pigments
Cadmium Sulfide
Calcium Arsenate
Calcium Carbide
Calcium Carbonate
Calcium Chloride
Calcium Hydroxide
Calcium Oxide
Calcium Phosphate
Carbon Dioxide
Carbon Monoxide
Chlorine & Caustic
Chlorosulfonic Acid
Chrome Green Pigment
Chrome Yellow Pigment
Chromic Acid
Chromic Oxide Pigment
Cobalt Compounds
Cobalt Oxide
Copper Sulfate
Cuprous Oxide
Ferric Chloride
Ferrous Sulfate
Fluorine
Helium
Hydrochloric Acid
Hydrogen
Hydrogen Fluoride
Hydrogen Peroxide
Iodine
Iron Blue Pigments
Iron Oxide Pigments
Lead Carbonate
Lead Nitrate
Lead Oxides
Lead Sulfate
Lithium Carbonate
Lithium Hydroxide
Magnesium Chloride
Magnesium Sulfate
Manganese Sulfate
Mercuric Chloride
Mercuric Oxide
Mercuric Sulfide
Mercurous Chloride
Molybdate Chrome Pigments
Nickel Sulfate
Nitric Acid
Nitrogen & Oxygen
Nitrous Oxide
Phosphate Rock
Phosphoric Acid
Phosphorus
Phosphorus Oxychloride
Phosphorus Pentasulfide
Phosphorus Pentoxide
Phosphorus Trichloride
Potassium Chlorate
Potassium Chloride
Potassium Dichromate
Potassium Iodide
Potassium Metal
Potassium Nitrate
Potassium Perchlorate
Potassium Permanganate
Potassium Sulfate
Silver Nitrate
Sodium Bicarbonate
Sodium Bisulfite
Sodium Borohydride
Sodium Bromide
Sodium Carbonate
Sodium Chlorate
Sodium Chloride
Sodium Chromate
Sodium Cyanide
Sodium Dichromate
Sodium Fluoride
Sodium Sulfide
Sodium Hydrosulfite
Sodium Hydroxide
Sodium Metal
Sodium Perchlorate
Sodium Phosphates
Sodium Silicate
Sodium Silicofluoride
Sodium Sulfite
Sodium Thiosulfate
Stannic Oxide
Stannous Chloride
Strontium Carbonate
Sulfur Chlorides
Sulfuric Acid
Sulfuryl Chloride
Superphosphoric Acid
Supported Catalysts
Thallium Carbonate
Thionyl Chloride
Titanium Dioxide
Ultramarine Pigments
Zinc Chloride
Zinc Oxide
Zinc Sulfate
Zinc Yellow Pigment

ISBN 0-8155-0726-7

351 pages

CORROSION INHIBITORS 1979
RECENT DEVELOPMENTS
by J.S. Robinson

Chemical Technology Review No. 132

There are both multipurpose and highly specialized corrosion inhibitors described in this new work. Corrosion is an ever-present problem in industry, but it is clear from the nearly 300 processes and techniques detailed here that research is making substantial strides in supplying products to overcome it. The book comprises chemicals, such as sequestering agents and oxygen scavengers; and physical barriers, such as coatings.

The author has arranged the processes according to their most significant end use, as shown below. The first chapter, for instance, covers substances used to overcome the problems encountered in water engineering. It encompasses both antiscalants and corrosion inhibitors, the latter often being required during scale removal operations.

It should be emphasized that some inhibitors serve in several capacities—the benzotriazole derivative found under lubricants may well be ideal for circulating water systems.

Chapter headings and **examples of some** important subtitles follow below. The number of processes per topic is shown in parentheses following chapter headings.

ISBN 0-8155-0757-7 **306 pages**

INCINERATION OF INDUSTRIAL HAZARDOUS WASTES AND SLUDGES 1979

by Marshall Sittig

Pollution Technology Review No. 63

This is another volume in our Pollution Technology Review series which is especially designed to provide help and advice for strict compliance with present and projected rules and regulations of the Resource Conservation and Recovery Act (RCRA) as interpreted by the EPA.

This book, dealing with incineration and related combustion processes, such as pyrolysis, can be of vital importance to the interests of the affected companies, who must see to it that incineration, combustion, and other burning operations are conducted with proper attention to complete destruction of the toxic materials, and efficient scrubbing of the effluent gases, followed by appropriate treatment of the scrubbing liquors. A condensed table of contents follows here:

ISBN 0-8155-0774-7 **348 pages**

LANDFILL DISPOSAL OF HAZARDOUS WASTES AND SLUDGES 1979

by Marshall Sittig

Pollution Technology Review No. 62

The Resource Conservation and Recovery Act (RCRA), passed 1976, created a Federal and State regulatory authority over both solid and hazardous wastes. The projected regulations will become fully effective by June 30, 1980. These will have profound effects on industrial waste disposal practices, particularly those for hazardous wastes.

The Department of Transportation has currently compiled a list of about 300 poisons, pesticides and priority pollutants considered to be hazardous waste materials.

In this book, the landfill technology and the directions for the disposal of unwanted hazardous and toxic substances are based on reports and guidelines mostly issued by the EPA. A condensed table of contents follows here.

ISBN 0-8155-0773-9 **365 pages**

CONTENTS AND SUBJECT INDEX

and it is preferred that the specific surface area be reasonably high, though this did not appear to be critical but is a preference for maximum activity. Preferred is a silica with a specific surface area ranging from such as about 10 to 100 m^2/g, more preferably from about 50 to 100 m^2/g.

While the silica supported catalyst can be prepared in any convenient fashion, one effective method is to impregnate the silica with a solution containing one or more rare earth metal salts which are convertible to the oxide on calcination in a molecular oxygen atmosphere. Typical and suitable of such rare earth metal salts are the bromates, halides, nitrates, sulfates, various organic complexes such as those derived from ethylenediaminetetraacetic acid, and the like, preferred being the nitrates for ease and convenience of dissolving and handling.

After impregnation of the support, the composite is dried, and calcined in a molecular oxygen-containing atmosphere, such as air, at a suitable calcining temperature, such as about 600° to 1500°F (315° to 816°C), suitably and preferably from 800° to 1200°F (about 426° to 649°C), for a time suitable to effectuate the conversion of the rare earth metal salt to the oxide, typically for such as about 1 to 20 hours.

After calcining, the catalysts can be activated at elevated temperatures in gases such as air, hydrogen and nitrogen and mixtures thereof. The choice of gas appears to be related to the catalyst. Praseodymium-containing catalysts are preferably activated in air, whereas cerium-containing supported catalysts are preferably activated in hydrogen, for example.

Example: A catalyst was prepared by impregnating 10 to 20 mesh (U.S. Sieve Series) catalytic grade silica having a specific surface area of about 88 m^2/g with an aqueous solution of praseodymium nitrate, drying the composite, and calcining the dried material at 900°F in air for two hours. The final catalyst was calculated to contain 10 wt % praseodymium oxide calculated as the metal and 90 wt % silica.

A tubular reactor was charged with 20 cc of the catalyst, the reactor was heated to 900°F and air was passed through it for two hours and then nitrogen overnight (about fifteen hours). The reactor was cooled to 705°F (374°C) and hexene-1 passed through it at atmospheric pressure for 0.7 hour at the rate of 0.5 LHSV. The effluent was cooled and the liquid portion collected in a wet ice trap and analyzed by gas-liquid chromatography.

The results showed the liquid product contained 10.8 wt % olefins lower in molecular weight than hexene and 19.6 wt % olefins higher in molecular weight than hexene. In terms of hexene converted, olefins lower in molecular weight than hexene constituted 35.5 wt % of the products and olefin higher in molecular weight than hexene constituted 64.5 wt % of the products.

Rare Earth Metal Phosphates

W.L. Kehl and R.J. Rennard, Jr.; U.S. Patent 3,752,878; August 14, 1973; assigned to Gulf Research & Development Company have found that aryl halides, such as chloroxylene, are hydrolyzed to the corresponding ring hydroxylated aryl compounds, such as xylenol, by contacting the aryl halides and steam with a rare earth metal phosphate catalyst, such as lanthanum phosphate, cerium phosphate and neodymium phosphate.