Industrial Water Treatment Chemicals and Processes

Developments Since 1978

Edited by M. J. Collie

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NOYES DATA CORPORATION
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FOREWORD

The detailed, descriptive information in this book is based on U.S. patents, issued from January 1979 through October 1982, that relate to industrial water treatment chemicals and processes. This title contains new developments since our previous title, *Industrial Wastewater Cleanup,* published in 1979.

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 recent developments in the field of industrial water treatment chemicals and processes.

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.

16 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. Most important technological advances are described in the patent literature.

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. Identifying potential new competitors.

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

16. Scrutiny of the patent literature has important profit-making potential.

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INTRODUCTION

The patents on which this book is based relate to various aspects of water treatment ranging from a chemical for the removal of a specific compound to a detailed process for the treatment of a wastewater containing multiple organic and inorganic substances.

The largest number of patents describe wastewater treatment. Many of these have application in specific industries, for example, the purification of paper, textile or chemical manufacturing wastes and food or beverage plant effluents. Others are intended for more general use while still others describe improvements in known processes.

Deposition of scale on and the corrosion of metal surfaces in contact with water or aqueous solutions continue to be problems in many industries. The book includes a large number of processes directed to correcting these problems.

Use of flocculants makes possible accelerated separation of suspended material, thus permitting recycling of water and obviating the need for settling ponds. Flocculants are also used as drainage aids, for example, in papermaking. The chapter on flocculants, coagulants and adsorbents describes work being done in these fields.

A chapter on biocides includes processes for disinfecting wastewater before discharging into waterways, as well as processes for the control of microorganisms in cooling towers or in stored materials such as paint and cutting fluids. Also included in this chapter are several compositions that act as scale or corrosion inhibitors in addition to being biocides.

Heavy metal ions must be removed before wastewaters are discharged into waterways. The chapter on metal removal and recovery addresses this problem, describing methods applicable to effluents from specific industrial processes and methods generally applicable.

Other chapters describe compositions and processes useful in the dewatering of coal slurries, drilling muds, phosphate slimes and other mineral slurries, and compositions to be used as flotation aids. Several flotation processes are also described.

SCALE AND CORROSION INHIBITORS

SCALE INHIBITORS

Mixtures of Polyanionic and Polycationic Polymers for Evaporative Desalination Units

Desalination is a process for removing soluble salts from water containing them to render such water potable or useful in operations where the original dissolved salt content is unacceptable. Desalination is an important process for providing potable water from seawater in arid areas where other sources of water are limited. Desalination is also an important process for removing salts from wastewaters so that such waters can be recycled or safely discharged into natural waters.

Desalination may be an evaporative process carried out in desalination units that may be operated under vacuum, at atmospheric pressure, or at superatmospheric pressure. The use of vacuum or superatmospheric pressures are more difficult and costly to employ in conjunction with desalination units and, accordingly, the preferred procedure of operation is essentially at atmospheric pressure. In operating such desalination units, the temperature of operation, which is dependent upon the operating pressure employed, influences the nature of scaling that occurs.

At atmospheric pressure a transition point occurs at a temperature between about 80° and about 90°C, below which the scale formation is due to calcium carbonate and above which the scale formation is due to magnesium hydroxide. While scale formation due to calcium carbonate can be controlled by a number of useful additives the problem of magnesium hydroxide scale or sludge control in evaporative desalination units has not been satisfactorily solved. Thus, although evaporative desalination units are potentially efficient in the desalination of seawaters and waters of high salt contents, the rapid formation of magnesium scaling or sludging reduces efficiency, necessitating shut-down and scale or sludge removal from the desalination units. The loss of operating time and the difficulties of scale or sludge removal severely limit the amount of water processed by a desalination unit in a given time period and add to the cost of processed water.

R.M. Goodman; U.S. Patents 4,147,627; April 3, 1979; 4,164,521; August 14, *1979; and 4,205,143; May 27, 1980; all assigned to American Cyanamid Company* provides a process for inhibiting formation of magnesium scale or sludge in evaporative desalination units which comprises adding to the water being processed an effective amount of a mixture of (1) a polyanionic polymer containing at least about 50 mol percent of repeating units derived from an acrylic acid and any balance of repeating units derived from one or more monomers compatible therewith, the acid units being in the form of at least one member selected from the group consisting of free acid radical, ammonium salt, and alkali metal salts, and (2) a polycationic polymer.

The polycationic polymer may be selected from the group consisting of (a) dimethylamine-polyamine-epichlorohydrin reaction product wherein the amount of the polyamine is from 0 to about 15 mol percent of the total amine content and the amount of the epichlorohydrin is from at least the molar equivalent of the total amine content up to the full functional equivalent of the amine content, (b) poly(dimethyldiallylammonium chloride), (c) quaternized derivatives of poly(dimethylaminoethyl methacrylate), and (d) poly[oxyethylene(dimethylimino)ethylene (dimethylimino)ethylene dichloride], the polyanionic polymer having a molecular weight in the range of about 500 and about 50,000, the polycationic polymer having a molecular weight in the range of about 1,500 and about 500,000, and the molar ratio of the polycationic polymer to the polyanionic polymer based on the average molecular weight of the repeating units therein being in the range of about 2:1 and about 25:1.

Use of the process in association with evaporative desalination units enables such units to be operated for greatly extended time periods at high efficiency. This result is highly surprising and completely unexpected in view of the fact that the polyanionic polymer is ineffective in the inhibition of magnesium floc formation when used alone and the polycationic polymer is completely ineffective as an antiscaling agent when used alone. In addition to its ability to inhibit magnesium hydroxide scale or sludge formation, the process is also effective against calcium carbonate scaling, thus providing protection against scale formation at a wide range of operating temperatures.

In carrying out the process, the mixed polymer composition is added to the water being processed in an evaporative desalination unit in an effective amount.

An effective dosage will generally be found in the range of about 0.1 to 100 parts polymer mixture per million parts of water being processed. A preferred range is generally about 5 to 50 ppm.

The process is more fully illustrated by the examples which follow wherein all parts and percentages are by weight unless otherwise specified.

Since the evaluation of scale inhibitors in commercial type desalination units involves large quantities of chemical additives, copious quantities of process water, considerable expenditures of power to effect vaporization, it is desirable to employ a small-size laboratory screening method whereby the suitability of proposed additives can be predicted with accuracy. The following laboratory method was employed in some of the examples which follow and subsequent large-size evaluations on commercial type equipment verified the accuracy of its predictions.

(1) To a 150 ml capacity beaker containing 68 ml of deionized water are added 5.4 ml of 0.10 N sodium hydroxide.

(2) To the solution obtained above are added 5 ml of a 900 ppm stock solution of the agent of test, giving 50 ppm on the final contents of the beaker.

(3) After thoroughly mixing the resulting composition, 11.55 ml of magnesium stock solution [6.0 grams of $Mg(NO_3)_2 \cdot 6H_2O$ in 1 ℓ of water] are added and heating to 90°C with stirring is effected.

(4) The beaker is then removed from the heat source and allowed to cool at ambient conditions.

A blank, no additive employed, run in this manner shows a white floc of hydrated magnesia which settles out in about twenty minutes. Ineffective scale inhibitors will have little or no effect on the rate of settling of hydrated magnesia. Effective scale inhibitors show significant increase in settling time of hydrated magnesia.

Example 1: Using the procedure described above, the following run was made. The polyanionic polymer was a 50 weight percent aqueous solution of a copolymer of 90 mol percent acrylic acid units in the form of the sodium salt and 10 mol percent of acrylamide units, the molecular weight being about 1,000. The polycationic polymer was a 50% aqueous solution of the reaction product of an amine composition consisting of 98 mol percent of dimethylamine and 2 mol percent of ethylenediamine with an amount of epichlorohydrin equal to the full functionality of the two amines, the product having a molecular weight of about 10,000. The mol ratio of polycationic polymer to polyanionic polymer was 2:1, and was obtained by adding three parts of the polycationic polymer to one part of the polyanionic polymer. A free-flowing homogeneous composition dilutable with water in all proportions was obtained. Evaluation of this composition as described in the procedure resulted in the prevention of magnesium hydroxide floc for 5 days.

Example 2: The procedure was again followed using the polyanionic polymer of Example 1 but substituting for the polycationic polymer therein a poly(dimethyldiallylammonium chloride) having a molecular weight of about 10,000, which was supplied in the form of a 20 wt % aqueous solution, the molar ratio of polycationic polymer to polyanionic polymer being 2:1 based on the average molecular weight of the repeating units of the polymers. The proportions of the mixture were one part of polyanionic polymer and 4.35 parts of polycationic polymer. A homogeneous solution was obtained which was dilutable with water in all proportions and was effective as a scale inhibitor in the procedure.

Example 3: The procedure of Example 1 was again followed in every material detail except that the polycationic polymer was a homopolymer of dimethylaminoethyl methacrylate quaternized with dimethyl sulfate and having a molecular weight of about 500,000. The proportions of polymers used was such as to provide a molar ratio of polycationic polymer to polyanionic polymer of 3:1 based on the average molecular weights of the repeating polymer units. The composition was an effective scale inhibitor based on the procedure.

Example 4: The procedure of Example 1 was again followed except that in place of the polycationic polymer used therein there was employed a poly[oxyethylene-(dimethylimino)ethylene (dimethylimino)ethylene dichloride] of molecular weight of about 3,400. The proportions of polymers were such as to provide a