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ANTIFOULING MARINE COATINGS

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Foreword

The detailed, descriptive information in this book is based on U.S. patents describing the chemical and technological development of antifouling marine coatings.

This book serves a double purpose in that it supplies detailed technical information and can be used as a guide to the U.S. 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 antifouling marine coatings, together with the underlying chemical and biochemical principles.

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."

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. One should have to go no further than this condensed information to establish a sound background before launching into research in this field.

Advanced composition and production techniques developed by Noyes Data Corporation are employed to bring these durably bound books to you in a minimum of time. The shortest possible production time is necessary to close the gap between "manuscript" and "completed book." Industrial technology is progressing so rapidly that time-honored, conventional typesetting, printing, binding and shipping methods can render a technical or scientific book quite obsolete before the potential user gets to see it.

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 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 technology, 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 cents a copy.

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

Contents and Subject Index

Introduction

One of the earliest needs for performance-oriented coatings was in the marine environment. Very early formulations were designed around known toxins such as copper and mercury compounds and the patent literature of the 19th century is replete with hundreds of formulations using these materials in creosote and natural drying oil formulations.

The two areas on a ship requiring specialty coatings are, of course, the bottom and the boot-topping area. The boot-topping area intermittantly exposed to both air and water, represents a particularly difficult surface to protect from the elements.

For ship bottoms, antifouling compounds based on copper, mercury and tin are commonly incorporated into somewhat water-sensitive binders to afford gradual breakdown of the film to allow for a sustained release of the poison.

This required self-erosion property necessitates frequent repainting of the ship bottom, depending on location and severity of exposure conditions. In general, boot-topping paints are designed to provide a high level of resistance to both salt water and weather. Typically phenolic resin-tung oil and vinyl resin combinations are used.

This book contains many patented processes which provide high performance antifouling coatings based on copper, mercury, tin and arsenic compounds, as well as a number of organic coating compositions. In all, several hundred different formulations are provided, along with references to the early process literature which contains many of the thoughts, concepts and basic information which led to today's commercial coatings.

Copper Compounds

COPPER OXIDE-BASED COATINGS

Rosin and Blown Fish Oil

W. J. Francis; U.S. Patent 2,989,407; June 20, 1961 describes a paint which is based on a rosin plasticized with blown fish oil as the matrix for the pigment ingredients, which forms a film of a controlled soluble matrix type that permits the gradual dissolution of the matrix in sea water at a rate suitable for concurrent release of the toxic particles in the pigment, thus resulting in effective antifouling action. The quantities or percentages by weight of the component ingredients of a black boot-topping coating composition are as follows.

Ingredient	Percent Range	Percent Preferred
Rosin	20.23 to 28.86	23.40
Blown fish oil	7.97 to 13.26	10.02
Zinc stearate	0.85 to 2.45	1.67
Cuprous oxide	27.78 to 34.60	28.40
Magnesium silicate	2.21 to 6.64	4.68
Mercuric oxide	0.88 to 5.27	3.68

(continued)

Ingredient	Percent Range	Percent Preferred
Lampblack	4.34 to 10.33	5.85
Coal tar naphtha	16.72 to 25.07	22.30

Cuprous sulfide or copper pigment (containing a minimum of 6% cuprous oxide) may be substituted for the cuprous oxide. Diatomaceous silica or other silica extender pigment may be used in place of magnesium silicate. Carbon black and black iron oxide may be used as alternate blackening pigments instead of lampblack.

From the above table, it is evident that the ratio of rosin to blown fish oil can be as low as about 1.5 and as high as about 3.6 by weight. A manner of preparing the coating can be understood from the following description for making about one hundred gallons from the ingredients listed in the following table.

Ingredient	Pounds
Rosin (gum or wood)	280
Blown fish oil	120
Coal tar naphtha	267
Zinc stearate	20
Cuprous oxide	340
Mercuric oxide	44
Magnesium silicate	56
Lampblack	70

The rosin and fish oil are heated together in a kettle to 300°F. until entirely liquid. The batch is then removed from the heat and the batch stirred while the coal tar naphtha is slowly added. The batch constituting the mixed vehicle is then allowed to cool to ordinary room temperature. It is in liquid form at such temperatures. A paste is then formed by adding the dry ingredients, comprising the pigments, to about 636 pounds of the mixed vehicle to form a paste of suitable consistency for grinding.

The paste is then ground on a roller mill or other suitable mill to obtain uniform dispersion and to obtain a minimum fineness of grind of 4 Hegeman gauge. The ground paint base is thinned with the remainder of the mixed vehicle, and then this batch is thoroughly mixed to give a homogeneous liquid paint. This paint can be placed in any suitable receptacles, preferably metal cans, for storage.

The paint is fluid and not thixotropic at ordinary temperatures so that little stirring is required prior to application by any of the common means, viz brushing, spraying and by roller. The paint dries rapidly after application, being dry to touch in about ten minutes and dried hard in about 1 1/2 to 3 1/2 hours.

The paint dries rapidly apparently because of its mercuric oxide ingredient which also functions as a toxic antifouling agent and also as a toughening agent for the film by partially reacting with the vehicle binder comprising the rosin, the blown fish oil, and the coal tar naphtha.

The paint retains its antifouling properties for considerable length of time. Tests have shown that the paint gives excellent film durability and provides protection against corrosion and against marine fouling organisms, such as algae and hydroids that attach to water-line surfaces of vessels, as well as shell fouling matter like barnacles, tubeworms and encrusting bryozoa that foul ship bottoms.

Steel panels painted with two coats of the paint were tested under sea immersion conditions and had satisfactory performance after 23 months, over three times as long as other black boot-topping paints. The antifouling paint retains its black color during long periods of service, whereas others become green after exposure to sea water.

The paint, based on rosin plasticized with blown fish oil as the matrix for the pigment ingredients, forms a film of a controlled soluble matrix type that permits the gradual dissolution of the

matrix in sea water at a rate suitable for the concurrent release of the toxic particles in the pigment, thus resulting in effective antifouling action.

Rosin and Wax

W.J. Francis; U.S. Patent 2,602,752; July 8, 1952 describes a rapid dry paint of the following composition and percentages of ingredients.

	Percent Range	Percent Preferred
Gum rosin	36.67 to 41.67	41.67
Paraffin wax	4.44 to 8.00	4.44
Ceresine wax	2.38 to 4.55	2.38
Copper linoleate	13.64 to 24.0	13.64
Cuprous oxide	32.46 to 37.87	32.46
Inert pigment (asbestine)	0 to 5.41	5.41

The primary function of the waxes is to reduce the viscosity of the composition to a suitable spraying consistency when heated in the range from 260° to 300°F. The paraffin also functions as a plasticizer for the rosin.

The ceresin wax (melting point 173° to 175°F.) increases the sag resistance properties of the applied composition, i.e., it helps prevent the sagging or flowing of the applied coating when high temperature conditions prevail or when subjected to direct sunlight.

The purpose of the metallic soap is to improve the physical properties of the film and promote adhesion and to improve the copper leaching characteristics of the film under sea water immersion conditions.

The rosin functions as the main resinous binder ingredient of the matrix. The cuprous oxide functions as the toxic ingredient for the antifouling paint. The magnesium silicate such as asbestine promotes better suspension of the total pigment in the paint, and also improves the antifouling action of the composition.

If the ceresine wax were eliminated from the composition, the paint film would have deficient sag resistance properties. If paraffin were eliminated, the composition would have too high a viscosity for spray application.

In preparing the composition the waxes and rosin are placed in a steam jacketed steel kettle and heated to approximately 250°F. until the ingredients are melted. The metallic soap is then added. This soap is selected from the group including copper naphthenate, copper linoleate, copper tallate, copper oleate and zinc naphthenate, with preference given to copper linoleate.

The mixture of heated waxes, rosin and soap is stirred slowly and continuously by mechanical means while the temperature is slowly increased to a value of around 300°F. When the batch is entirely liquefied, cuprous oxide (or metallic copper) and asbestine are slowly sifted into the mix while maintaining the agitation and the temperature at about 300°F. for a time period of at least 15 minutes after all the ingredients are in the kettle so as to insure adequate dispersion.

The finished product is then drained off into drums and allowed to cool and solidify; after which the solid plastic may be broken into small chunks for transportation.

In use the chunks of plastic are melted in an open kettle provided with a steam jacket for heating to a temperature range of 250° to 350°F. At this temperature the composition has a low viscosity and may therefore be sprayed on the hull or other base. Preferably in hull use, the hull should have received, prior to antifouling paint application, a coating of anticorrosive paint, the antifouling paint being applied over the anticorrosive layer.

The paint spreads readily to a smooth laye. of about 30 mils thickness which is above 5 to 10 times the thickness of the usual antifouling paint film.

The properties of the melted paint are such that it maintains good stability while being maintained in a molten state. On application to the hull surface it dries rapidly with a total absence of sagging. In fact, its nonsagging property is an outstanding characteristic of the paint, it being unaffected by temperatures as high as 140°F. maintained for 24 hours and as high as 162°F. for short time intervals.

Moreover, only a single coat is necessary, the paint smoothing down to a uniform layer approximately 30 mils thick. Tests have indicated that the paint has a penetration at 70°F. of 84.6 (ASTM standard), a viscosity range between 260° and 300°F. of 74 to 35 cp. respectively, no embrittlement of film or settling of pigments after 8 hours of heating at 300°F., capacity for spraying as low as 270°F., complete adhesion after 90°F., base bending at 77°F., over a 1/2 inch rod, resistance to shock in temperature range 35° to 77°F., crack resistant at Dry Ice temperature and normal adhesion of 22.5 lbs./sq. in.

The overall usefulness of the paint as an antifouling medium is apparent from the fact that the toxic action is maintained as shown by actual test for time periods of over three years with the paint still effective at the end of this period. Tests indicate a steady state leaching rate per month of 28.2, using the test method described by Ketchum, Ferry, Redfield and Burns (Industrial & Engineering Chemistry, vol. 37, pp. 456).

Phenol-Formaldehyde Hot Melts

A.S. Pitre and J.R. Saroyan; U.S. Patent 2,579,610; Dec. 25, 1951 describe an antifouling coating which continuously exposes a toxic surface, which erodes away by dissolving and/or disintegrating under the frictional attack of relatively moving water at least as rapidly as surface toxicity is leached out whereby a continuously toxic surface is exposed.