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Volatile Corrosion Inhibitors

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December 1964

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VOLATILE CORROSION INHIBITORS

ABSTRACT

Significant reports covering the period since 1962 were selected for this study, with reference to relevant earlier works. Recent government R&D on volatile corrosion inhibitors (VCI) has generally proceeded along three lines: extension of tests defining the protective value of these materials for longer storage periods to steel equipment, tolerances of various nonferrous materials and finishes toward tarnishing or corrosion by these materials, and effectiveness of exterior packaging materials in extending use of these inhibitors to more severe exposures of water vapor and liquid. Volatile corrosion inhibitors in the form of salts, dissolved in oils, or coated on paper within enclosed shipment parcels or storage spaces offer improved corrosion protection to bare steel while it is in a ready condition for withdrawal and immediate use.

REVIEW OF RESEARCH REPORTS

Introduction

For the past several years government agencies have been keenly interested in better corrosion protection in storage and more rapid withdrawal of equipment in a condition ready for use. Continuing progress in the use of volatile corrosion inhibitors has resulted from studies by these agencies in three major areas: evaluation of time in which steel is fully protected under varying external conditions, effect of inhibitor materials upon nonferrous metals, and the effect of the outside package materials. These studies, which are available from the Clearinghouse for Federal Scientific and Technical Information, Department of Commerce, have potentially wide application in delivering products to the consumer in more ready-to-use condition.

Corrosion inhibitors are employed to prevent damage to the surface of metals during stages of packaging, storage, shipment and use of equipment. This damage results from the attack on the metal surface by moisture in liquid or vapor form and by the presence of acids or soluble salts.

Volatile corrosion inhibitors provide protection for simple to complicated metallic assemblies so that these packaged items can be used immediately without the tedious and costly procedures normally associated with the removal of preservatives containing oil or grease. Other methods of protection, such as storage in controlled low humidity warehouses or in completely impermeable packaging materials, are not usually required with properly used volatile corrosion inhibitors.

Volatile corrosion inhibitors are amine salts of weak inorganic acids and amine-organic acid complexes. Contained in trays or cloth bags, or coated on paper and placed within enclosed equipment or packages, they have the power of preventing the corrosion of stored steel.

These compounds act as vapor sources for the transfer of benzoate, nitrite, or other corrosion-inhibiting compound radicals to the surface of the metal to be protected. The amine part (or radical) of these compounds contributes to the low volatility, and in addition to providing corrosion-inhibiting action of its own, serves as an alkalizer or neutralizer of traces of acid vapors which might be present.

The selection of these compounds depends on the humidity, salinity, porosity of packaging, infiltration of outside atmosphere to which the packaged steel equipment may be exposed, as well as the vapor pressure of the compound at the temperature of shipment and storage. There is also some risk of tarnishment and corrosion of nonferrous metals such as zinc, magnesium, and cadmium and their alloys.

Commonly used compounds are dicyclohexylamine nitrite (DCHN), cyclohexylamine carbonate (CHC), and mixtures of sodium nitrite and urea. A qualitative comparison of the compounds and their use (PB-111 407P) lists the following ammonium or amine positive radicals: dicyclohexyl, cyclohexyl, amyl, isoamyl, diisopropyl, isopropyl, dibutyl, monethyl, diethyl, triethyl, and naphthyl. The following negative radicals are also used: nitrite, benzoate, butyrate, phosphonate, sulfonate, salicylate, carbonate, and carbamate. Some of these compounds are proprietary in nature.

A recent and comprehensive bibliographic guide (AD-600 643P) on the general subject "Vapor Phase Corrosion Inhibitors for Nonferrous and Ferrous Metals" was compiled in 1963 by the Prevention of Deterioration Center, National Academy of Sciences. This guide lists 153 references (1947-63) including patents, U. S. Government reports, and technical magazines. General surveys of the literature also include a comprehensive 1954 review, PB-111 407P, "Volatile Rust Inhibitors" by Hayward R. Baker of the Naval Research Laboratory.

Protection of Steel

The most significant contribution of volatile corrosion inhibitors has been their demonstrated utility in protecting bare steel equipment from corrosion over long periods during shipment and storage.

The Army Chemical Center sponsored a study (AD-259 458P) in this area. Utility of these inhibitors on bare steel using paper carriers, aluminum foil, Mylar, as well as crystalline or liquid salts was established for at least a 5-year period. Supplementary preservative oils and greases may be used with cast iron or phosphated surfaces. On complex assemblies, utility of these inhibitors has been demonstrated for preserving internal combustion engines, guns and small arms, containers and tankage. However, zinc, lead, silver, aluminum, cadmium, and copper may be tarnished or corroded by some or all the volatile corrosion inhibitors. Decorative or functional colored conversion coating applied to aluminum, copper and zinc may also be adversely affected by all volatile corrosion inhibitors.

Volatile organic compounds similar in type to vapor corrosion inhibitors can function as lubricants for high-speed ball bearing operations. The appli-

cation of VCI in small or individual containers is usually most practical. However, the protection in bulk or small item packaging is not effective without proper control of venting or leakage of the exterior packaging.

The Rock Island Arsenal, U.S. Army, has sponsored a study over 10 years, (PB-171 516P) evaluating the corrosion protection afforded by both volatile corrosion inhibitors and petrolatum type compounds on ferrous and non-ferrous ordnance materials. Volatile corrosion inhibitor papers were satisfactory for the preservation of gun and howitzer tubes and brought about a savings in time and labor because the tubes were ready for immediate use upon removal of the paper, with no degreasing operation required. Cadmium specimens were most severely attacked by the inhibitor that was composed of a combination of sodium nitrite and urea. Care should be exercised in the packaging of cadmium parts with volatile corrosion inhibitors; however, the other nonferrous metals tested exhibited only minor stain or tarnish.

The Army Ordnance Tank Automotive Command sponsored tests completed in 1962 (AD-282 328P) on installed engines as components of combat vehicles in outdoor storage. After at least three years of protection by volatile corrosion inhibitors—added either to the oil or blown into the cylinders in crystal form—only one of the eight test engines would not start. This failure was attributed to improper timing and not to corrosion. The oil treated with these inhibitors proved far superior to untreated oils after three years' storage.

Protection of Nonferrous Metals

The most adverse effect of volatile corrosion inhibitors is the effect of tarnish or even attack on many nonferrous metals. However, service experience is usually better on nonferrous components than indicated by laboratory tests.

A comprehensive bibliographic guide (AD-601 238P) on "Corrosion Inhibitors for Nonferrous Metals" was compiled in 1960 by the Prevention of Deterioration Center, National Academy of Sciences. This guide lists about five hundred references for the period 1947-1959 including patents, U.S. Government reports, and technical magazine articles. This guide, however, includes reports on many other types of corrosion inhibitors besides the volatile types.

The Rock Island Arsenal Laboratory has made a study (AD-427 151P) evaluating volatile corrosion inhibitors for a period of up to eight years in outdoor, shed, and indoor storage in order to determine the protection provided to packaged metal panels with various finishes. It was shown that these inhibitors provided no significant additional protection to nonferrous finishes such as cadmium and zinc plating beyond that given by regular Kraft paper packaging. Addition of a dip coating wax on the paper-wrapped metal panels and a well sealed outer packaging provided the best measure of protection. Chromium plated finishes required either exterior packaging or wax coatings on the volatile corrosion inhibitor paper in order to remain free of tarnish. For phosphated finishes the inhibitor papers provided no improvement over plain paper wrapping.

Severe corrosion of untreated zinc, cadmium, and magnesium may result from exposure to volatile corrosion inhibitors. Chromate or anodic treatments of these metals may prevent corrosion by some of the inhibitors.

Anodizing usually provides good resistance of aluminum to corrosion by the inhibitors. Blackened copper may show a dull, faded appearance when exposed to VCI.

With longer exposures, these inhibitors cause increased staining, softening, or peeling of the magnesium fluoride or zinc sulphide films on coated optical equipment. VCI does not inhibit fungi attack on stored equipment in humid atmospheres.

Exterior Packaging Materials

The protection to uncoated steel provided by a volatile corrosion inhibitor depends on the near absence of moisture and on the continuous condensation of the compound's vapor on the metal surface. If the VCI papers or oils are to be effective, the exterior packaging should be nearly impermeable to moisture or other weathering agents.

Using steel rifle components with a manganese phosphate finish as the materials to be protected, the Springfield Armory Laboratory (AD-295 474P) investigated the effectiveness of volatile corrosion inhibitors in both outdoor humid storage and polyester exterior packaging. A waterproof-vaporproof packaging composed of heat-sealable polyester material and volatile corrosion inhibitor provided satisfactory protection for twelve months in a humidity cabinet, and longer protection in an outdoor shed. Packages that were not vaporproof did not stand up as well in these tests.

The Rock Island Arsenal (AD-421 514P) studied the effect of indoor and outdoor storage upon the properties of exterior packaging materials used with volatile corrosion inhibitors. While there was no appreciable effect on tensile strength, tearing strength, and water resistance of packaging there was some increase in its vapor transmission and loss-of-seam strength after storage for five years. Some of the older polyvinylidene chloride and Kraft paper exterior packaging materials deteriorated at seals during outdoor storage for two years. However, material produced according to the more recent MIL-B-121 government specifications was found satisfactory for five-year test periods.

The Rock Island Arsenal (AD-425 370P) made another study of panels sealed in exterior transparent plastic films for one-year exposure. Bare steel panels sealed in these plastic bags were free of rust after one year of indoor heated storage. VCI inserts provided protection to bare steel panels when the plastic film packages were kept in a humidity cabinet at 100°F, and 95 to 100% relative humidity; however, when the VCI was lost through small openings or in reaction with the bag materials, rusting occurred. Polyethylene (0.004 inch) and polyvinyl chloride acetate copolymer (0.008 inch) bag materials provided the best external packaging for protecting bare steel panels in the humidity cabinet tests.

Present applications of volatile corrosion inhibitors either coated in paper or dissolved in oil offer excellent protection during shipment and storage of such steel equipment as gun tubes, containers, tanks, components of gasoline and diesel engines, and electronic equipment. These parts are ready for immediate use when the external packing is removed.

Miscellaneous Guides

Some of the volatile corrosion inhibitors are reported in the technical

magazine literature according to their proprietary names and corresponding industrial firms. Recent sources of information are:

"Protective Papers for Corrosion Control of Metals," by H. W. Mumm and W. S. Grimes. TAPPI, Vol. 45, No. 8, p. 129A-131A, August 1962.

Corrosion (Volume 2, Corrosion Control), by L. L. Shreir, 1963. Published by John Wiley & Sons, Inc., New York, N. Y.

RECENT BIBLIOGRAPHY AND ABSTRACTS
(1962-64)

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AD-282 328P Ordnance Tank-Automotive Command, Detroit, Mich. ENGINE CORROSION STUDY ON INSTALLED ENGINES AS A COMPONENT OF A COMBAT VEHICLE IN OUTDOOR STORAGE AT ANNISTON ORDNANCE DEPOT, ANNISTON, ALABAMA, J. DeGroot, June 62, 36p., CFSTI \$5.60.

VCI oil proved far superior to the presently used MIL-L-21260 oil after a minimum of 3 years outdoor storage under actual conditions. Of 24 cylinders (2 test engines) using the VCI oil, 17 were corrosion free after 3 years. The other 7 cylinders developed spotty and not too severe corrosion during the 3rd year of storage. MIL-L-21260 oil displayed sufficient corrosion on 12 of 24 cylinders to question satisfactory operation of the engine after reassembly without considerable rework and/or salvage. Half of the cylinders showed corrosion in the first year. There was no apparent attack from the VCI oil or VCI crystals on nonferrous or nonmetallic components of the engine.

AD-295 474P Springfield Armory, Mass. INVESTIGATION OF PACKAGING METHODS AND SUBMETHODS WITH VOLATILE-CORROSION-INHIBITOR-TREATED MATERIALS, G. Pributsky, Aug. 62, 45p., CFSTI \$1.25.

Various submethods with volatile-corrosion-inhibitor-treated materials in the packaging of small arms components were investigated. Packages were stored under two conditions: (1) in an outdoor shed to simulate minimum warehouse storage and (2) in a static humidity cabinet to simulate tropic storage. Heat-sealable polyester film with volatile-corrosion-inhibitor innerwrap provided satisfactory protection in the humidity cabinet for one year. Results of this investigation indicate that packaging submethods other than those specified in MIL-I-8574 can be satisfactorily used with VCI preservatives. Test procedures are described and results given.

AD-421 514P Rock Island Arsenal Lab., Rock Island, Ill. NATURAL AGING OF BARRIER MATERIALS AT ROCK ISLAND ARSENAL, L. W. Lynch, July 63, 33p., CFSTI \$1.00.

The effect of natural aging on the properties of selected barrier materials conforming to Military Specification JAN-P-117, MIL-B-121 and MIL-B-131 has been determined. The materials tested have been in storage for intervals up to nine years at Rock Island Arsenal. The properties are compared with specification requirements and original properties. Certain properties of JAN-P-117, Type II and JAN-P-117, Type I, Class C were seriously deteriorated within two years. MIL-B-121 and MIL-B-131 materials were not appreciably affected by the storage. Physical properties and water resistance properties were generally not affected, material resistance to moisture vapor and grease were reduced and the seam construction was adversely affected by the longterm storage.

AD-425 370P Rock Island Arsenal Lab., Rock Island, Ill. **PACKAGING IN TRANSPARENT BAGS**, L. H. Wagner, Aug. 63, 44p., CFSTI \$1.25.

Eighteen transparent plastic films of various thicknesses were made into bags. Bare steel panels, panels overwrapped in vinylidene chloride copolymer, panels coated with an emulsifiable rust preventative and panels protected with VCI materials were sealed in the bags. These packs were then subjected to fresh water immersion, static and dynamic humidity, cyclic exposure and one year of indoor storage tests to determine the suitability of plastic bags for packaging applications. The extent, nature and intensity of the rusting of the test specimens were noted through the transparent bag materials.

The control packs, after one year of indoor exposure at ambient temperature, provided adequate protection without the use of VCI materials. It was also determined that the packs were unable to provide adequate protection to the control panels when immersed in fresh water and exposed to high humidity conditions. Cyclic exposure revealed that the emulsifiable rust preventative coating was unable to withstand exposure at high temperature. Incompatibility between polystyrene and the vinylidene chloride copolymer overwrap was noted at high temperature. A yellowish coloration was also noted on several plastic bags containing VCI materials.

AD-427 151P Rock Island Arsenal Lab., Rock Island, Ill. **THE USE OF VOLATILE CORROSION INHIBITORS WITH FERROUS AND NON-FERROUS METAL FINISHES**, R. E. Johnson, May 63, 47p., CFSTI \$1.25.

Four VCI materials were evaluated up to eight years in outdoor, shed, and indoor storage to determine the degree of protection provided to packaged ferrous and nonferrous metal panels with various finishes, and to determine the necessity of providing a well sealed package to reduce the loss of VCI vapors. One of the VCI materials was found to be superior to all other materials evaluated. It was shown that the VCI materials provided no significant protection to nonferrous finishes, such as cadmium and zinc plate. The addition of an overwrap of MIL-B-121, Grade C barrier material and a coating of VV-S-190 dipcoating wax to the VCI wrapped panels provided the greatest amount of protection to both ferrous and nonferrous finishes.

AD-600 643P Prevention of Deterioration Center, NAS-NRC, Washington, D. C. **BIBLIOGRAPHY ON VAPOR PHASE CORROSION INHIBITORS FOR NONFERROUS AND FERROUS METALS**, H. Janecka, Nov. 63, 22 p., CFSTI 75 cents.

Listing of 153 government reports, patents, and technical magazine references (1947-1963) on vapor phase inhibitors.

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PB-111 407P U. S. Naval Research Lab., Washington, D.C. VOLATILE RUST INHIBITORS, H. R. Baker, March 54, 21p., LC \$4.00, microfilm \$2.25.

PB-136 411P Frankford Arsenal Lab., Philadelphia, Pa. GASOLINE STORAGE TANK-VAPOR PHASE CORROSION INHIBITOR TEST, W. J. Shields and A. Gallaccio, Aug. 52, 17p., LC \$3.30, microfilm \$2.40.

PB-143 295P Container Labs., Washington, D. C. EVALUATION OF VOLATILE CORROSION INHIBITORS FOR PRESERVATION AND PACKAGING, PART I. LITERATURE SURVEY AND PRELIMINARY INVESTIGATION, G. S. Mustin, Jan. 58, 87p., LC \$13.80, microfilm \$4.80.

PB-143 440P Rock Island Arsenal Lab., Rock Island, Ill. CHARACTERISTICS OF VCI MATERIALS WHEN APPLIED AS PACKAGING MEDIA, F. H. Wayne, Feb. 59, 15p., LC \$3.30, microfilm \$2.40.

PB-144 387P Rock Island Arsenal Lab., Rock Island, Ill. GUIDE FOR PRACTICAL PRESERVATION WITH VCI, R. L. LeMar, July 59, 30p., LC \$4.80, microfilm \$2.70.

PB-146 838P Rock Island Arsenal Lab., Rock Island, Ill. AN EVALUATION OF VOLATILE CORROSION INHIBITED OILS FOR THE INTERNAL PRESERVATION OF MACHINE TOOLS IN UNCONTROLLED STORAGE, R. E. Johnson, Nov. 59, 24p., LC \$4.80, microfilm \$2.70.

PB-146 992P Springfield Armory, Mass. INTERACTION OF PLASTICS WITH VOLATILE CORROSION INHIBITORS, R. L. Keleher and A. Hitchins, April 57, 20p., LC \$3.30, microfilm \$2.40. *Call*

PB-147 338P Rock Island Arsenal Lab., Rock Island, Ill. THE EFFECT OF VOLATILE CORROSION INHIBITORS ON MIL-B-131 BARRIER MATERIALS, E. S. Burke, Feb. 60, 21p., LC \$4.80, microfilm \$2.70.

PB-147 431P Rock Island Arsenal Lab., Rock Island, Ill. CHARACTERISTICS OF VCI MATERIALS WHEN APPLIED AS PACKAGING MEDIA, L. H. Wagner, April 60, 18p., LC \$3.30, microfilm \$2.40.

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PB-151 122P Rock Island Arsenal Lab., Rock Island, Ill. VCI OILS: PROPERTIES AND PROPOSED QUALITY CONTROL TESTS, R. L. LeMar, June 58, 61p., CFSTI \$1.75.

PB-151 766P Rock Island Arsenal Lab., Rock Island, Ill. VCI BIBLIOGRAPHY AND ABSTRACTS, R. L. LeMar, Oct. 58, 117p., CFSTI \$2.50.

PB-154 612P Naval Civil Engineering Lab., Port Hueneme, Calif. USE OF VOLATILE CORROSION INHIBITORS FOR PRESERVING THE INTERIOR SURFACE OF STEEL PIPE, C. V. Brouillette, 1958, LC \$3.30, microfilm \$2.40.

PB-171 516P Rock Island Arsenal Lab., Rock Island, Ill. THE USE OF VOLATILE CORROSION INHIBITORS AS A PRESERVATIVE MEDIUM FOR LONG TERM STORAGE OF ORDNANCE MATERIAL. ADDENDUM VII. RESULTS AFTER TEN YEARS OF EXPOSURE, R. E. Johnson, Feb. 61, 49p., CFSTI \$1.25.

PB-181 174P Coating and Chemical Lab., Aberdeen Proving Ground, Aberdeen, Md. IMPROVED MULTIPURPOSE CORROSION INHIBITOR, C. B. Jordan, Jan. 62, 21p., CFSTI 75 cents.

AD-259 458P Container Labs., Washington, D. C. THE SELECTION AND USE OF VOLATILE CORROSION INHIBITORS FOR THE PRESERVATION OF CHEMICAL CORPS EQUIPMENT AND MATERIAL, J. B. Weaver, June 61, 11p., CFSTI \$1.60.

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Inquiries on reports and services are to be directed to Clearinghouse, U.S. Department of Commerce, Springfield, Va. 22151 or to any Commerce field office (listed on inside back cover).