Volatile inhibitors of atmospheric corrosion. IV. Evolution of vapor-phase protection in the light of patent literature

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Abstract

The review analyzes the patent literature dealing with metal protection by volatile corrosion inhibitors (VCIs) and materials based thereon. It has been found inhibitors of atmospheric corrosion with vapor pressure above $10^{-5}$ mmHg can be used as VCIs, including nitrogen-containing bases of various nature, salts of nitrogen-containing bases with some inorganic or organic acids, organic nitro compounds, esters of organic and inorganic acids, heterocyclic nitrogen-containing compounds, etc. Vapor-phase metal protection is also performed using non-volatile compounds and formulations that can release compounds of the above types upon hydrolysis. VCIs for temporary protection can be used in the form of active compounds, solutions, packaging materials, porous emitters, inhibited air, or in special forms intended for the protection of specific product types. VCIs can be used for permanent protection of metal articles within polymer coatings (paints) and working liquids (hydraulic, cooling liquids, etc.).

Key words: volatile corrosion inhibitors, patent literature, vapor-phase protection of metals.

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Volatile corrosion inhibitors (VCIs) are among the most efficient and cost-effective classes of means used to protect metals from atmospheric corrosion. The physicochemical aspects of VCI protective action are covered in a number of reviews [1–5]. Analysis of these reviews makes it possible to create VCIs in a purposeful way in order to solve specific practical problems. However, development of VCIs with predefined properties also requires an analysis of existing developments, i.e., patent literature. An analysis of this kind became the purpose of this publication.

This review was carried out using the database of http://worldwide.espacenet.com, the largest Internet resource in this field. The review covers the main technical solutions in the vapor-phase protection of metals since the time of VCI invention and until the end of the first decade of our century. We tried to follow the chronological order in the presentation of the events, though sometimes we had to deviate from it in order to generalize a situation concerning some specific direction of VCI development.
The first patent dealing with VCIs was obtained in Great Britain in 1948 (the priority date is 1944). Shell Dev company proposed to use salts of nitrous acid with primary, secondary, tertiary amines or quaternary ammonium bases as VCIs. According to [6], organic isologues of ammonium can be used for corrosion protection instead of amines. Furthermore, the patent covers the use of organic esters of nitrous acid in the packaging of metal articles.

The prospects of the new approach to temporary protection was obvious and the number of patents dealing with vapor-phase protection of metals by inhibitors grew rapidly.

In 1947, Bataafche Petroleum company submitted a patent application which was the first to suggest VCIs within packaging materials, such as paper, cardboard, cotton, wool, silk or viscose fabric, etc. These materials were treated with vapors or aerosols of VCIs such as nitrophenol or aliphatic nitro compounds. The patent also specifies that the above packaging materials can be modified with paraffin, wax, bitumen or rubber-like compounds in order to reduce their permeability by VCI vapors [7]. It should be noted that inhibited packaging materials thus far remain one of the most technologically efficient forms of VCI application.

Another patent [8] with application priority of 1948 recommends to use VCI solutions it spray form for preservation of articles. This form of VCI application is also rather popular even today.

The use of VCIs within packaging paper that allows packaging and preservation of metal articles to be combined was further developed in a new Shell Dev patent [9]. The employees of this company developed a paper inhibited with salts of cycloaliphatic amines, e.g., cyclohexylamine, with carboxylic (lauric and benzoic) acids. The major difference of this material from those developed previously is that it can protect not only ferrous but also some non-ferrous metals.

In 1950, the idea to use VCIs within protective coatings arose. It was suggested [10] to incorporate the inhibitors described in [6] and [7] into a polymeric coating (a copolymer of vinyl chloride and vinylidene chloride) for protection of metal articles from corrosion and wear. The expediency of this solution is not obvious. Most often, contact inhibitors rather than VCIs are needed for modification of polymeric coatings. On the other hand, situations are known where the ability of a coating to provide vapor-phase protection plays the decisive role in the product selection.

A VCI that was new at the time, viz., a mixture of dicyclohexylamine and morpholine caprilates with mineral oil, was described in [11]. It was intended for application within inhibited paper. Apparently, the mineral oil within the impregnating liquid prevented paper from water absorption and the associated loss of mechanical properties, i.e., the drawback that many today’s packaging papers still have.

The issue of VCI toxicity was not so acute in the 50th of the past century, therefore the use of volatile organic chromates for temporary protection [12] did not arouse a strong
rejection among the people of those times. It should however be admitted that chromate-containing VCIs did not find broad practical application even then.

Meanwhile, the areas of VCI application continued to expand. In 1957, Celanese Corp. patented a hydraulic fluid modified with a contact inhibitor (mercaptobenzothiazole) and a VCI selected from monoethanolamine salicylate and diisopropylamine, diisobutylamine, and dicyclohexylamine nitrates [13]. This fluid did not cause metal corrosion not only in the fluid bulk but also above it. This is apparently one of the first examples of VCI application for permanent rather than temporary metal protection.

Somewhat later [14], it was suggested to add a VCI to water along with a conventional contact inhibitor in order to protect pipelines and metallic vessels both in the gas and liquid phases simultaneously. It was recommended to use cyclohexylamine and morpholine as the VCIs. In the light of later data [15, 16], this does not appear to be the optimal choice. However, under certain conditions, even these additives can provide efficient steel protection above their aqueous solutions.

Starting from [17], inhibited air came into common use in corrosion protection. In accordance with that patent, the metal articles to be preserved were passed through a stream of heated air saturated with vapors of dicyclohexylamine nitrite (DAN) and/or cyclohexylamine carbonate (CCA). Inhibitor vapors condensed on the articles to provide a uniform VCI layer on the surface. Inhibited air, though combined with other VCIs, even now appears to be the optimum form of vapor-phase protection of bulky articles, such as gas turbines, military equipment, etc. It is worthy of note that this patent was the first to mention DAN and CCA, the inhibitors that subsequently became very popular in practice.

In [18], it was suggested to use a VCI (polyamine) as an additive to hydrocarbons during distillation. The inhibitor ensured corrosion protection of all parts of fractionating columns.

In the beginning of 1960s, Daubert Chemical Co patented a fundamentally new inhibited packaging material, namely, a polymer film capable of vapor-phase protection [19]. The film was transparent and thus allowed the state of the articles being protected to be monitored visually. During production, the film base impermeable for inhibitor vapors was passed over a roll that wetted it with VCIs, namely aliphatic (capronic, caprylic, pelargonic, or enanthic) or aromatic (benzoic, toluic, tert-butylbenzoic) carboxylic acids. Though the efficiency of the compounds used as the VCIs is doubtful, two-layer films of this kind are superior to many today’s materials where a VCI is introduced into the polymer matrix during extrusion. Production of the latter has considerable limitations concerning the content of the inhibitor that can upset the isolating properties of the film.

The idea to create efficient and versatile anticorrosion polymer films was elaborated in a slightly later patent of the same company. In [20], a material that protected a broad range of ferrous and non-ferrous metals was suggested. The protection of non-ferrous metals, such as copper and copper alloys, cadmium, etc., was provided by addition of benzotriazole (BTA). This was likely the first time that BTA was mentioned as a VCI in
patent literature. Even now, this inhibitor is widely used in the practice of vapor-phase protection of non-ferrous metals, including copper and copper alloys.

It became clear as early as in the 1960s that application of VCIs for temporary or permanent metal protection is justified in the majority of situations, provided that the space to be protected can be sealed, at least partially. Moreover, the VCI formulations that existed by that time allowed rather a wide range of problems to be solved. For example, it was suggested in [21] to use CCA for the protection of steel cables in the ducts of concrete structures. Morpholine or DAN were used within an antifreeze formulation in order to protect metals in vapor phase [22] and as a component of a liquid for corrosion protection of double walled metal tanks [23].

A sealed container with VCIs for packing and storage of metal articles is patented in [24], a tool box is patented in [25], and a package for cutting implements, in [26]. It was suggested to use steel tubes containing a VCI in their inside cavity as a welding wire [27]. It is remarkable that specific VCIs are not named in these patents.

However, the scope of VCI formulations continued to expand. In late 1960s, Daubert Chemical Co, which in that period was intensively developing the methods and means for metal vapor-phase protection, patented a versatile inhibitor [28] containing: at least one volatile aliphatic and aromatic nitro compound (nitropropane, nitro- and dinitrobenzenes), as well as a heterocyclic amine (triazole). The other inhibitor components (imidazolines of fatty acids, esters of polyhydric alcohols, etc.) ensured efficient contact protection of metals.

The same company proposed dicyclohexylammonium and morpholine benzoates or dicyclohexylammonium caprylate as VCIs for packaging polymeric films [29]. Substituted benzimidazoles [30], as well as mixtures of BTA and tolyltriazole [31, 32] were suggested as VCIs.

Some inventions of those times ascribed the capability to provide vapor-phase protection to non-volatile compounds. For example, alkylbenzotriazoles with C_3–C_20 chain were patented [33] as inhibitors (including volatile ones) of corrosion and tarnishing of copper and copper alloys. Considering the very low volatility of these compounds, their activity as VCIs appears doubtful. Calcium, magnesium, and sodium dichromates that are also compounds with low volatility were claimed as VCIs [34].

A short time later, requirements for the vapor pressure of compounds intended as VCIs were formulated in the literature. According to [35], an inhibitor should have a vapor pressure above 10^{-5} mmHg in order to have a capability for vapor-phase protection. However, this did not prevent developers from further errors since saturated vapor pressure has not yet been determined for many types of corrosion inhibitors.

It should be recognized that a considerable progress in development of the theory as well as methods and means of vapor-phase protection of metals is associated with the studies of Soviet scientists. According to the practice of those times, the majority of inventions concerning VCIs made in the countries of Eastern Europe could not published. Even now, there is virtually no information about them in patent literature. Nonetheless,
such products as G-2 (hexamethyleneimine meta-nitrobenzoate), IFKhAN-1 (an aminoketone) [36], a nitrite–urotropin formulation [37] and many others that are still popular in corrosion protection were developed around the 60s–70s.

In 1973, scientists from the Institute of physical chemistry of the USSR Academy of Sciences obtained patents [38, 39] for a method for metal protection from atmospheric corrosion involving the use of VCIs (primary, secondary or tertiary amines) applied on solid porous carriers, i.e., zeolites or silica gels. The idea is that the use liquid compounds in preservation activities is not always convenient. However, this invention overcomes the above inconvenience. Furthermore, both zeolites and silica gels that have undergone preliminary thermal treatment can absorb moisture, which considerably facilitates metal protection with VCIs.

VCIs on silica gel and zeolites are popular even today. For example, VCIs of IFKhAN series are produced on silica gel [40].

A USA patent [41] proposes the use of an aliphatic ester of an amino acid applied on silica gel, zeolites, or paper for metal protection from atmospheric corrosion. Later, Cortec Corp. patented inhibitor-containing drying materials [42–44] in which VCIs were applied on silica gel granules. The use of zeolites with VCIs is stipulated in patent [45].

It is interesting that “ZAO NTO Priborservis” company rather recently obtained a patent [46] where zeolites were also proposed as VCI carriers. The VCI itself is not specified in the invention description. From our point of view, this fact again confirms the statement that patent legislation and/or the procedures used by patent offices leave the possibility to register proprietary rights for well known, widely applied, and even previously patented technical solutions, provided that certain simple rules are followed.

In the 70s, the technique of vapor-phase metal protection by inhibitors was developing intensely. In 1974, Aicello Chemical Co patented a polymer film modified by salt-type VCIs [47]. It was the first time that an inhibitor was incorporated into a polymer at the stage of film extrusion. Subsequently, it was this technology that became the most popular [48].

In [49] it was suggested to protect ferrous metal articles using a nitrite-amide formulation applied on paper. Amides themselves have low vapor pressure. However, they can undergo hydrolysis with release of ammonia [35].

Fuji Photo Film Co Ltd used VCIs to treat a ferromagnetic metal powder in order to protect it from corrosion [50]. Starting from this patent, wide application of VCIs in data storage systems on magnetic media started. Japanese experts [51, 52] proposed to apply a VCI on the leader tape end in tape cassettes. This prolonged service life and improved reliability. It is also recommended to use a VCI [53–55, 70] or a VCI along with desiccants [56] for corrosion protection of recorders using magnetic media. In [57] it is recommended to incorporate BTA in the adhesive tape joining the recordable part of magnetic tape with the trailing end. NDA, diisopropylamine nitrite, CCA, or BTA were proposed for magnetic tape protection [58].
The boom of the “fashion” for VCIs occurred in late 70s – 80s of the past century. It showed itself as an increase in the number of patents and sometimes in the use of VCIs where they are not too necessary. For example, it is recommended in [59] to use DAN in a formulation for metal surface treatment. We believe that non-volatile nitrites could be used in this case with equal success. Likewise, we believe that addition of VCIs to a formulation for pipe insulation [60] is not quite justified.

New methods of VCI application appear which are nearly never used today. For example, it was suggested to protect internal cavities of metal articles by VCI-modified materials whose volume can expand to fill the cavity, e.g., compacted cotton and some others [61].

A considerable number of inventions concerning devices and methods for detection of VCIs in a volume being protected were made in that period of time. One of the inconveniences of vapor-phase metal protection by inhibitors is that, in the majority of cases, it is hard to distinguish a system where a VCI is present from a system from which a VCI has already escaped. Therefore, Vedale Ltd. developed a special oxidative-type indicator that changes color after a VCI has evaporated. Based on its color one can judge on the necessity to re-preserve the article [62]. The problem of visual monitoring of the presence of VCI is also handled by the methods developed by Matsushita Electric Ind Co Ltd (Japan) [63, 64]. It should be noted that the problem itself is eliminated if VCIs are used as pellets or granules containing no binding agents. For example, a material of this kind, namely, a pelletized mixture of ammonium carbonate and hydrocarbonate, was proposed [65]. It should however be noted that the efficiency of metal protection by ammonium carbonates as VCIs leaves a lot to be desired.

A number of patents of those times deal with VCIs applied on porous polymer supports. For example, it was suggested [66] to perform vapor-phase protection of metals using foamed polymer plates impregnated with a solution of NDA and BTA in an alcohol. Prior to use, the material was dried in order to remove the solvent. Obviously, such materials based on foamed or porous plastics could protect metal articles not only from corrosion but also from mechanical damage by acting as dampers. Preparation of such materials is covered in [67 – 76]. According to [67], ammonium nitrite is introduced as a powder to synthetic polymer foam that, moreover, has good heat-insulating properties. In [69], a microporous fabric containing a VCI is recommended for packaging and protection of metal parts from corrosion and mechanical damage. A multilayer protective material containing a foamed polymer layer modified with a VCI is described in [70]. In some cases, materials similar to those described above have an adhesion layer for convenience of use [71, 77, 78]. Japanese companies Sekisui Plastics and Kyoeisha Chemical developed special foam-forming polymer granules containing an aminocarboxylate VCI for the production of foamed inhibited materials [79].

In general, many inhibited foamed materials of that period do not contain any new VCI formulations. The VCI is just not specified in the majority of patents.
NDA is still widely used in the practice of metal vapor-phase protection [80, 81]. At those times, the issue of nitrite toxicity was not as urgent as today, while the inhibitive efficiency of NDA toward the corrosion of ferrous metals is very high.

However, in general, the scope of formulations for metal vapor-phase protection is expanding intensely. The majority of new VCIs are mixtures of compounds already known as such or their homologues, selected to expand the scope of metals they protect or with consideration for a synergistic enhancement of the protective effects of the components. In fact, a mixture of ammonium nitrobenzoates or amines with ethyleneurea [82], a BTA and organic amine salt or a salt of a benzoic acid derivative and an organic amine [83], a mixture of CCA and BTA [84], and a mixture of soda, potash and ammonium hydrocarbonate [85] were patented. A salt of dialkylaminooethanol and caprylic acid combined with hexamethylenetetramine was claimed in [86]. Hexamethylenetetramine is non-volatile; however, it absorbs water to release ammonia into the atmosphere. A combination of a substituted benzoic acid salt with ammonia or an amine mixed with substituted BTA, a substituted triazole, and a salt of a substituted benzoic acid with an alkaline metal was recommended within inhibited paper [87]. It was proposed to use a mixture of dicyclohexylammonium and/or diisopropylammonium nitrites with BTA and/or tolyltriazole applied on calcium silicate as a VCI for ferrous and non-ferrous metals [88]. A mixture of VCIs (NDA, cyclohexylamine, diisopropylammonium nitrite, BTA, tolyltriazole) with a water-absorbing polymer, e.g., polyacrylate, was claimed as a formulation for metal protection [89]. Shin Jung Ind Co Ltd (Corea) proposed rather a complex mixture to hinder the atmospheric corrosion of iron–zinc alloys. The VCI contains a salt of monoethanolamine with a carboxylic acid (benzoic, lauric, or methylcaprilyc), a salt of dimethylamine with an aromatic carboxylic acid (benzoic, phthalic, isophthalic, or terephthalic), urea, sodium nitrite, and ammonium hydrocarbonate [90]. Some components of this mixture can hardly be regarded as volatile compounds. However, this is justified if they are used in the form of packaging paper that can directly contact the surface being protected. The same applicant recommends to protect galvanized steel using a mixture of a salt of benzoic acid and a volatile amine, urea, sodium nitrite, and soda [91]. Maintaining the component ratio specified in the patent ensures a synergistic enhancement of the protective effect.

More ingenious formulations are proposed in [92, 93]. A VCI that is an adduct of glycols with dicyclohexylamine is proposed in [92]. Nippon Mining Co patents flavonoids, natural phenol compounds, as VCIs [93].

The VCI application fields and methods expanded in that period, but only to a small extent.

In [94, 95], VCIs are considered as additives to working fluids for metal protection in the vapor phase. In [96], it is suggested to use primary amines in order to protect steam generators from corrosion caused by oxygen and carbon dioxide. Obviously, compounds that are nearly not volatile at room temperature can be used as VCIs in this case. The authors of patent [96] believe that the optimum hydrocarbon chain length ranges from 10
to 22 atoms. It was proposed to use various volatile (aliphatic, aromatic, alicyclic) amines, sometimes combined with contact inhibitors, in aerosol formulations [97–99]. An interesting technical solution is contained in [100]: it is proposed to use rods impregnated or coated with a VCI to protect articles with extended internal cavities. This invention was recently further developed by using polymer braids with a VCI to protect thin metal tubes. In [101], Japanese experts propose to use VCIs, in particular BTA, to protect steel reinforcement in concrete. This was perhaps the first step toward the development of migrating inhibitors that would appear much later, in the end of 1990s. In order to protect aluminum foil used in the manufacture of capacitors, it was proposed to use one or more VCI(s) selected from BTA, CCA, NDA, or diisopropylammonium nitrite [102]. A VCI as a paint component was proposed in [103]. A VCI as a paint component was proposed in [103]. This technical solution is concordant with the one mentioned above [75].

Packaging materials containing VCIs, primarily polymer films, had been developed rather intensely [87, 90, 91, 104–113]. Experts from Byelorussia have patented an anticorrosion material, viz., a polyethylene film plastisized with mineral oil and containing an oil-soluble inhibitor [105, 108]. The oil-soluble inhibitor is a mixture of contact-type and volatile components (salts of cyclo- or dicyclohexylamine and an organic acid or a lower heteroalkylated amine). A method for manufacturing an oil-plastisized polyethylene film shaped as a tube by extrusion with tube inflation was patented in [106]. It is proposed to introduce an oil-soluble VCI into the tube. A similar technology for producing inhibited film is described in [109]; however, in this case the film is modified with a VCI in electrostatic field.

The 1990s demonstrated a high interest in vapor-phase protection like the time period considered above. However, the requirements for the VCIs become noticeably tighter. Decreasing the toxicity and environmental impact became a matter of great importance.

At the same time, companies appeared that specialized almost totally in development and sales of VCIs and VCI-based materials. In the first place, Cortec Corporation (USA) should be mentioned. According to the results of 1990, it is among the hundred most fast-growing USA companies. Up to 40% sales on the world market belong to it. However, it has a fair number competitors. It became clear that a business of vapor-phase protection of metals could bring a very good profit. High competition in this area affects the features of patent literature.

As before, patents aim at protection of proprietary rights, but their formulas and descriptions are composed in such a way so as to cover as broad area as possible but not to disclose any real information about the invention. To a considerable extent, this occurs because companies from Eastern Europe, where proprietary rights are poorly protected, have joined the world market of metal protection means. It is nearly impossible to monitor whether a particular company uses others’ inventions. Under these conditions, some companies cease to patent their inventions in order to prevent information leakage to competitors. For example, none of the VCIs recommended for practical use [40] (including IFKhAN and VNKh-L series formulations) was reflected in the patent literature at those
times. Other claimants strive to obscure the essence of their inventions as much as possible. Often, in order hinder the search, patents are attributed to international classification classes only indirectly related to the essence of an invention. On the other hand, the patent legislation itself, at least in CIS countries, has flaws allowing one to patent nearly anything. We have already presented some examples above. And still, analysis of patent literature of those times provides not only a general idea of the development trends in this field but also information about specific developments.

An important trend involves attempts to make vapor-phase metal protection as convenient as possible for consumers of any level. Cortec Corporation patents a special package for VCIs in the form of powder made of a material that is permeable to inhibitor vapors but not to the powder particles [114]. Such VCI emitters can be used both in industry and at home. A case for fire arms with a vapor-phase protection function is proposed in [115]. A sealant material protecting a metal in the gas phase is proposed in [116]. Means for the vapor-phase protection of threaded joints are described in [117–120]. It is notable that the VCI composition in these inventions is not often reported.

Specific inhibitor formulations are provided in [42–44, 121–130]. A contact and vapor-phase corrosion inhibitor is proposed in [121]. Isopropylamine nitrite and CCA, that is, a combination of inhibitors with high and low vapor pressure, is used as the VCI in this patent. Apparently, one of these is supposed to provide a large protection radius and the other one, protection durability. In [122], a substituted aminotriazole is recommended as a VCI for ferrous and non-ferrous metals. A hydrocarbon radical with a chain length from 1 to 12 carbon atoms can serve as the substituent. According to the inventors, this VCI has high thermal stability, which is significant in the creation of polymer materials modified with VCIs. Cortec Corporation patented a VCI for iron, copper and their alloys. The VCI contains anhydrous sodium molybdate, ammonium molybdate, and molybdate of a primary or secondary aliphatic amine with no more than seven carbon atoms, as well as sodium nitrite and BTA [123]. In all appearance, it is the first application of molybdates in the vapor-phase protection of metals. This compound does not possess high volatility. The vapor pressure required for protection is most likely provided by the amine component of the formulation. However, the capability for contact protection when the inhibitor is used within packaging materials apparently justifies the considerably high cost of molybdates. All the foregoing also pertains to patent [124] where an amine molybdate is the only VCI component for polymer films. The existence of both patents is explained by the fact that both claims were submitted on the same day and have the same priority date. A team of researchers from Tula Technical university (Russia) patented a VCI based on an adduct that is formed upon interaction of ortho-nitrophenol, BTA and cyclohexylamine [125]. The product contains no toxic nitrites, but the safety of nitrophenol is quite doubtful. Chronologically, a series of patents by Cortec Corporation follows next. They propose combinations of VCIs and drying agents [42–44, 126–131]. A mixture of anhydrous sodium, ammonium and amine molybdates with BTA and sodium nitrate or a mixture of amine benzoates with amine nitrates and BTA was used as the VCI in all these materials.
is notable that nitrates are neither corrosion inhibitors nor drying agents, so the meaning of this component is not clear. Perhaps, these rather inert compounds were added in order to ensure the patent purity of the formulations. It is interesting that a VCI in fact identical to the formulations described above but containing nitrite rather than nitrate was claimed in Japan in mid-1990s [132]. Mitsubishi Motors Corp. patented a VCI based on butynediol [133]. An aromatic mercaptothiazole or triazole in combination with a water-soluble polysubstituted phenol and ascorbic acid or their salts constitute a formulation proposed as a VCI by German experts [134]. Kurita Water Ind Ltd. recommends to protect steam condensate lines using a mixture of an aliphatic lactone, p-hydroxybenzoate, methyl anthranilate, cyclohexyl acetate, and eugenol [135].

It is of note that, along with these formulations, VCIs that have been known for a long time are also used, e.g., NDA [136, 137].

A broad spectrum of new materials for the vapor-phase protection of metal articles appeared. A number of patents [138–148] concerned new VCI-containing packaging materials. The films patented in [145–148] are interesting as they feature an improved resistance against tear and puncture. It is very important since the durability of article protection with inhibited polymer materials is often limited by their mechanical properties. Patent [149] protects the proprietary rights of Japanese experts for a paint with vapor-phase protection capability. Conversely, in [150] VCIs are proposed as a component of an efficient paint remover. A principally new material [151] claimed as a VCI is a master batch (super-concentrate) for the production of polymeric inhibited articles. However, it is unlikely that films with vapor-phase protection capability can be made using this approach since a mixture of an alkali metal nitrite, benzoate and molybdate is intended as the VCI. The vapor pressures of these compounds are below the threshold required for vapor-phase protection.

Cortec Corporation patented a few inventions where materials for metal protection are based on recovered polymers [152, 153] or paper [154] modified with VCIs. Corrosion protection and waste management problems are solved concurrently.

In general, the trends of 1990s–2000s include the environmental safety of vapor-phase metal protection and convenience for consumers. Cortec Corporation patented biodegradable films and packages for VCIs [155–157]. Polymeric starch-based resins, polyactic acid polyesters, and polycaprolactone were used as the basis. The VCI for the films consists of amine salts, ammonium benzoate, triazole derivatives, tall oil imidazolines, alkaline metal molybdates, as well as salts of alkaline metals with dibasic acids [155, 156]. The VCI according to [157] comprises amine salts, triazole derivatives, and salts of alkaline metals with dibasic acids.

The same company developed a VCI for the protection of boilers and similar equipment from corrosion during downtimes. The VCI contains a mixture of sodium, ammonium, monoethanolamine, and cyclohexylamine benzoates with sodium sebacate and BTA [158]. The VCI is placed in water-soluble containers with perforated walls. The use
of containers with standard masses makes it unnecessary for the consumer to weigh the inhibitor. As the system is reactivated, the inhibitor and the container dissolve in water.

An increase in the number of Russian developments is yet another trend of those times [46, 159–164].

In fact, a versatile volatile inhibitor based on nitrophenols (*ortho-* or *para-*), BTA, triethylamine or cyclohexylamine, and isopropanol is patented in [159]. A very similar formulation [125] contains no toxic nitrites but does contain nitrophenols. The inhibitor has a fungicide effect.

1-Phenyl-1-(piperidinomethyl)benzotriazole [160] is a new versatile inhibitor from Russian developers. This individual compound is a product of fine organic synthesis possessing very low volatility. Apparently, vapor-phase protection is provided in this case by residual original compounds or by products of hydrolytic destruction of the compound. According to [165], this is possible for Schiff and Mannich bases.

OJSC “Kompaniya Slavich” patents an inhibited polymer film [161]. The Cesa-Cor 9103 superconcentrate was used to make it capable of vapor-phase protection. Data on its composition are missing. Cyclohexylamine chromate was used as the contact inhibitor. It can hardly be called a contemporary material in the 21st century. Another packaging material of the same company was proposed in [163]. It also contains a contact inhibitor and a VCI (VNHk-L-20).

Yet another formulation containing a nitrophenol is described in [162]. The VCI also contains alkylimidazolines, triethylamine, and isopropanol.

A versatile mixed inhibitor of synergistic action is described in [164]. The VCI was developed in late 1990s at IFKhE RAN. The formulation contains an amine, a heterocyclic nitrogen-containing compound, and a ketone. The experts from this company still prefer not to patent newer developments.

As before, VCIs are not described specifically in many patents of those times. Examples: packaging materials with VCIs, including films, papers, foam polymers etc. [166–180]; cardboard [181]; adhesive tape and self-adhesive films [182–184]; a container-diffuser for inhibitor [185]; a cover for tool [186]; protective plastic caps for protection of metal screw fasteners [187]; bearings with VCI-modified polymer inserts [188, 189]; a method for protection of bolt joints [190]; a skate guard [191]. Likewise, the VCI composition was not specified in [192–200]. All these materials have some technical solution novelty, but it is insignificant from the point of view of vapor-phase protection.

Nearly the same situation exists for patents that contain information about VCI composition. This mainly concerns the use of already known VCIs in new systems or mixed formulations whose components are known as VCIs or should definitely manifest a capability for vapor-phase protection.

BTA or tolyltriazole are used as additives to “gold” paint [201]. It contains bronze powder that can change color due to oxidation. VCIs slow down this undesirable change in color. Obviously, the inhibitor volatility is not important in this case. A contact inhibitor could have been used instead of a VCI.
Patent [202] describes a mixed VCI that can be used in the preparation of protective materials. The VCI comprises sodium and ammonium benzoates, sodium nitrite, BTA, dicyclohexylamine, as well as toluene, water and morpholine as the solvents.

A mixture of an inorganic nitrite, polysubstituted phenol, a dihydroxybenzoate acid ester, tocopherol, and a bicyclic terpene or a substituted naphthalene were proposed as a versatile VCI to protect iron, chromium, nickel, tin, zinc, aluminum, and copper [203].

Most likely, the last reference to nitrites in patent literature was made in [202–205]. It is a typical feature of new VCIs that nitrites are no longer used.

The corrosion inhibitor proposed in [206] contains at least one of the following compounds: a tertiary amine, CCA, BTA, or a quaternary ammonium base. The volatility of quaternary ammonium bases has not been thoroughly studied. However, they were used as VCI components even back in [6].

Japanese experts propose a formulation containing volatile inhibitors and contact inhibitors for impregnation of paper [207]. It comprises the following components: a salt of a primary or secondary alkanolamine with an aliphatic carboxylic acid (C₆–C₁₂); a salt of a primary, secondary or tertiary alkanolamine with sebacic acid; a salt of dimethylethanolamine, diethylethanolamine or morpholine with a carboxylic acid (C₆–C₁₂); BTA or tolyltriazole.

It is proposed [208] to protect metal articles using drying agents combined with VCIs selected from phenols, hydroquinones, aliphatic or aromatic amines, thiazoles, triazoles, imidazoles, or their mixtures.

Patent [209] protects the proprietary rights for a VCI-containing liquid. It contains sodium benzoate, gelatin, carboxyethyl cellulose, glycerol, propylene glycol, BTA, and triethanolamine. BTA is the only component here that can provide the vapor-phase protection of metals.

The same is true for biodegradable films proposed by Korean company Sunwoodpack Co Ltd [210–214]. They have rather complex compositions containing only BTA or tolyltriazole as volatile compounds. This is insufficient for efficient vapor-phase protection of ferrous metals.

Patent [215] concerns VCIs comprising an aliphatic monocarboxylic acid (C₆–C₁₀), an aliphatic dicarboxylic acid (C₆–C₁₀), a primary aromatic amide, an aliphatic ester of hydroxybenzoic acid, and a benzimidazole containing substituents at the benzene ring. The inhibitor protects a broad range of metals, viz., iron, chromium, nickel, tin, zinc, aluminum, copper, magnesium, and their alloys. The capability to protect magnesium alloys is a rare property for VCIs that is in considerable demand in practical applications.

Yet another versatile VCI has been patented by Korean company Sambu Tech Co Ltd. It is intended for the production of anti-corrosion paper [216]. It consists of a mixture of BTA, an aminotriazole, a salt of an aliphatic amine with an aliphatic acid, and a solvent, namely, an aqueous solution of hexamethylenetetramine and an alkaline or alkaline-earth metal carbonate.
Despite the studies on the volatility of inhibitors belonging to various classes [217–220], it still occurs in patent literature that the capability for vapor-phase protection is ascribed to purely contact-type inhibitors. For instance, a glycerol solution of sodium benzoate, sodium molybdate and dextrin is proposed as an ecologically safe VCI [221]. This formulation does not contain any components that possess a vapor pressure required for vapor-phase protection.

An ammonium salt of aliphatic dicarboxylic acids was proposed as a VCI for ferrous and non-ferrous metals [222].

Rti Engineering Co Ltd. (Korea) proposes a VCI containing a mixture of five groups of components [223]. The first group comprises triethylamine, morpholine, monoethanolamine, and dimethylethanolamine. The second group comprises silicic acid and benzoic acid. The third group involves octanoic acid or sebacic acid. The fourth group comprises BTA, tolyltriazole and trimethylthiahydroxypyrazole. And finally, the fifth group comprises sodium or ammonium benzoates. Numerous formulations can be composed of these compounds. The specific combination used by the company in practice is unclear.

A VCI-related component that is new in patent literature was introduced in formulations by Metpro Technical Services Ltd [224]. It is an ester of phosphoric acid. In combination with amines, organic acids (caprylic or nonylic) and silica gel, it provides efficient protection of metals in the gas phase.

A polymer film modified by a mixed VCI is proposed for the protection of metal articles [225]. The inhibitor comprises borax, ammonium molybdate, and cyclohexylamine laurate. In this case, vapor phase protection is provided by ammonia and cyclohexylamine. The other inhibitor components have low volatility.

The most recent patents available in open access correspond to the end of the first decade of the 21st century. In all appearance, analysis of later patent literature will reveal new development trends in this field. The information considered above allows us to make the following general conclusions:

1. The following compounds can be used as VCIs:
   - inhibitors of atmospheric corrosion with vapor pressure above $10^{-5}$ mmHg, including compounds and formulations of compounds belonging to the following classes:
     - nitrogen-containing bases of various nature (including various amines, quaternary ammonium bases, Schiff bases, Mannich bases, etc.),
     - salts of nitrogen-containing bases and some inorganic (including nitrous, carbonic, chromic, molybdenic, etc.) or organic acids (including various mono- and dicarboxylic acids, phenols, etc.),
     - organic nitro compounds (including nitrophenol, aliphatic nitro compounds, etc.),
– esters of organic and inorganic acids (including carboxylic acids, chromic acid, phosphoric acid, etc.),
– heterocyclic nitrogen-containing compounds (triazoles, imidazoles, thiazoles of various nature, etc.),
♦ non-volatile compounds and formulations that can release compounds of the above types upon hydrolysis (including hexamethylenetetramine, urea, their mixtures with sodium nitrite, etc.).

2. VCIs for temporary protection can be used as:
♦ active compounds,
♦ solutions (aqueous or non-aqueous),
♦ packaging materials (including papers, polymer films, specialized containers, etc.),
♦ porous emitters (including those based on foamed and porous plastics, silica gels, zeolites, etc.),
♦ inhibited air,
♦ special forms intended for the protection of a specific product type.

3. VCIs can be used for permanent protection of metal articles within:
♦ polymer coatings (paints, etc.);
♦ working liquids (hydraulic, cooling liquids, etc.).

References
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8. Pat. 665466 GB, IPC B65B33/04. Improvements in methods of packaging and preservation of metal articles and equipment, such as aero-engines.

10. Pat. 699077 GB, IPC C09D127/06, C08L15/00. *Improvements in or relating to the protection of articles against corrosion, abrasion or the like*. Applicant: B. B. CHEM CO LTD, I. R. Cooper and A. D. Woods. Publication date: 28.10.1953. Priority date: 18.03.1950.


174. Pat. 102006014551 DE, IPC B65D51/30, B65D81/26. Cap or cover for closing storage or transporting container for accommodating corrosion-sensitive freight, has electronic storage unit that is read out and recordable in contactless manner, where storage unit is connected with cap or cover. Inventor: G. Stottmeister. Applicant: CORPAC DEUTSCHLAND GMBH & CO K. Publication date: 27.09.2007, Priority date: 20.03.2006.


178. Pat. 102009013959 DE, IPC B65D65/14, B65D65/40, B65D65/42. Packaging materials for corroдобе metal objects e.g. steel, stainless steel, comprises plastic film forming outer covering, inner layer and adhesive layer connecting plastic film with inner layer, comprising volatile corrosion inhibitor. Applicant: NORDENIA DEUTSCHLAND GRONAU. Publication date: 16.09.2010, Priority date: 09.03.2009.


196. Pat. 102006005666 DE, IPC B29C65/02, B32B27/18, B65D25/18. *Foil, useful for the manufacture of hoods that is useful for closing of storage- or transport-containers, comprises at least a volatile corrosion inhibitor, where the foil is elastically extensible*. Inventor: G. Stottmeister. Applicant: CORPAC DEUTSCHLAND GMBH & CO K. Publication date: 09.08.2007, Priority date: 31.01.2006.


