AD/A-000 237

USE OF CORROSION INHIBITORS IN THE PRODUCTION OF PACKING PAPER FOR PROTECTION OF METAL PARTS

S. A. Balezin, et al

Army Foreign Science and Technology Center
Charlottesville, Virginia

20 May 1974

AD A000237

DEPARTMENT OF THE ARMY
U.S. ARMY FOREIGN SCIENCE AND TECHNOLOGY CENTER
220 SEVENTH STREET NE.
CHARLOTTESVILLE, VIRGINIA 22901

TRANSLATION

In Reply Refer to:
FSTC-HT-23-230-74
DIA Task No. T741801

Date: 20 May 1974

ENGLISH TITLE: Use of Corrosion Inhibitors in the Production of Packing Paper for Protection of Metal Parts

SOURCE: Ingibitory korrozii metallov (sbornik 3), Moscow, 1969, pp. 276-86

CIRC: CSP 72519123

AUTHOR: Balezin, S. A., Babich, L. V., Shekhter, Yu. N., Khoroshilova, L. D.

LANGUAGE: Russian

COUNTRY: USSR

REQUESTOR: GE - Prelle

TRANSLATOR: Leo Kanner Associates, Redwood City, CA (DPS)

ABSTRACT:

The possibility of producing a single-layer anticorrosion wrapping paper for metal parts, by means of addition of various kinds of additives to the paraffinning compound, was investigated. Effective protection from atmospheric corrosion of ferrous and nonferrous metal parts, by means of paraffinned wrapping paper containing corrosion inhibitors, was demonstrated. Formulas for the protective layer of paraffinned wrapping papers for metal parts were presented. It was found that wrapping metal parts with inhibitor paper and then paraffinned paper increases the corrosion resistance of the paper to a negligible extent in the majority of cases.

16

For protection of metal parts from corrosion during shipment and storage, atmospheric corrosion inhibitors are widely used. Under these conditions, both volatile and contact inhibitors can be used.

The "contact" inhibitors include substances which have a protective effect under conditions of direct contact with the surface of the metal being protected. Volatile inhibitors protect metal parts from corrosion in the vapor phase; therefore, they frequently are called vapor phase inhibitors.

A large number of water-soluble and oil-soluble compounds are used at the present time as inhibitors of atmospheric corrosion of metals.

Water-soluble inhibitors of metal corrosion, forming true solutions in water, but not dissolving in mineral oils, are used in the form of water solutions and powders, and they are applied to wrapping paper [1].

The following requirements should be placed on this group of atmospheric corrosion inhibitors: a specific vapor tension, metal surface sorption and their solubility in water media, considering that there is a thin film of moisture on the surface of the metal under almost any conditions [2].

The protective effect of inhibitors is connected to a great extent with their surface-active properties. An increase in surface activity of inhibitors strengthens their protective effect. The effective concentration of them is sharply reduced in this case [3].

One of the principal characteristics of a volatile inhibitor is the pressure of its saturated vapor. It should be sufficient to create a protective concentration of inhibitor vapors in the space surrounding the metal being protected and not too high, in order to guarantee prolonged protection.

In leading up to a summary of many years of use of water-soluble inhibitors for protection of metals from atmospheric corrosion, it should be noted that both fatty and aromatic organic amines and their salts with weak organic and inorganic acids are the most effective. These are substances, the molecules of which are formed by ionic or polar bonds, and their hydrophilic groups assist in solution of the inhibitor in water.

Oil-soluble inhibitors are organic substances consisting of two parts: a quite high molecular weight, branched hydrocarbon radical, providing for solubility of the entire molecule in oil, and a functional group (or several groups), providing the protective properties of a given compound [4].

Nitro and amino groups, as well as sulfonate and oxygen-containing ones--ester, carboxyl, carbonyl and hydroxyl groups--can emerge as such functional groups.

The mechanism of action of oil-soluble inhibitors have been studied very little. The fundamental difference between water- and oil-soluble inhibitors of corrosion affecting their mechanism of action and protective properties consists of the fact that oil-soluble inhibitors, in distinction from water-soluble ones, do not dissociate. Apparently, for this reason, they cannot have a significant effect on the electrode processes taking place in an atmosphere of corrosion, and they act on the metal in another manner. Thus, for example, while sodium nitrite and dicyclohexylammonium nitrite have much in common in the mechanism of action, both have passivating properties, both stimulate corrosion of some nonferrous metals, oil-soluble inhibitors, for example, nitrated oil, differ sharply from them. They protect ferrous and nonferrous metals.

In this manner, despite the fact that water- and oil-soluble corrosion inhibitors frequently have one and the same functional groups, their mechanisms of action are completely different: the first act in a water medium, for example, in a moisture film on the surface of the metal; the second prevent penetration of the moisture to the metal surface.

The adsorption film created by oil-soluble corrosion inhibitors on the surface of the metal can physically prevent penetration of moisture and reactive substances, they can have hydrophobic properties, and they can displace moisture from the metal surface. In some cases, the molecules of an oil-soluble inhibitor can chemically bind reactive components of the environment. Thus, basic alkali earth metal sulfonates (having excess alkalinity above the stoichiometric) can bind reactive gases (sulfur dioxide, hydrogen sulfide) and, as a consequence of this, protect the metal from corrosion.

Under conditions of warehouse storage and transportation of metal parts, the carriers of oil-soluble inhibitors are oils and greases and the carriers of water-soluble inhibitors most often are the wrapping paper. Paper continues to be the cheapest packaging material at the present time.

An essential defect of regular inhibitor paper is its high gas and vapor permeability.

To provide more reliable protection of metal parts, they are wrapped additionally in paraffinned paper. Another method of increasing the protective properties of inhibitor paper is the manufacture of multilayer paper.

The purpose of this work was the creation of a single-layer inhibitor wrapping paper, guaranteeing protection from corrosion of parts of ferrous and nonferrous metals during the transportation and warehouse storage periods.

Experimental Section

For solution of the problem stated, three series of corrosion tests were carried out on ferrous and nonferrous metals (steel 20, copper M3, brass L62):

I. Corrosion tests of samples of metals wrapped in kraft paper impregnated with inhibitor solution;

II. Corrosion tests of metal samples wrapped in inhibitor paper and in paraffinned paper over it;

III. Searching for an additive to the paraffin, which would increase the anticorrosion protective properties of paraffinned paper.

All corrosion tests were carried out in a heat and humidity chamber, under variable storage conditions.

To conduct the first two series of tests, we used substances soluble in water or alcohol, known to be effective inhibitors in neutral media.

Samples of kraft paper were immersed in a solution with a specific concentration of inhibitor, then dried at room temperature, after which the gravimetric content of inhibitor in the paper was determined in g/m^2. If the content of inhibitor in the paper proved to be insufficient, the sample was impregnated several times in the same solution until the optimum concentration was achieved.

The corrosion tests were conducted over a period of 100 hours in a heat and humidity chamber at 100% relative humidity and variable storage conditions. For a period of 2 hours a day, the temperature was maintained at 45°C and, during the remaining time of the day, natural cooling to 20°C took place. The state of the metal surface was evaluated by a 10-point system (see Table 2), after 100 hcurs of testing.

TABLE 1: CHARACTERISTICS OF INHIBITOR SOLUTIONS USED FOR IMPREGNATING KRAFT WRAPPING PAPER

a п/п. №№	b Наименование ингибитора	c Конц. раств., %	d pH р-ра	e Содержание ингибитора в бумаге, г/м²	f Примечание
1	Бензоат натрия	10	7,2	13,26	
2	Бензоат аммония	10	6,7	13,15	
3	Нитрит дициклогексиламина	5	5,4	10,39	
4	Хромат циклогексиламина .	g насыщенный раствор	6,8	13,11	
5	Хромат гексаметилендиамина	10	8,25	14,16	
6	Бензотриазол	5	5,5	12,52	h спиртовый раствор

Key: a. Number
b. Inhibitor name
c. Solution concentration, %
d. Solution pH
e. Inhibitor content in paper, g/m^2
f. Note
g. Saturated solution
h. Alcohol solution

1. Sodium bonzoate
2. Ammonium benzoate
3. Dicyclohexylamino nitrite
4. Cyclohexylamino chromate
5. Hexamethylenediamine chromate
6. Benzotriazole

[Translator's note: Commas in tabulated figures are equivalent to decimal points.]

The results of the tests carried out (Table 3) show that additional wrapping of the samples in paraffinned paper has a very insignificant effect on the corrosion behavior of the metal samples tested, in the majority of cases. These data permit it to be concluded that this method of wrapping, which frequently is used at present, is inadvisable. The results of tests of paper inhibited with ammonium benzoate and hexamethylenediamine chromate were somewhat unexpected. Additional wrapping of samples in paraffinned paper reduces the protective properties of the inhibitor paper.

TABLE 2: SCALE FOR DETERMINATION OF CORROSION DAMAGE TO STEEL, COPPER AND BRASS

Points	External Appearance of Samples		
	Steel	Copper	Brass
0	No change	No change	No change
1-2	Appearance of 2 or 3 corrosion points on ends.	Appearance of 2 or 3 rust spots, Surface bright.	Indelible strips.
3-4	Increase in number of corrosion points on ends.	Formation of thin oxide layer without loss of shine.	Single corrosion points. Tarnishing of surface.
5-6	Appearance of 1-2 corrosion points on sample surface.	Tarnishing of surface and appearance of separate foci of corrosion.	Corrosion and temper color.
7-8	Increase in number of corrosion foci.	Increase in number of corrosion spots.	Significant corrosion of part of surface of sample.
9-10	Heavy corrosion of entire surface of sample.	Considerable corrosion of entire surface of sample.	Considerable corrosion of entire surface of sample.

On the basis of visual observations, this can be explained in the following manner: paper impregnated with ammonium benzoate is very hygroscopic and, after a day of testing in the heat and humidity chamber, it becomes moist. The samples became covered with drops of water inside the wrapping, but the surface of the steel remains shiny and is not corroded during the entire test period.

Under these conditions, an optimum protective concentration of inhibitor evidently is created. Paraffinned paper, decreasing the vapor permeability of the wrapping, decreases the protective properties of the ammonium benzoate under these conditions.

The decrease in time of protective effect on nonferrous metals by paper inhibited with hexamethylenediamine chromate, with additional wrapping of the samples in paraffinned paper, apparently can be explained in this same manner. During corrosion tests in the heat and humidity chamber, drops of condensed moisture do not form on the surfaces of the samples, but the inhibitor paper itself is strongly wetted.

TABLE 3: PROTECTIVE PROPERTIES OF INHIBITOR PAPER

a №№ п/п.	b Ингибитор	c Серия опыта	d Сталь		e Медь		f Латунь	
			g время до наступления коррозии, сутки	h оценка поверхности, балл	g время до наступления коррозии, сутки	h оценка поверхности, балл	g время до наступления коррозии, сутки	h оценка поверхности, балл
1	Контроль (крафт-бумага без ингибитора)		1	10	12	5	12	7
2	Бензоат натрия	I II	60 100	1 0	9 9	8 4	9 9	8 4
3	Бензоат аммония	I II	100 30	0 2	— —	— —	— —	— —
4	Нитрит дициклогексиламмония	I II	100 100	0 1	20 40	6 2	15 15	4 4
5	Хромат циклогексиламмония	I II	100 100	0 0	25 25	4 3	25 40	2 2
6	Хромат гексаметилендиамина	I II	10 10	2 2	100 30	1 3	100 60	0 1
7	Бензотриазол	I II	14 90	4 1	100 100	0 1	6 30	2 1

Key:

a. Number
b. Inhibitor
c. Test series
d. Steel
e. Copper
f. Brass
g. Time to onset of corrosion, days
h. Evaluation of surface, points

1. Control (kraft paper without inhibitor)
2. Sodium benzoate
3. Ammonium benzoate
4. Dicyclohexylammonium nitrite
5. Cyclohexylammonium chromate
6. Hexamethylenediamine chromate
7. Benzotriazole

The next series of tests was devoted to selection of the additive to the paraffin which would increase the anticorrosion protective properties of paraffinned paper. For this purpose, those additives to the paraffin mass should be selected which would act on the metal surface as contact inhibitors, or which would sharply decrease the vapor permeability of the paraffinned paper and increase its elasticity.

We investigated oil-soluble inhibitors as additives, which are successfully used by the "Neftegaz" plant, as an inhibiting grease, as well as certain organic amines and their salts, which have low solubility in oil.

The oil-insoluble inhibitors were introduced into the paraffinning compound in the form of a suspension, produced by means of an ultrasonic unit. Paper base ODP-35, made of 100% unbleached sulfate cellulose (GOST[1] 5175-53), and grade B paraffin (GOST 784-53) were used for paraffinning.

To increase the elasticity of the cover layer of paraffin, together with the oil-soluble inhibitors, we mixed spindle oil (GOST 1707-51) and petrolatum (GOST 4096-54) with the paraffin. The results of the investigation are presented in Tables 4, 5, and 6.

[1] [GOST--All-Union State Standard.]

TABLE 4: COMPARATIVE EFFECTIVENESS OF PARAFFINNED PAPER SAMPLES

№№ п.п.	Добавка в парафин	Концентрация, %	Время до начала коррозии, сутки: сталь	медь	латунь
1	2	3	4	5	6
1	Контроль (парафинированная бумага)	—	7	40	40
2	Окисленный петролатум	3	19	50	50
3	Окисленный петролатум Веретенное масло	3 20	27	55	55
4	Окисленный петролатум Петролатум	3 30	29	120	52
5	Окисленный петролатум Масляный раствор сульфоната кальция	1,5 8,5	10	50	40
6	Окисленный петролатум Нитрованное масло Пиреполимеры	1,5 5,5 3	42	60	55
7	Окисленный петролатум Нитрованное масло Олеат алюминия	1,5 7,5 0,5	40	45	45
8	Окисленный церезин	3	17	30	12
9	Окисленный церезин Веретенное масло	3 20	24	55	40
10	Окисленный церезин Петролатум	3 30	7	12	5
11	Присадка — ингибитор коррозии Акор *	10	100	120	60
12	Хромат гексаметилендиамина	2	22	120	120
13	Вазелиновое масло Октадециламин	63 3	100	—	30
14	Вазелиновое масло Бензоат моноэтаноламина Триэтаноламин Олеиновая кислота	17 1 1 1	50	29	79
15	Вазелиновое масло Латекс	63 3	60	—	32

TABLE 4 (continued)

Key:

a. Number
b. Paraffin additive
c. Concentration, %
d. Time to start corrosion, days
e. Steel
f. Copper
g. Brass
h. Control (paraffinned paper)
i. Oxidized petrolatum
j. Spindle oil
k. Petrolatum
l. Oil solution of calcium sulfonate
m. Nitrated oil
n. Pyropolymers
o. Aluminum oleate
p. Oxidized ceresin
q. Additive, Akor corrosion inhibitor[1]
r. Hexamethylenediamine chromate
s. Mineral oil
t. Octadecylamine
u. Monoethanolamine benzoate
v. Triethanolamine
w. Oleic acid
x. Latex

TABLE 5: EFFECT OF ADDITIVES TO PARAFFIN ON ANTICORROSION PROTECTIVE PROPERTIES OF PARAFFINNED WRAPPING PAPER

a №№ п/п	b Добавки в парафин	c Концентрация, %	d Состояние поверхности, баллы					
			e сталь		f медь		g латунь	
			h после 60-ти суток	i После 120-ти суток	h после 60-ти суток	i После 120-ти суток	h После 60-ти суток	i После 120-ти суток
1	2	3	4	5	6	7	8	9
1	j Контроль (парафинированная бумага) . . .	—	10	—	5	6	5	6
2	k Окисленный петролатум	3	6	8	4	7	3	4
3	k Окисленный петролатум . . . . l Веретенное масло . . .	3 20	5	8	1	4	1	4
4	k Окисленный петралатум . . . . m Петролатум	3 30	5	5	0	0	3	3
5	k Окисленный петролатум . . . . m Масляный раствор сульфоната кальция . .	1,5 8,5	1	1	1	1	1	2

[1]Akor additive has the following composition: nitrated oil, 85.7%; technical stearin, 9.5%; technical lime (calculated as CaO), 4.8%.

Table 5 (continued)

1	2	3	4	5	6	7	8	9
6	k Окисленный петролатум o Нитрованное масло p Пиррополимеры	1,5 5,5 3	6	6	0	4	3	6
7	k Окисленный петролатум o Нитрованное масло q Олеат алюминия	1,5 7,5 0,5	1	1	1	4	1	5
8	r Окисленный церезин	3	5	—	4	4	3	3
9	r Окисленный церезин l Веретенное масло	3 20	2	2	1	2	1	1
10	r Окисленный церезин m Петролатум	3 30	5	5	5	5	2	3
11	s Присадка — ингибитор коррозии Акор	10	0	1	0	0	1	1
12	t Хромат гексаметилендиамина	2	4	7	0	0	1	1
13	u Вазелиновое масло v Октадециламин	63 3	0	1	—	—	1	1
14	u Вазелиновое масло w Бензоат моноэтаноламина x Триэтаноламин y Олеиновая кислота	17 1 1 1	2	—	4	—	5	—
15	u Вазелиновое масло z Латекс	63 3	1	—	—	—	1	—

Key:

a. Number
b. Paraffin additive
c. Concentration, %
d. State of surface, points
e. Steel
f. Copper
g. Brass
h. After 60 days
i. After 120 days
j. Control (paraffinned paper)
k. Oxidized petrolatum
l. Spindle Oil
m. Petrolatum
n. Oil solution of calcium sulfonate
o. Nitrated oil
p. Pyropolymers
q. Aluminum oleate
r. Oxidized ceresin
s. Additive, Akor corrosion inhibitor
t. Hexamethylenediamine chromate
u. Mineral oil
v. Octadecylamine
w. Monoethanolamine benzoate
x. Triethanolamine
y. Oleic acid
z. Latex

TABLE 6: VAPOR PERMEABILITY OF PARAFFINNED PAPER

a №№ п/п	b Добавки в парафин	c Концент-рация, %	d Паропро-ницае-мость, г/м²
1	Контроль (бумага парафинированная, лабораторные образцы)	2	44
2	Окисленный петролатум	3	29
3	Окисленный петролатум	3	
	Веретенное масло	20	51
4	Окисленный петролатум	3	
	Петролатум	30	12
5	Окисленный петролатум	1,5	
	Масляный раствор сульфоната кальция	8,5	58
6	Окисленный петролатум	1,5	
	Нитрованное масло	5,5	
	Пирополимеры	3	55
7	Окисленный петролатум	1,5	
	Нитрованное масло	7,5	
	Олеат алюминия	0,5	32
8	Окисленный церезин	3	30
9	Окисленный церезин	3	
	Веретенное масло	20	55
10	Окисленный церезин	3	
	Петролатум	30	45
11	Присадка Акор	10	20
12	Хромат гексаметилендиамина	2	46
13	Вазелиновое масло	63	
	Октадециламин	3	115
14	Вазелиновое масло	17	
	Бензоат моноэтаноламина	1	
	Триэтаноламин	1	
	Олеиновая кислота	1	87

Key:

a. Number
b. Paraffin additive
c. Concentration, %
d. Vapor permeability, g/cm²
e. Control (paraffinned paper, laboratory samples)
f. Oxidized petrolatum
g. Spindle oil
h. Petrolatum
i. Oil solution of calcium sulfonate
j. Nitrated oil
k. Pyropolymers
l. Aluminum oleate
m. Oxidized ceresin
n. Akor additive
o. Hexamethylenediamine chromate
p. Mineral oil
q. Octadecylamine
r. Monoethanolamine benzoate
s. Triethanolamine
t. Oleic acid

The investigations conducted demonstrated that introduction of corrosion inhibitors into the paraffinning compound considerably increases the protective anticorrosion effect of paraffinned wrapping paper.

Samples of metals wrapped in paraffinned paper containing Akor additive, hexamethylenediamine chromate (nonferrous metals) were not corroded over a period of four months of testing under severe conditions. Oxidized petrolatum, combined with other additives, also has good protective properties.

For conduct of natural tests, the following compositions of the protective layer of the wrapping paper can be recommended:

For Steel and Nonferrous Metals

A. 1. Paraffin - 90%

   2. Akor additive - 10%

B. 1. Paraffin - 30%

   2. Mineral Oil - 63%

   3. Octadecylamine - 7%

For Copper and Brass

A. 1. Paraffin - 98%

   2. Hexamethylenediamine chromate - 2%

For Copper

1. Paraffin - 67%
2. Petrolatum - 30%
3. Oxidized petrolatum - 3%

For Steel

1. Paraffin - 90.5%
2. Nitrated oil - 7.5%
3. Oxidized petrolatum - 1.5%
4. Aluminum oleate - 0.5%

Conclusions

1. The possibility of producing a single-layer anticorrosion wrapping paper for metal parts was investigated.

2. The possibility of effective protection of ferrous and nonferrous metal parts from atmospheric corrosion was demonstrated, using paraffinned wrapping paper containing corrosion inhibitors.

3. It was determined that introduction of certain additives to the protective layer of paraffinned wrapping paper reduces its vapor permeability.

4. A formula for the protective layer of paraffinned wrapping paper for metal parts was developed.

5. The comparative effectiveness of the protective action of wrapping paper, impregnated with various atmospheric corrosion inhibitors, was investigated.

6. It was determined that, in preservation of metal parts with inhibitor paper, additional wrapping of them in paraffinned paper increases the corrosion resistance of the paper to only a negligible extent, in the majority of cases.

It was noted that the protective properties of certain samples of inhibitor paper (ammonium benzoate and hexamethylenediamine chromate inhibitors) is sharply reduced by isolating them from the external medium with paraffinned paper.

BIBLIOGRAPHY

1. Balezin, S. A., L. V. Babich, in the collection Ingibitory korrozii metallov [Metal Corrosion Inhibitors], Sudostroyeniye Press, Leningrad, 1965.

2. Balezin, S. A., Collection No. 2 Ingibitory korrozii [Corrosion Inhibitors], VSNTO, Profizdat Press, 1957.

3. Golyanitskiy, O.I., scientific-technical collection Zashchitnyye pokrytiya [Protective Coatings], Issue 1, Moscow, 1962.

4. Shekhter, Yu. N., Zashchita metallov ot korrozii [Protection of Metals from Corrosion], Khimiya Press, 1964.