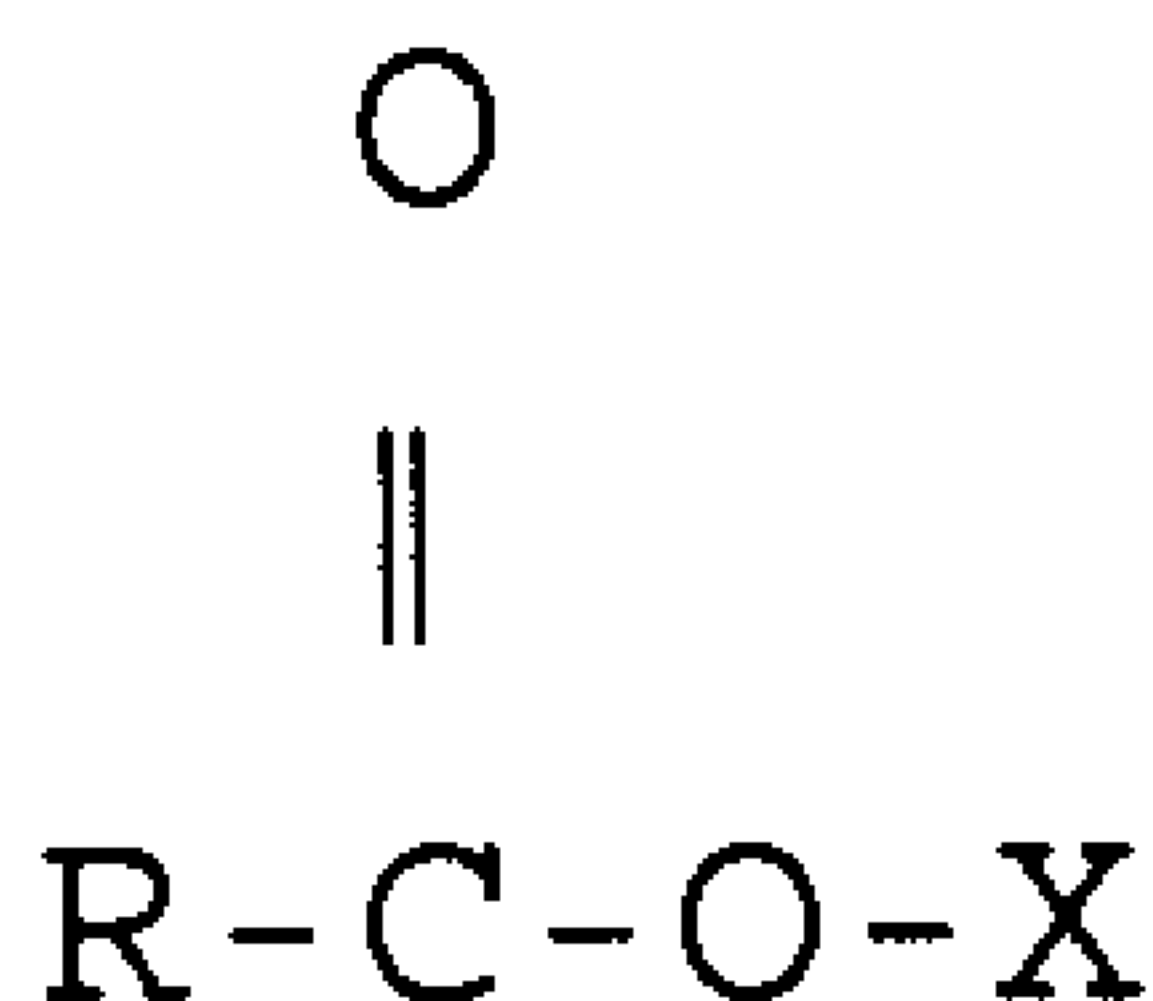




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(54) Titre : COMPOSITIONS IGNIFUGES STABILISEES ET INHIBANT LA CORROSION ET PROCEDES ASSOCIES
(54) Title: STABILIZED, CORROSION-INHIBITED FIRE RETARDANT COMPOSITIONS AND METHODS



(57) **Abrégé/Abstract:**

An improved fire retardant composition with improved stability and/or corrosion resistance is provided herein. Such composition contains a fire retardant salt, a gum thickener, an aqueous liquid carrier and at least one non-toxic water-soluble additive. That non-toxic, water-soluble additive is at least one carboxylic acid or salt thereof, having the structural formula (see above formula). In that structural formula R is an unsubstituted phenyl group, or a substituted phenyl group, or an unsubstituted carbon chain containing conjugated unsaturation, or a substituted carbon chain containing conjugated unsaturation, and X is hydrogen or a metal. The additive component is present in an amount which is effective to improve the stability of the composition and/or to reduce the corrosivity of the composition to iron. Preferred compositions contain benzoic acid, or sorbic acid, or a mixture of benzoic acid and sorbic acid.



ABSTRACT

An improved fire retardant composition with improved stability and/or corrosion resistance is provided herein. Such composition contains a fire retardant salt, a gum thickener, an aqueous liquid carrier and at least one non-toxic water-soluble additive. That non-toxic, water-soluble additive is at least one carboxylic acid or salt thereof, having the structural formula

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R-C-O-X.

In that structural formula R is an unsubstituted phenyl group, or a substituted phenyl group, or an unsubstituted carbon chain containing conjugated unsaturation, or a substituted carbon chain containing conjugated unsaturation, and X is hydrogen or a metal. The additive component is present in an amount which is effective to improve the stability of the composition and/or to reduce the corrosivity of the composition to iron. Preferred compositions contain benzoic acid, or sorbic acid, or a mixture of benzoic acid and sorbic acid.

(a) TITLE OF THE INVENTION

STABILIZED, CORROSION-INHIBITED FIRE RETARDANT
COMPOSITIONS AND METHODS

(b) TECHNICAL FIELD TO WHICH THE INVENTION RELATES

5 This invention relates to fire retardant compositions,
which are especially adapted for preventing and fighting
wildfires. More particularly, the invention relates to such
compositions which have improved stability. In another
respect, the invention relates to such compositions which have
10 reduced corrosivity to ferrous metals. The invention further
relates to fire retardant compositions which are specially
adapted to prevent, and/or to prevent the spread of, wildfires
and which are especially suited to aerial application.

(c) BACKGROUND ART

15 A wide variety of fire retardant compositions which are
used to prevent or combat the spread of wildfires (forest
fires, range fires, etc.) have been proposed. Generally, such
compositions contain a fire retardant salt (e.g., ammonium
phosphate, monobasic ammonium phosphate (MAP) and/or dibasic
20 ammonium phosphate (DAP), ammonium polyphosphate, ammonium
sulphate, and the like), an aqueous liquid vehicle, and
various functional additives which improve specific character-
istics of the composition. These functional additives may
include, e.g., thickeners (to improve the aerial drop and fuel
25 coverage characteristics), corrosion inhibitors (to reduce the
corrosivity of the compositions to metal components of storage
and application equipment), colouring agents (to improve the
accuracy and coverage of successive aerial applications),
stabilizing agents (to prevent separation of the various
30 components of the composition during storage and transport),
spoilage inhibitors (to prevent microbial decomposition of
certain components), etc.

 Illustrative examples of such prior art fire retardant
compositions are disclosed in U.S. Patents Nos. 3,196,108
35 (Nelson) and 3,730,890 (Nelson), 3,960,735 (Lacey), 4,176,071

(Crouch), 3,634,234 (Morgenthaler), 3,257,16 (Langguth),
4,822,524 (Strickland), 4,447,336 (Vandersall) and 4,839,065
(Vandersall).

5 As illustrated by the Crouch '316, Strickland '524,
Morgenthaler '234 and Vandersall '336 patents, various natural
and synthetic gums are advantageously used to thicken fire
retardants compositions. Fire retardant compositions
containing such cellulosic thickeners are, however, notably
10 susceptible to instability, causing the components to lose
viscosity over extended storage periods. Unfortunately, the
other functional additives, may cause or contribute to such
instability problems. Thus, it has been observed that reduced
corrosivity and improved stability are contradictory
15 requirements for certain additives for fire retardants that
are thickened with natural or synthetic galactomanan gum
components.

Certain prior art functional additives which provide a
measure of corrosion and/or stability control have been
identified as having adverse impacts on human health and are
20 listed as such by various governmental fire fighting agencies.
In particular, the use of thiourea in fire retardants has been
prohibited by the United States Forest Service.

(d) DESCRIPTION OF THE INVENTION

25 It would be highly desirable, and it is an object of a
first aspect of this invention, to provide a non-toxic
corrosion inhibitor for gum-thickened fire retardants which
did not degrade the long-term stability of the compositions.

It would also be highly desirable, and it is an object of
a second aspect of the invention, to provide a non-toxic
30 viscosity stabilizer for gum-thickened fire retardants which
did not degrade the corrosion characteristics of the
compositions.

In particular, it would be highly desirable, and it is an
object of a third aspect of the invention, to provide a non-
35 toxic functional additive for gum-thickened fire retardants

which improves both the corrosivity and stability of gum-thickened fire retardants.

5 It would further be highly desirable, and it is an object of a fourth aspect of this invention, to provide fire retardant compositions, specially adapted for aerial application, which are thickened with a carbohydrate thickening agent, e.g., galactomanan or derivitized galactomanan thickening agent, e.g., guar gum, hydroxypropyl guar, and the like, yet which have a combination of reduced
10 corrosivity and increased stability.

Sodium benzoate is known to inhibit corrosion of iron in the near neutral range, e.g., steel in aerated distilled water, and is known to inhibit corrosion of steel in water at pH 7.5 containing 17 ppm NaCl (Corrosion and Corrosion
15 Control, Uhlig & Revie (Wiley), pp. 266, et seq.). Sodium benzoate may have been disclosed in a publication as a corrosion inhibitor in fire retardants, which is thickened with an unknown type of thickening agent. However, there is no known prior art which teaches its use in stabilizing and/or
20 inhibiting corrosivity of fire retardants containing gum thickeners, as disclosed herein.

It has now been discovered that gum-thickened, fire retardant compositions, containing a selected corrosion inhibitor additive, reduces the corrosivity of the composition
25 to ferrous metals without sacrificing and, in some cases, even improving, the stability of such compositions. In addition, gum-thickened fire retardant composition have been discovered, containing a selected stabilizing agent for gum-thickened fire retardants which improves the stability (viscosity loss)
30 characteristics of the composition, without sacrificing and, in certain instances even improving, the ferrous metal-corrosion characteristics of the composition.

Briefly, the improved gum-thickened fire retardant compositions of a first broad aspect of this invention include
35 a fire retardant salt, a gum thickener, an aqueous liquid

carrier and an additive comprising at least one non-toxic, water-soluble carboxylic acid or salt thereof having the structural formula



10 wherein R is a substituted or unsubstituted phenyl group, or a substituted or unsubstituted carbon chain containing conjugated unsaturation, and X is hydrogen or a metal, the additive being present in an amount which is effective to reduce the corrosivity of the composition to iron.

15 In one preferred embodiment of the invention, the additive is benzoic acid. In a second preferred embodiment of the invention, the additive is sorbic acid. In a third preferred embodiment of the invention, the additive is a mixture of benzoic acid and sorbic acid.

20 The carboxylic acid or salt thereof may be a mixture of a non-toxic, water-soluble aromatic carboxylic acid or salt thereof and a non-toxic, water-soluble substituted or unsubstituted straight or branched-chain carboxylic acid or salt thereof. By one specific variation thereof, the mixture is of sodium benzoate and sorbic acid. The combination of such
25 aromatic and straight/branched-chain components appears to provide the optimum combination of corrosion inhibition and stability enhancement.

Representative examples of aromatic carboxylic acids, which may be employed in the practice of aspects of this
30 invention, include benzoic acid, salicylic acid and phenyl acetic acid.

Representative examples of straight or branched-chain carboxylic acids, which may be employed in the practice of aspects of the invention, include sorbic acid, cinnamic acid
35 (3-phenyl-2-propenoic acid), maleic acid, succinic acid

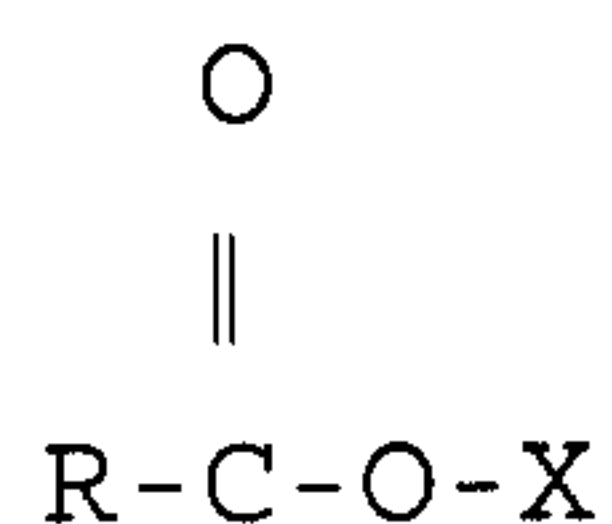
derivatives having a side chain with conjugated unsaturation and 2-furoic acid.

5 Other suitable aromatic and straight or branched-chain carboxylic acids/salts can be identified without undue experimentation by those skilled in the art having regard for this disclosure.

10 In addition to the above-described novel fire retardant compositions, the invention in a second of its broad aspects, also contemplates methods for manufacturing novel fire retardant compositions, in which the additive compound is mixed with the other components of the fire retardant composition to provide the final improved composition.

15 The present invention, in such second broad aspect, provides an improvement in a method of manufacturing a fire retardant composition, the composition including components comprising a fire retardant salt, a gum thickener, a liquid carrier and a corrosion inhibitor, the improvement comprising including, as the corrosion inhibitor, at least one non-toxic water-soluble carboxylic acid or salt thereof having the structural formula

20



25 wherein R is an unsubstituted phenyl group, or a substituted phenyl group, or an unsubstituted carbon chain containing conjugated unsaturation, or a substituted carbon chain containing conjugated unsaturation, and X is hydrogen or a metal, in an amount effective to reduce the corrosivity of the composition.

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By a first variant of this second broad aspect of this invention, the method comprises including, as the corrosion inhibitor, benzoic acid.

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By a second variant of this second broad aspect of this invention, the method comprises including, as the corrosion inhibitor, sorbic acid.

By a third variant of this second broad aspect of this invention, the method comprises including, as the corrosion inhibitor, benzoic acid.

By a fourth variant of this second broad aspect of this invention, the method comprises including, as the corrosion inhibitor, the combination of benzoic acid and sorbic acid, and also comprises using amounts thereof which are also effective to improve the stability of the composition.

(e) AT LEAST ONE MODE FOR CARRYING OUT THE INVENTION

The following examples illustrate the practice of various aspects of this invention. In each example, the indicated components of the fire retardant formulation are mechanically mixed by any one of several mixing techniques which are well-known in the art to provide the indicated final compositions. Upon testing these compositions by standardized methods for compliance with U.S. Forest Service procurement specifications for viscosity loss and iron corrosion rate, the indicated results are observed. Corrosion rate is measured by NACE weight loss method using 4130 mild steel, partial immersion at 120°F., 90-day immersion.

EXAMPLE 1Formulation: Ammonium Sulphate-Lightfast

	<u>Ingredient</u>	<u>Weight % in Final Retardant</u>
5	Ammonium sulphate	14
	Tetrasodium hexacyanoferrate	0.32
	Diammonium Phosphate	0.95
	Hydroxypropyl guar	0.82
10	Xanthan gum	0.008
	Iron Oxide (Fe ₂ O ₃)	0.13
	sorbic acid	(as below)
	sodium benzoate	(as below)
15	water	balance

Table 1

	% sorbic acid	% sodium benzoate	% original viscosity retained	Fe Corrosion Rate (mils/yr)
20	0	0	15	23.5
25	0.10	0	64	6.4
	0	0.10	59	
	0	0.30	-	10 ⁻
	0	0.50	-	5.5
	0	0.70	-	3
30				

EXAMPLE 2Formulation: Ammonium Sulphate - Fading

	<u>Ingredient</u>	<u>Weight % in Final Retardant</u>
35	Ammonium Sulphate	14
	Diammonium Phosphate	0.95
40	Tetrasodium hexacyanoferrate	0.32
	Carbohydrate thickener	0.83
	Fading Pigment	0.13
	Iron oxide (Fe ₂ O ₃)	0.03
	Bactericide/Spoilage Inhibitor	0.10
45	defoamer/antifoamer	0.06
	sorbic acid	as below
	sodium benzoate	as below
50	water	balance

% sorbic acid	% sodium benzoate	% initial viscosity retained	Fe Corrosion Rate mils/yr
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10

0	0	5.6	29.3
0.3	0	9.7	12
0.6	0	11.1	6
0	0.75	9.4	2
0	1.5	12.2	4
0.3	0.75	17.5	2
0.6	0.75	18.9	1.7
0.3	1.5	20.4	2
0.6	1.5	23	1.5

25 Formulation: Ammonium Phosphate/Ammonium Sulphate -
 Lightfast

	<u>Ingredient</u>	<u>Weight % in Final Retardant</u>
30	Ammonium Sulphate	8.4
	Diammonium Phosphate	3.2
	Hydroxypropyl guar	0.82
	Iron Oxide (Fe ₂ O ₃)	0.13
35	bactericide/spoilage inhibitor	0.10
	sorbic acid	as below
	sodium benzoate	as below
40	water	balance

Table 3

	% sorbic acid	% sodium benzoate	% initial viscosity retained	Corrosion rate mils/yr
5	0	0	4	8.5
	0	0.4	15	3.1
	0	0.8	20	1.6
	0	1.2	22	2.7
	0.1	0	16	3.8
10	0.1	0.4	28	1.7
	0.1	0.8	30	2.5
	0.1	1.2	23	3.5

15 The formulations set forth below are mixed, yielding satisfactory iron corrosion and stability results.

EXAMPLE 4

This example illustrates the practice of an aspect of the invention in connection with compositions similar to those disclosed in the Vandersall U.S. Patent No. 4,983,326.

20

Weight % in

	Components	Dry Concentrate	Liquid Concentrate	Final Mix
25	Mixture of ammonium salts with N-P ratio of at least 1.25 (ammonium phosphate, ammonium sulphate or mixtures thereof)	70.13-87.05	32.57-40.56	7.64-9.3
30				
35	Tricalcium Phosphate	2.01	0.94	0.22
	Galactomannan Gum thickener	7.24	3.39	0.78
40	Polyalkylene derivatives of propylene glycol	0.13	0.06	0.01
45	Colourant LIGHTFAST™ (iron oxide, titanium dioxide)			

EXAMPLE 4 (Continued)

Weight % in				
5	Components	Dry Concentrate	Liquid Concentrate	Final Mix
10	or fading (DAY-GLO _{TM} (122-9180) or mixtures thereof	1.89	0.68	0.20
15	Tetrasodium hexacyano ferrate (II)	0-0.5	0-0.23	0-0.05
20	Carboxylic acid or mixtures sorbic acid/salt, benzoic acid/salt, cinnamic acid/salt or combinations thereof)	0.18-16.6	0.08-8.8	0.02-2.00
25	Sodium Benzoate	0.09-9.3	0.04-4.3	0.01-1.00
	Water	none	balance	balance

EXAMPLE 6

30 This example illustrates the practice of an aspect of the invention with corrosion inhibitor-stabilizer components other than sodium benzoate and sorbic acid.

	<u>Components</u>	<u>Wt. % Dry</u>	<u>Wt. % Final Mix</u>
35	Ammonium Sulphate	84.89-79.42	12.92-12.09
	Ammonium Phosphate (DAP, MAP or mixture thereof)	6.81- 6.37	1.04- 0.97
40	Galactomannan Gum	5.40	0.82
45	Colourant (LIGHTFAST TM (iron oxide or titanium dioxide) or fading (e.g., DAY-GLO _{TM} pigment 122-9180) or a mixture of both	1.05	0.16

EXAMPLE 6 (Continued)

	<u>Components</u>	<u>Wt. % Dry</u>	<u>Wt. % Final Mix</u>
5	Anti-microbial mixture (66% methyl paraben and 33% propyl paraben)	0.65	0.08
10	Cinnamic Acid or salt	0.66-6.57	0.01-1.00

EXAMPLE 7

15 This example illustrates a liquid concentrate formula
suitable for dilution with water to a final retardant salt
concentration that meets combustion retarding effectiveness in
a given fire situation. The galactomannan gum is pre-
dispersed in a non-aqueous carrier to make a liquid
concentrate thickener solution and can be added at a variable
rate directly to the final mixed product to achieve a desired
20 viscosity.

	<u>Components</u>	<u>Weight % in Liquid Concentrate</u>	<u>Final Mix</u>
	Ammonium Polyphosphate	91.5-79.00	5.0-25.0
25	Suspending agent	3.5	0.19-0.97
	TSHCF	0-4.5	0.08-1.24
30	Colorant Lightfast (iron oxide or titanium dioxide) or fading (e.g., DAY-GLO _{TM} pigment 122-9180) or a mixture of both	5.62-1.12	0.31
35	Galactomannan Gum thickener	-	0.2-0.80
40	Carboxylic Acid or mixture (66% methyl paraben and 33% propyl paraben)	0.18-7.25	0.01-2.00
	water	none	balance

CLAIMS

1. In a fire retardant composition, which includes a fire retardant salt, a gum thickener, and a liquid carrier, the improvement comprising:

5 an additive which is at least one non-toxic, water-soluble carboxylic acid or salt thereof having the structural formula



wherein R is an unsubstituted phenyl group, or a substituted phenyl group, or an unsubstituted carbon chain containing conjugated unsaturation, or a substituted carbon chain containing conjugated unsaturation, and X is hydrogen or a metal,

15

said additive being present in said composition in an amount which is effective to reduce corrosivity of said composition.

20 2. The composition of claim 1, in which said additive is benzoic acid.

3. The composition of claim 1, in which said additive is sorbic acid.

25 4. The composition of claim 1, in which said additive is the combination of benzoic acid and sorbic acid.

5. The composition of claim 4, in which said benzoic acid and said sorbic acid are present in the amount effective to both reduce the corrosivity of said composition and to improve the stability of said composition.

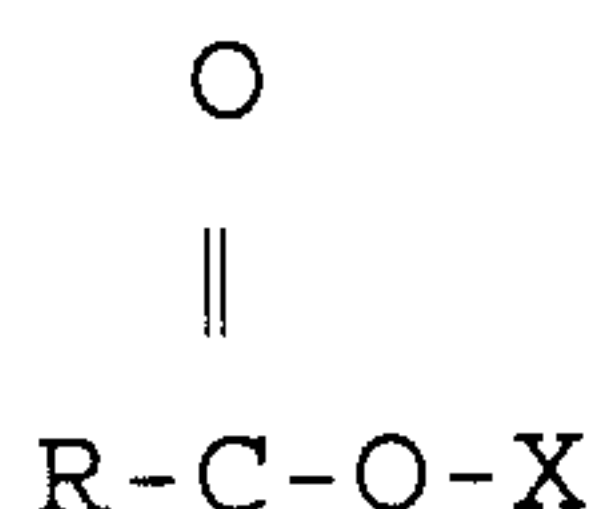
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6. In a method of manufacturing a fire retardant composition, said composition including components comprising

35

a fire retardant salt, a gum thickener, a liquid carrier and a corrosion inhibitor, the improvement comprising:

including, as said corrosion inhibitor, at least one non-toxic water-soluble carboxylic acid or salt thereof having the structural formula



wherein R is an unsubstituted phenyl group, or a substituted phenyl group, or an unsubstituted carbon chain containing conjugated unsaturation, or a substituted carbon chain containing conjugated unsaturation, and X is hydrogen or a metal, in an amount effective to reduce the corrosivity of said composition.

7. The method of claim 6 which comprises including, as said corrosion inhibitor, benzoic acid.

8. The method of claim 6 which comprises including, as said corrosion inhibitor, sorbic acid.

9. The method of claim 6 which comprises including, as said corrosion inhibitor, benzoic acid.

10. The method of claim 6 which comprises including, as said corrosion inhibitor, the combination of benzoic acid and sorbic acid, and using the amounts thereof which are also effective to improve the stability of said composition.

11. In a method of retarding or extinguishing a wildfire, the step of aerially applying the composition of claim 1, claim 2, claim 3, claim 4 or claim 5 to vegetation.

