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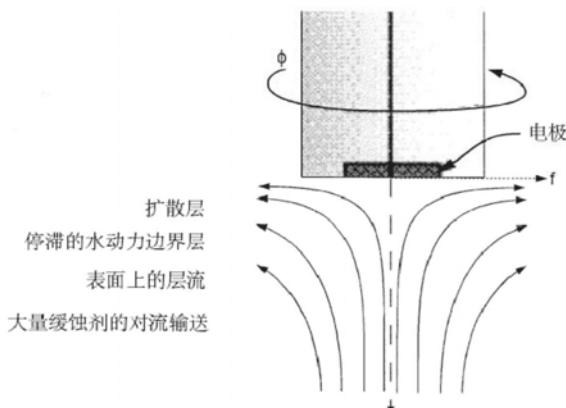
权利要求书37页 说明书54页 附图7页

(54) 发明名称

包含硫醇缓蚀剂的聚乙烯醇缩丁醛涂料

(57) 摘要

提供了制剂、涂料和用于在基底上涂布缓蚀制剂的方法。缓蚀制剂包括 (a) 至少一种树脂，(b) 至少一种布朗斯台德酸和 (c) 至少一种含硫缓蚀剂。



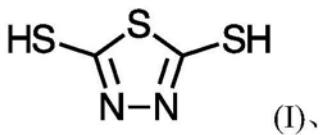
1. 一种缓蚀制剂, 其由下列组成:

- (a) 聚乙烯醇缩丁醛树脂;
- (b) 酸催化剂, 其包括至少一种布朗斯台德酸; 和
- (c) 至少一种含硫缓蚀剂, 其包括噻二唑化合物,

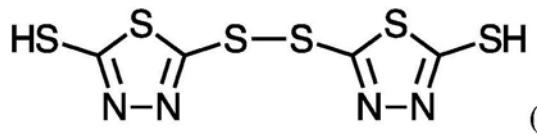
其中所述至少一种布朗斯台德酸选自: H_3PO_4 、 H_2SO_4 、 HX , 其中X是Cl、Br或F, 和 HNO_3 , 或其组合。

2. 根据权利要求1所述的缓蚀制剂, 其中所述至少一种布朗斯台德酸包括 H_3PO_4 。

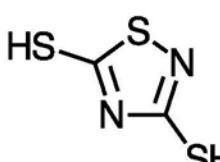
3. 根据权利要求1所述的缓蚀制剂, 其中所述噻二唑化合物选自结构(I)-(V):



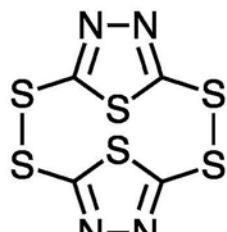
(I),



(II),

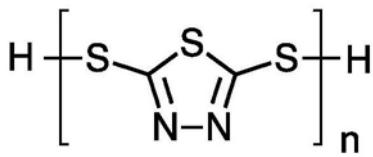


(III)



(IV)

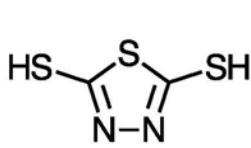
和



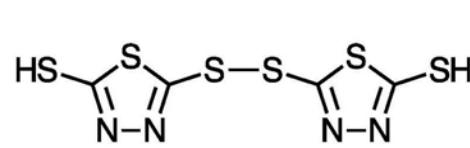
(V),

或其组合, 其中结构(V)的n等于或大于2。

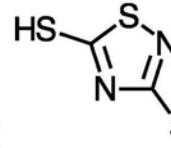
4. 根据权利要求1所述的缓蚀制剂, 其中所述噻二唑化合物选自:



(I),



(II) 和



(III),

或其组合。

5. 根据前述权利要求中任一项所述的缓蚀制剂, 其中所述至少一种含硫缓蚀剂包括含有金属的噻二唑化合物。

6. 根据权利要求5所述的缓蚀制剂, 其中所述含有金属的噻二唑化合物选自:

2,5-二巯基-1,3,4-噻二唑二钾盐、聚[Zn:2,5-二巯基-1,3,4-噻二唑(1:1)]、[Al:2,5-二巯基-1,3,4-噻二唑(1:3)]、[Al:2,5-二巯基-1,3,4-噻二唑(3:1)]、聚[Zn:(双-(2,5-二硫-1,3,4-噻二唑)(1:1))]、聚[Fe:2,5-二巯基-1,3,4-噻二唑)(1:1)]、聚[Al:2,5-二巯基-1,3,4-噻二唑(1:1)]、和聚[Cu:2,5-二巯基-1,3,4-噻二唑(1:1)]、或其组合。

7. 根据权利要求5所述的缓蚀制剂, 其中所述含有金属的噻二唑化合物是聚[Zn:2,5-二巯基-1,3,4-噻二唑(1:1)]。

8. 根据权利要求1-4和6-7中任一项所述的缓蚀制剂, 其中:

所述聚乙烯醇缩丁醛树脂以范围为从8%wt/wt至99%wt/wt的量存在;

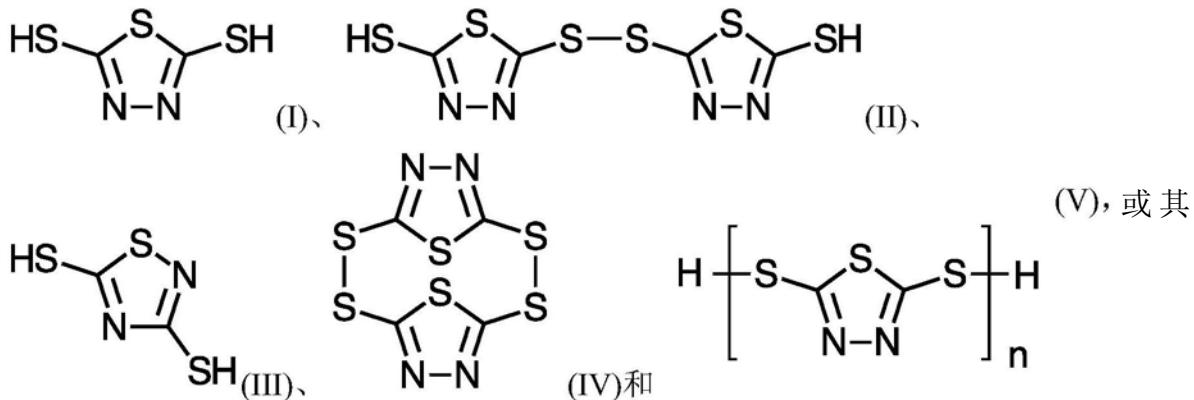
所述至少一种布朗斯台德酸以范围为从1%wt/wt至10%wt/wt的量存在; 并且

所述至少一种含硫缓蚀剂以范围为从0.01%wt/wt至30%wt/wt的量存在，其中所述缓释制剂中组分的百分含量的总和为100%。

9. 根据权利要求8所述的缓蚀制剂，其中：

所述至少一种布朗斯台德酸包括H₃PO₄。

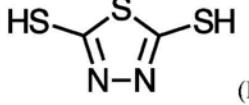
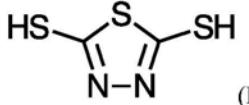
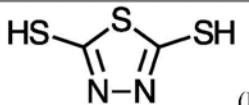
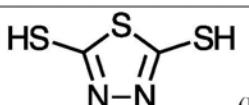
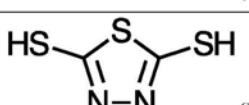
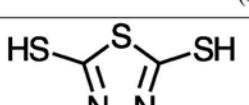
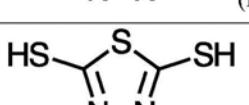
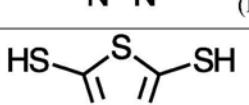
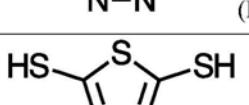
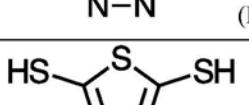
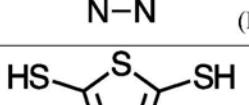
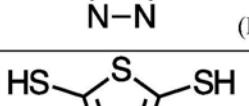
10. 根据权利要求9所述的缓蚀制剂，其中所述至少一种含硫缓蚀剂选自：



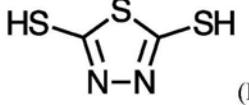
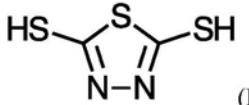
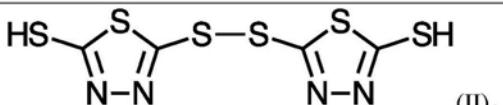
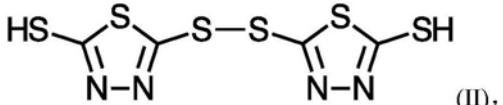
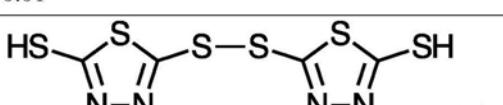
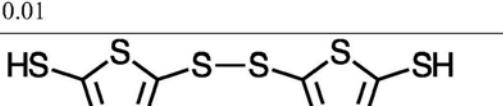
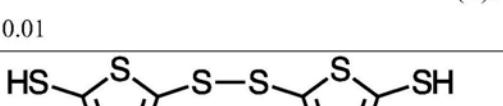
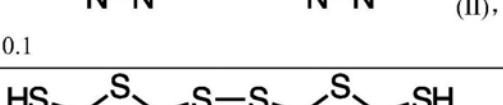
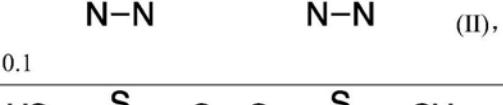
组合，其中结构(V)的n等于或大于2。

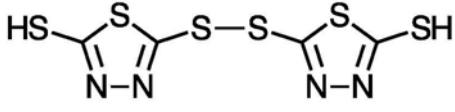
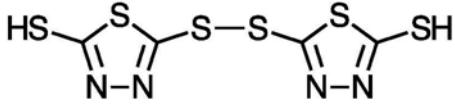
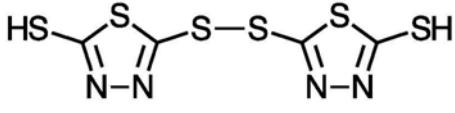
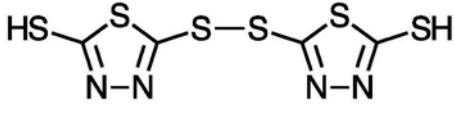
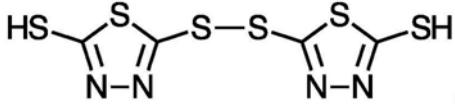
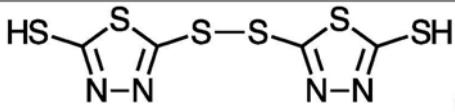
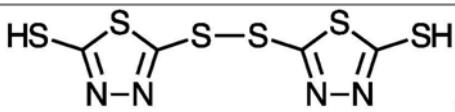
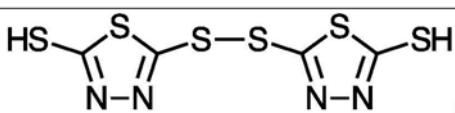
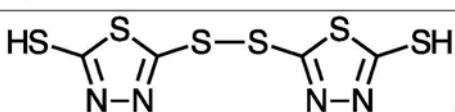
11. 根据权利要求10所述的缓蚀制剂，其中所述缓蚀制剂是制剂(1)-(140)中的至少一种：

制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
1	74.99	(I), 0.01	10.0
2	79.99	(I), 0.01	6.0

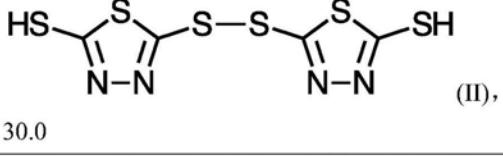
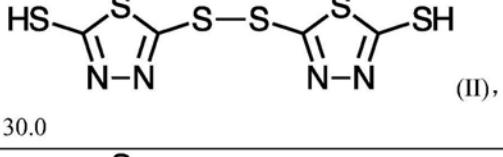
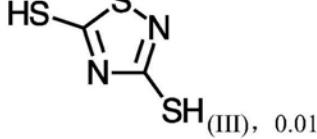
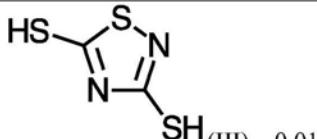
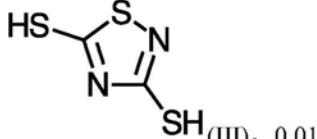
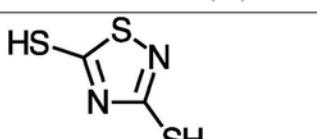
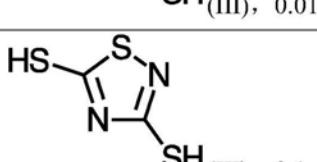
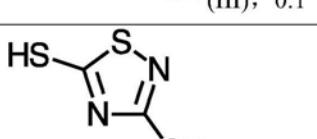
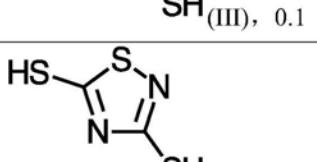
制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
3	89.99	 (I), 0.01	4.0
4	98.99	 (I), 0.01	1.0
5	74.9	 (I), 0.1	10.0
6	79.9	 (I), 0.1	6.0
7	89.9	 (I), 0.1	4.0
8	98.9	 (I), 0.1	1.0
9	74.6	 (I), 0.4	10.0
10	50.0	 (I), 0.4	6.0
11	8.2	 (I), 0.4	3.2
12	20.6	 (I), 0.4	1.0
13	70.0	 (I), 5.0	10.0
14	74.4	 (I), 5.0	6.0

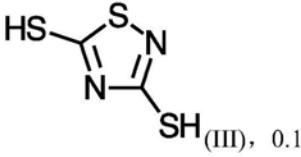
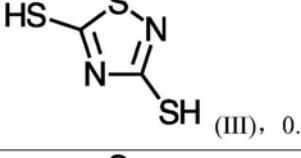
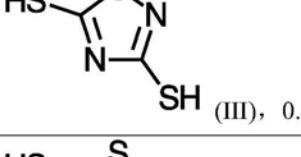
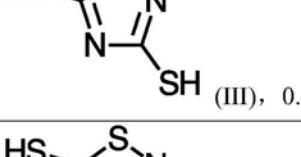
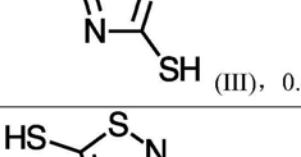
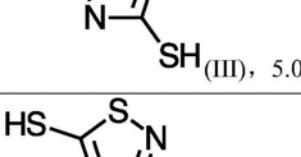
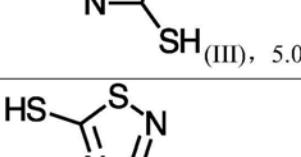
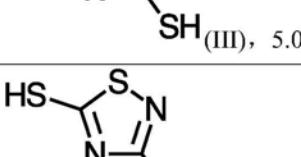
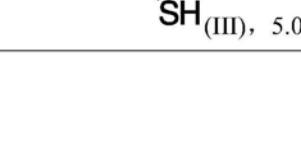
制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
15	85.0	 (I), 5.0	4.0
16	94.0	 (I), 5.0	1.0
17	65.0	 (I), 10.0	10.0
18	75.0	 (I), 10.0	6.0
19	80.0	 (I), 10.0	4.0
20	89.0	 (I), 10.0	1.0
21	55.0	 (I), 20.0	10.0
22	65.0	 (I), 20.0	6.0
23	70.0	 (I), 20.0	4.0
24	79.0	 (I), 20.0	1.0
25	50.0	 (I), 30.0	10.0
26	55.0	 (I), 30.0	6.0

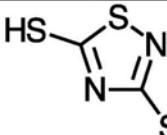
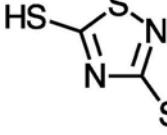
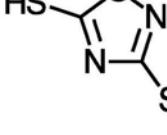
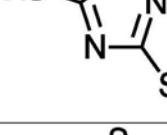
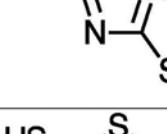
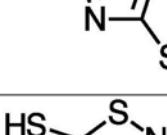
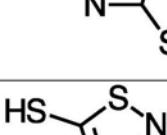
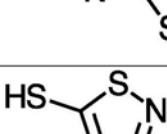
制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
27	60.0	 (I), 30.0	4.0
28	69.0	 (I), 30.0	1.0
29	74.99	 0.01 (II),	10.0
30	84.99	 0.01 (II),	6.0
31	89.99	 0.01 (II),	4.0
32	98.99	 0.01 (II),	1.0
33	74.9	 0.1 (II),	10.0
34	84.9	 0.1 (II),	6.0
35	89.9	 0.1 (II),	4.0
36	98.9	 0.1 (II),	1.0

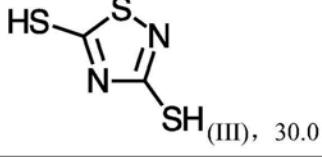
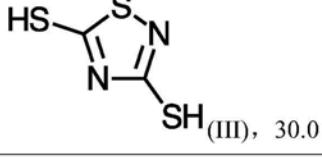
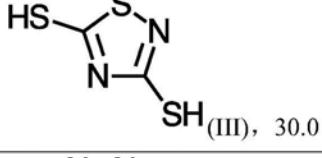
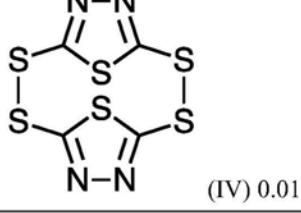
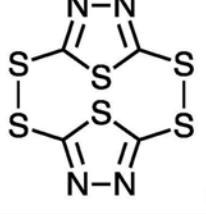
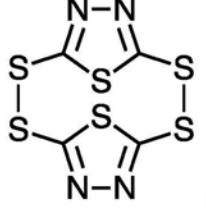
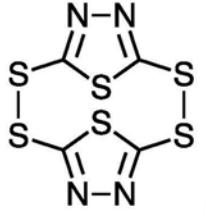
制剂	聚乙稀醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
37	74.6	 (II), 0.4	10.0
38	50.0	 (II), 0.4	6.0
39	8.2	 (II), 0.4	3.2
40	20.6	 (II), 0.4	1.0
41	70.0	 5.0 (II),	10.0
42	74.4	 5.0 (II),	6.0
43	85.0	 5.0 (II),	4.0
44	94.0	 5.0 (II),	1.0
45	65.0	 10.0 (II),	10.0

制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
46	70.0	 10.0	6.0
47	80.0	 10.0	4.0
48	89.0	 10.0	1.0
49	55.0	 20.0	10.0
50	60.0	 20.0	6.0
51	70.0	 20.0	4.0
52	79.0	 20.0	1.0
53	50.0	 30.0	10.0
54	55.0	 30.0	6.0

制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
55	60.0		4.0
56	69.0		1.0
57	74.99		10.0
58	84.99		6.0
59	89.99		4.0
60	98.99		1.0
61	74.9		10.0
62	84.9		6.0
63	89.9		4.0

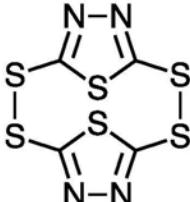
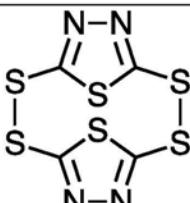
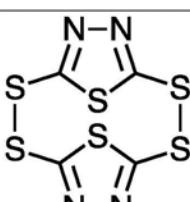
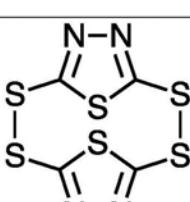
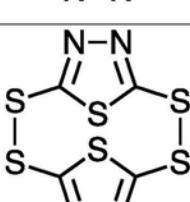
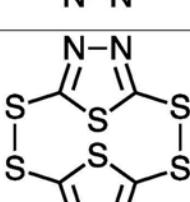
制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
64	98.9	 (III), 0.1	1.0
65	74.6	 (III), 0.4	10.0
66	50.0	 (III), 0.4	6.0
67	8.2	 (III), 0.4	3.2
68	20.6	 (III), 0.4	1.0
69	70.0	 (III), 5.0	10.0
70	74.4	 (III), 5.0	6.0
71	85.0	 (III), 5.0	4.0
72	94.0	 (III), 5.0	1.0

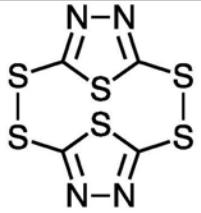
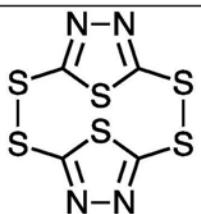
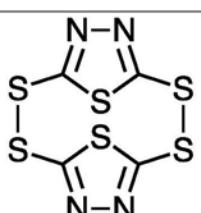
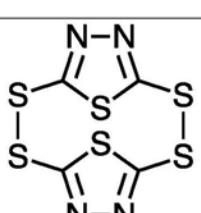
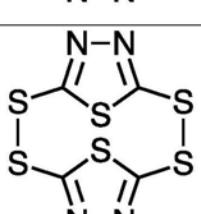
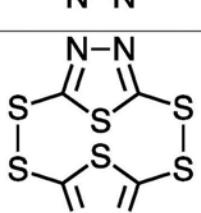
制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
73	65.0	 (III), 10.0	10.0
74	70.0	 (III), 10.0	6.0
75	80.0	 (III), 10.0	4.0
76	89.0	 (III), 10.0	1.0
77	55.0	 (III), 20.0	10.0
78	60.0	 (III), 20.0	6.0
79	70.0	 (III), 20.0	4.0
80	79.0	 (III), 20.0	1.0
81	50.0	 (III), 30.0	10.0

制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
82	55.0	 (III), 30.0	6.0
83	60.0	 (III), 30.0	4.0
84	69.0	 (III), 30.0	1.0
85	74.99	 (IV) 0.01	10.0
86	84.99	 (IV) 0.01	6.0
87	89.99	 (IV), 0.01	4.0
88	98.99	 (IV), 0.01	1.0

制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
89	74.9	<p>(IV), 0.1</p>	10.0
90	84.9	<p>(IV), 0.1</p>	6.0
91	89.9	<p>(IV), 0.1</p>	4.0
92	98.9	<p>(IV), 0.1</p>	1.0
93	74.6	<p>(IV), 0.4</p>	10.0
94	50.0	<p>(IV), 0.4</p>	6.0

制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
95	8.2	<p>(IV), 0.4</p>	3.2
96	20.6	<p>(IV), 0.4</p>	1.0
97	70.0	<p>(IV), 5.0</p>	10.0
98	74.4	<p>(IV), 5.0</p>	6.0
99	85.0	<p>(IV), 5.0</p>	4.0
100	94.0	<p>(IV), 5.0</p>	1.0

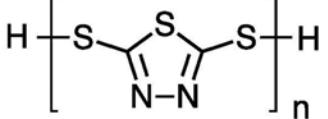
制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
101	65.0	 (IV), 10.0	10.0
102	70.0	 (IV), 10.0	6.0
103	80.0	 (IV), 10.0	4.0
104	89.0	 (IV), 10.0	1.0
105	55.0	 (IV), 20.0	10.0
106	60.0	 (IV), 20.0	6.0

制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
107	70.0	 <p>(IV), 20.0</p>	4.0
108	79.0	 <p>(IV), 20.0</p>	1.0
109	50.0	 <p>(IV), 30.0</p>	10.0
110	55.0	 <p>(IV), 30.0</p>	6.0
111	60.0	 <p>(IV), 30.0</p>	4.0
112	69.0	 <p>(IV), 30.0</p>	1.0

制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
113	74.99	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 0.01	10.0
114	84.99	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 0.01	6.0
115	89.99	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 0.01	4.0
116	98.99	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 0.01	1.0
117	74.9	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 0.1	10.0
118	84.9	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 0.1	6.0
119	89.9	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 0.1	4.0
120	98.9	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 0.1	1.0
121	74.6	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 0.4	10.0

制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
122	50.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 0.4	6.0
123	8.2	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 0.4	3.2
124	20.6	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 0.4	1.0
125	70.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 5.0	10.0
126	74.4	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 5.0	6.0
127	85.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 5.0	4.0
128	94.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 5.0	1.0
129	65.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 10.0	10.0
130	70.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 10.0	6.0

制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
131	80.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 10.0	4.0
132	89.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 10.0	1.0
133	55.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 20.0	10.0
134	60.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 20.0	6.0
135	70.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 20.0	4.0
136	79.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 20.0	1.0
137	50.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 30.0	10.0
138	55.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 30.0	6.0
139	60.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})=\text{N}-\text{C}(\text{S})=\text{N}\right]_n-\text{H}$ (V), 30.0	4.0

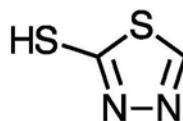
制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
140	69.0		1.0 (V), 30.0

12. 一种基底涂料,其包括根据前述权利要求中任一项所述的缓蚀制剂。

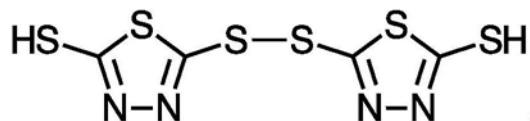
13. 根据权利要求12所述的基底涂料,其中所述至少一种布朗斯台德酸选自:H₃PO₄、H₂SO₄、HX,其中X是Cl、Br或F,和HNO₃,或其组合。

14. 根据权利要求12所述的基底涂料,其中所述至少一种布朗斯台德酸包括H₃PO₄。

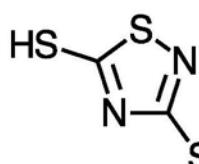
15. 根据权利要求12所述的基底涂料,其中所述噻二唑化合物选自结构(I)-(V):



(I)、



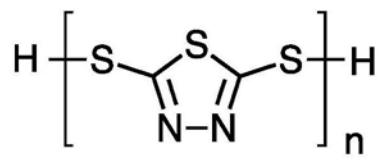
(II)、



或其组合。

(III)、

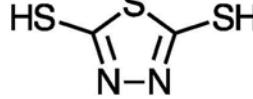
(IV) 和



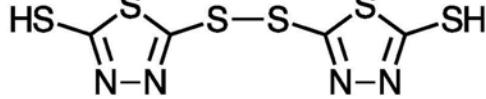
(V), 或其

组合,其中结构(V)的n等于或大于2。

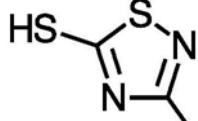
16. 根据权利要求12所述的基底涂料,其中所述噻二唑化合物选自:



(I) 、



(II) 和



或其组合。

(III),

17. 根据权利要求12所述的基底涂料,其中所述至少一种含硫缓蚀剂包括含有金属的噻二唑化合物。

18. 根据权利要求17所述的基底涂料,其中所述含有金属的噻二唑化合物选自:

2,5-二巯基-1,3,4-噻二唑二钾盐、聚[Zn:2,5-二巯基-1,3,4-噻二唑(1:1)]、[Al:2,5-二巯基-1,3,4-噻二唑(1:3)]、[Al:2,5-二巯基-1,3,4-噻二唑(3:1)]、聚[Zn:(双-(2,5-二硫-1,3,4-噻二唑)(1:1))]、聚[Fe:2,5-二巯基-1,3,4-噻二唑)(1:1)]、聚[Al:2,5-二巯基-1,3,4-噻二唑(1:1)]、和聚[Cu:2,5-二巯基-1,3,4-噻二唑(1:1)]、或其组合。

19. 根据权利要求17所述的基底涂料,其中所述含有金属的噻二唑化合物是聚[Zn:2,5-二巯基-1,3,4-噻二唑(1:1)]。

20. 根据权利要求12-19中任一项所述的基底涂料,其中:

所述聚乙烯醇缩丁醛树脂以范围为从50%wt/wt至99%wt/wt的量存在；

所述至少一种布朗斯台德酸以范围为从1%wt/wt至10%wt/wt的量存在；并且

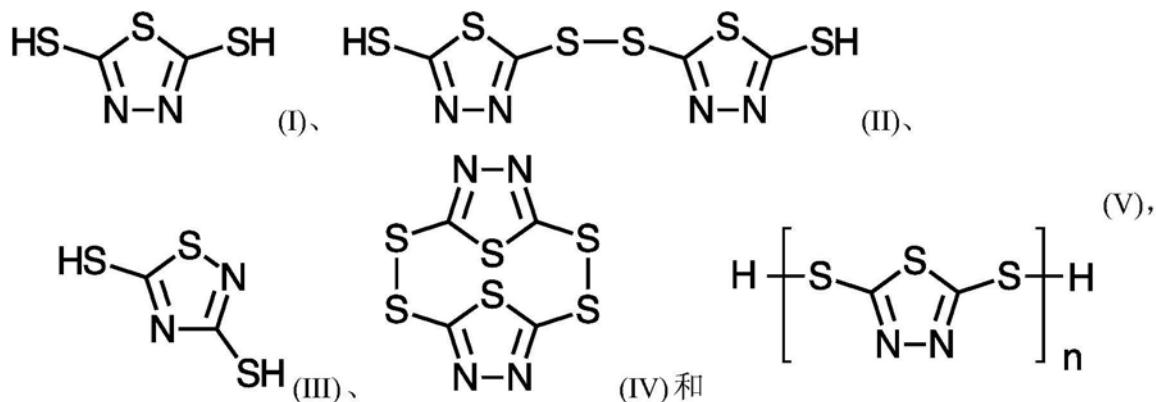
所述至少一种含硫缓蚀剂以范围为从0.01%wt/wt至30%wt/wt的量存在，

其中所述基底涂料中组分的百分含量的总和为100%。

21. 根据权利要求20所述的基底涂料，其中：

所述至少一种布朗斯台德酸包括 H_3PO_4 。

22. 根据权利要求21所述的基底涂料，其中所述至少一种含硫缓蚀剂选自：

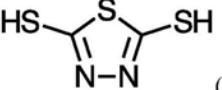
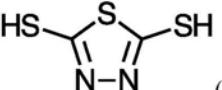
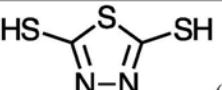
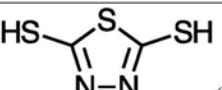
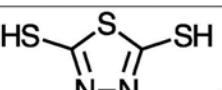
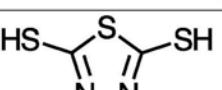
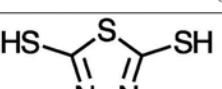
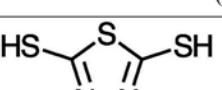
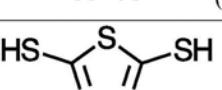
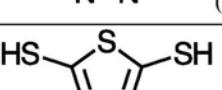
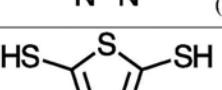
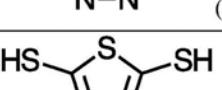


或其组合，其中结构(V)的n等于或大于2。

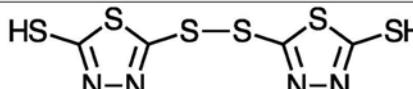
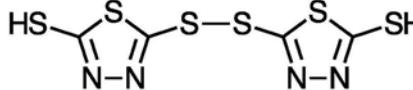
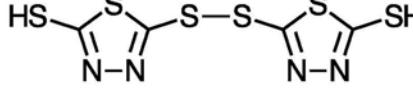
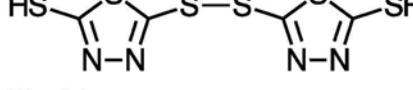
23. 根据权利要求22所述的基底涂料，其中所述缓蚀制剂是制剂(1)-(140)中的至少一种：

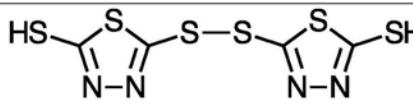
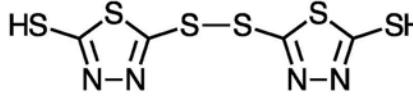
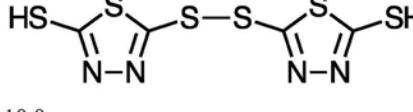
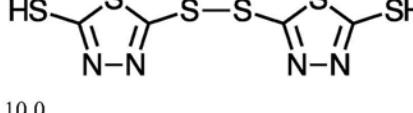
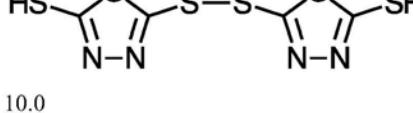
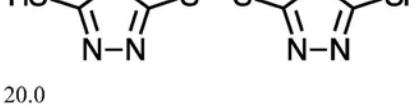
制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H_3PO_4 %wt/wt
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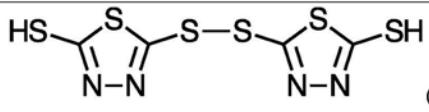
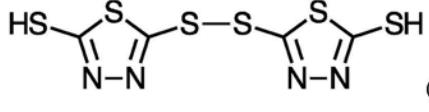
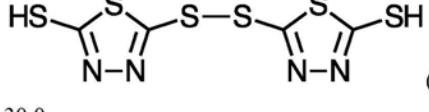
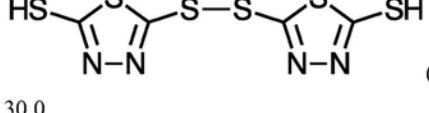
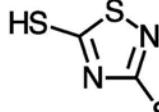
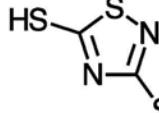
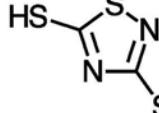
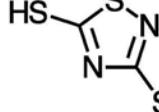
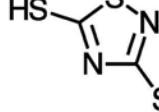
制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
1	74.99	 (I), 0.01	10.0
2	79.99	 (I), 0.01	6.0
3	89.99	 (I), 0.01	4.0
4	98.99	 (I), 0.01	1.0
5	74.9	 (I), 0.1	10.0
6	79.9	 (I), 0.1	6.0
7	89.9	 (I), 0.1	4.0
8	98.9	 (I), 0.1	1.0
9	74.6	 (I), 0.4	10.0
10	50.0	 (I), 0.4	6.0
11	8.2	 (I), 0.4	3.2
12	20.6	 (I), 0.4	1.0

制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
13	70.0	 (I), 5.0	10.0
14	74.4	 (I), 5.0	6.0
15	85.0	 (I), 5.0	4.0
16	94.0	 (I), 5.0	1.0
17	65.0	 (I), 10.0	10.0
18	75.0	 (I), 10.0	6.0
19	80.0	 (I), 10.0	4.0
20	89.0	 (I), 10.0	1.0
21	55.0	 (I), 20.0	10.0
22	65.0	 (I), 20.0	6.0
23	70.0	 (I), 20.0	4.0
24	79.0	 (I), 20.0	1.0

制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
25	50.0	 (I), 30.0	10.0
26	55.0	 (I), 30.0	6.0
27	60.0	 (I), 30.0	4.0
28	69.0	 (I), 30.0	1.0
29	74.99	 0.01 (II),	10.0
30	84.99	 0.01 (II),	6.0
31	89.99	 0.01 (II),	4.0
32	98.99	 0.01 (II),	1.0
33	74.9	 0.1 (II),	10.0
34	84.9	 0.1 (II),	6.0

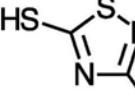
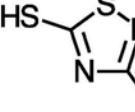
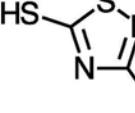
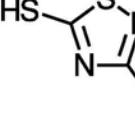
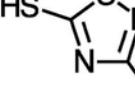
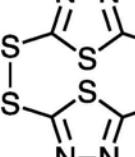
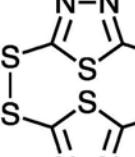
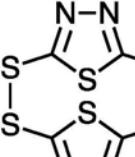
制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
35	89.9	 0.1 (II),	4.0
36	98.9	 0.1 (II),	1.0
37	74.6	 (II), 0.4	10.0
38	50.0	 (II), 0.4	6.0
39	8.2	 (II), 0.4	3.2
40	20.6	 (II), 0.4	1.0
41	70.0	 5.0 (II),	10.0
42	74.4	 5.0 (II),	6.0
43	85.0	 5.0 (II),	4.0

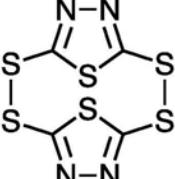
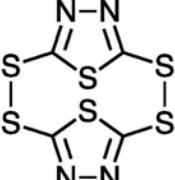
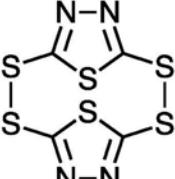
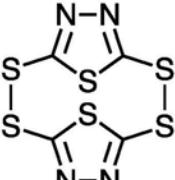
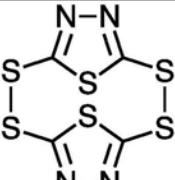
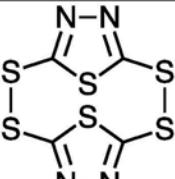
制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
44	94.0	 (II), 5.0	1.0
45	65.0	 (II), 10.0	10.0
46	70.0	 (II), 10.0	6.0
47	80.0	 (II), 10.0	4.0
48	89.0	 (II), 10.0	1.0
49	55.0	 (II), 20.0	10.0
50	60.0	 (II), 20.0	6.0
51	70.0	 (II), 20.0	4.0
52	79.0	 (II), 20.0	1.0

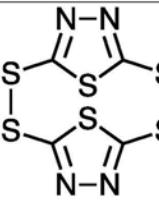
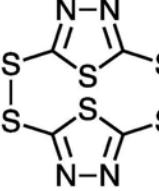
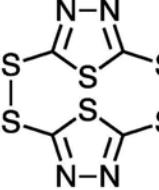
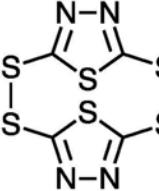
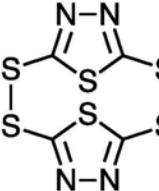
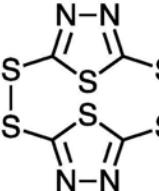
制剂	聚乙稀醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
53	50.0	 30.0	(II), 10.0
54	55.0	 30.0	(II), 6.0
55	60.0	 30.0	(II), 4.0
56	69.0	 30.0	(II), 1.0
57	74.99	 SH _(III) , 0.01	10.0
58	84.99	 SH _(III) , 0.01	6.0
59	89.99	 SH _(III) , 0.01	4.0
60	98.99	 SH _(III) , 0.01	1.0
61	74.9	 SH _(III) , 0.1	10.0

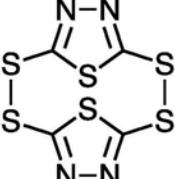
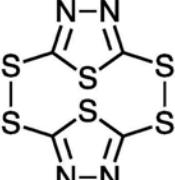
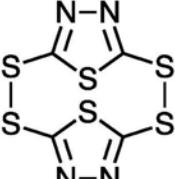
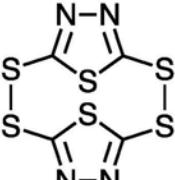
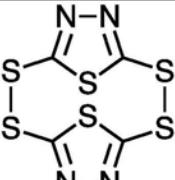
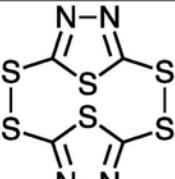
制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
62	84.9	 (III), 0.1	6.0
63	89.9	 (III), 0.1	4.0
64	98.9	 (III), 0.1	1.0
65	74.6	 (III), 0.4	10.0
66	50.0	 (III), 0.4	6.0
67	8.2	 (III), 0.4	3.2
68	20.6	 (III), 0.4	1.0
69	70.0	 (III), 5.0	10.0
70	74.4	 (III), 5.0	6.0

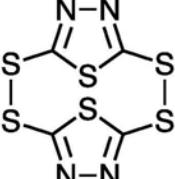
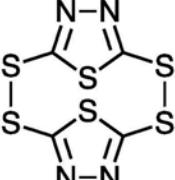
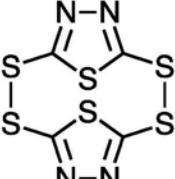
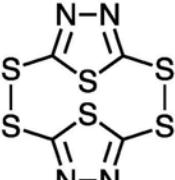
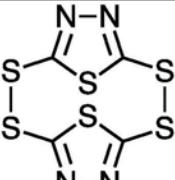
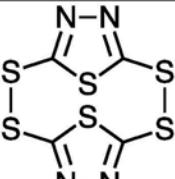
制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
71	85.0	SH _(III) , 5.0	4.0
72	94.0	SH _(III) , 5.0	1.0
73	65.0	SH _(III) , 10.0	10.0
74	70.0	SH _(III) , 10.0	6.0
75	80.0	SH _(III) , 10.0	4.0
76	89.0	SH _(III) , 10.0	1.0
77	55.0	SH _(III) , 20.0	10.0
78	60.0	SH _(III) , 20.0	6.0
79	70.0	SH _(III) , 20.0	4.0

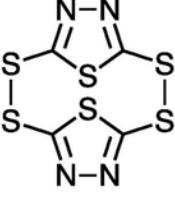
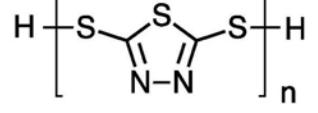
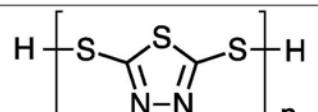
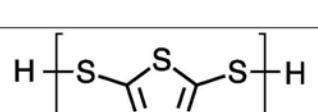
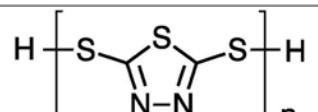
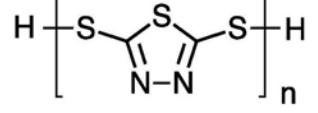
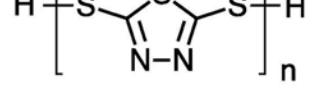
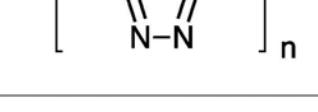
制剂	聚乙稀醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
80	79.0	 (III), 20.0	1.0
81	50.0	 (III), 30.0	10.0
82	55.0	 (III), 30.0	6.0
83	60.0	 (III), 30.0	4.0
84	69.0	 (III), 30.0	1.0
85	74.99	 (IV) 0.01	10.0
86	84.99	 (IV) 0.01	6.0
87	89.99	 (IV), 0.01	4.0

制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
88	98.99	 <p>(IV), 0.01</p>	1.0
89	74.9	 <p>(IV), 0.1</p>	10.0
90	84.9	 <p>(IV), 0.1</p>	6.0
91	89.9	 <p>(IV), 0.1</p>	4.0
92	98.9	 <p>(IV), 0.1</p>	1.0
93	74.6	 <p>(IV), 0.4</p>	10.0

制剂	聚乙稀醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
94	50.0	 (IV), 0.4	6.0
95	8.2	 (IV), 0.4	3.2
96	20.6	 (IV), 0.4	1.0
97	70.0	 (IV), 5.0	10.0
98	74.4	 (IV), 5.0	6.0
99	85.0	 (IV), 5.0	4.0

制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
100	94.0	 (IV), 5.0	1.0
101	65.0	 (IV), 10.0	10.0
102	70.0	 (IV), 10.0	6.0
103	80.0	 (IV), 10.0	4.0
104	89.0	 (IV), 10.0	1.0
105	55.0	 (IV), 20.0	10.0

制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
106	60.0	 (IV), 20.0	6.0
107	70.0	 (IV), 20.0	4.0
108	79.0	 (IV), 20.0	1.0
109	50.0	 (IV), 30.0	10.0
110	55.0	 (IV), 30.0	6.0
111	60.0	 (IV), 30.0	4.0

制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
112	69.0	 <p>(IV), 30.0</p>	1.0
113	74.99	 <p>(V), 0.01</p>	10.0
114	84.99	 <p>(V), 0.01</p>	6.0
115	89.99	 <p>(V), 0.01</p>	4.0
116	98.99	 <p>(V), 0.01</p>	1.0
117	74.9	 <p>(V), 0.1</p>	10.0
118	84.9	 <p>(V), 0.1</p>	6.0
119	89.9	 <p>(V), 0.1</p>	4.0

制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
120	98.9	$\text{H}-\left[\text{S}-\text{C}(\text{S})-\text{N}=\text{N}-\text{C}(\text{S})-\text{S}\right]_n\text{H}$ (V), 0.1	1.0
121	74.6	$\text{H}-\left[\text{S}-\text{C}(\text{S})-\text{N}=\text{N}-\text{C}(\text{S})-\text{S}\right]_n\text{H}$ (V), 0.4	10.0
122	50.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})-\text{N}=\text{N}-\text{C}(\text{S})-\text{S}\right]_n\text{H}$ (V), 0.4	6.0
123	8.2	$\text{H}-\left[\text{S}-\text{C}(\text{S})-\text{N}=\text{N}-\text{C}(\text{S})-\text{S}\right]_n\text{H}$ (V), 0.4	3.2
124	20.6	$\text{H}-\left[\text{S}-\text{C}(\text{S})-\text{N}=\text{N}-\text{C}(\text{S})-\text{S}\right]_n\text{H}$ (V), 0.4	1.0
125	70.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})-\text{N}=\text{N}-\text{C}(\text{S})-\text{S}\right]_n\text{H}$ (V), 5.0	10.0
126	74.4	$\text{H}-\left[\text{S}-\text{C}(\text{S})-\text{N}=\text{N}-\text{C}(\text{S})-\text{S}\right]_n\text{H}$ (V), 5.0	6.0
127	85.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})-\text{N}=\text{N}-\text{C}(\text{S})-\text{S}\right]_n\text{H}$ (V), 5.0	4.0
128	94.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})-\text{N}=\text{N}-\text{C}(\text{S})-\text{S}\right]_n\text{H}$ (V), 5.0	1.0

制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
129	65.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})-\text{N}=\text{N}-\text{C}(\text{S})-\text{S}\right]_n\text{H}$ (V), 10.0	10.0
130	70.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})-\text{N}=\text{N}-\text{C}(\text{S})-\text{S}\right]_n\text{H}$ (V), 10.0	6.0
131	80.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})-\text{N}=\text{N}-\text{C}(\text{S})-\text{S}\right]_n\text{H}$ (V), 10.0	4.0
132	89.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})-\text{N}=\text{N}-\text{C}(\text{S})-\text{S}\right]_n\text{H}$ (V), 10.0	1.0
133	55.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})-\text{N}=\text{N}-\text{C}(\text{S})-\text{S}\right]_n\text{H}$ (V), 20.0	10.0
134	60.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})-\text{N}=\text{N}-\text{C}(\text{S})-\text{S}\right]_n\text{H}$ (V), 20.0	6.0
135	70.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})-\text{N}=\text{N}-\text{C}(\text{S})-\text{S}\right]_n\text{H}$ (V), 20.0	4.0
136	79.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})-\text{N}=\text{N}-\text{C}(\text{S})-\text{S}\right]_n\text{H}$ (V), 20.0	1.0
137	50.0	$\text{H}-\left[\text{S}-\text{C}(\text{S})-\text{N}=\text{N}-\text{C}(\text{S})-\text{S}\right]_n\text{H}$ (V), 30.0	10.0

制剂	聚乙烯醇缩丁 醛%wt/wt	含硫缓蚀剂 %wt/wt	H ₃ PO ₄ %wt/wt
138	55.0	$\text{H}-\left[\begin{array}{c} \text{S} \\ \\ \text{N}-\text{N} \\ \\ \text{S} \end{array}\right]_n \text{H}$ <p style="text-align: center;">(V), 30.0</p>	6.0
139	60.0	$\text{H}-\left[\begin{array}{c} \text{S} \\ \\ \text{N}-\text{N} \\ \\ \text{S} \end{array}\right]_n \text{H}$ <p style="text-align: center;">(V), 30.0</p>	4.0
140	69.0	$\text{H}-\left[\begin{array}{c} \text{S} \\ \\ \text{N}-\text{N} \\ \\ \text{S} \end{array}\right]_n \text{H}$ <p style="text-align: center;">(V), 30.0</p>	1.0

24. 一种在基底上施加缓蚀剂的方法, 其包括:

涂布所述基底, 其中涂料包括根据权利要求1所述的缓蚀制剂; 和
固化所述涂料。

25. 根据权利要求24所述的方法, 其中涂布所述基底包括以下至少一种: 浸渍、刷涂、流
涂、丝网印刷、狭缝式模头挤出涂布、凹版涂布、粉末涂布、喷涂和旋转涂布所述涂料至所述
基底上。

26. 根据权利要求24或25所述的方法, 其中所述固化所述涂料包括使所述涂料经历范
围为从65°F 至160°F 的温度。

包含硫醇缓蚀剂的聚乙烯醇缩丁醛涂料

技术领域

[0001] 描述了缓蚀制剂和基底涂料。具体而言，本公开内容提供了涉及包含硫醇缓蚀剂的聚合物树脂的制剂和基底涂料。

背景技术

[0002] 六价铬(Cr[VI])化合物是有效的缓蚀剂。在过去的70年间，Cr[VI]化合物已经被用于底漆、涂料和密封剂中以防止金属基底和合金的腐蚀。在航空航天工业中，Cr[VI]化合物是用于涂布航空航天铝合金的最普遍和最有效的缓蚀剂系统。

[0003] Cr[VI]化合物还是已知的致癌物质。与Cr[VI]基缓蚀剂系统一起工作的那些人经历显著的健康风险。Cr[VI]材料和废料的储存、维护和处置的政府监督和法规遵从对工业强加另外的负担。

[0004] 对于具有缓蚀特性的Cr[VI]替换材料存在需要。

发明内容

[0005] 在第一方面中，描述了一种缓蚀制剂。缓蚀制剂包括(a)至少一种树脂，(b)至少一种布朗斯台德酸和(c)至少一种含硫缓蚀剂。

[0006] 在第二方面中，描述了包括缓蚀制剂的基底涂料。缓蚀制剂包括(a)至少一种树脂，(b)至少一种布朗斯台德酸和(c)至少一种含硫缓蚀剂。

[0007] 在第三方面中，描述了一种抑制基底上的腐蚀的方法。该方法包括两个步骤。第一步骤是在基底上布置涂料。该涂料包括缓蚀制剂。缓蚀制剂包括(a)至少一种树脂，(b)至少一种布朗斯台德酸和(c)至少一种含硫缓蚀剂。第二步骤包括固化该涂料。

附图说明

[0008] 图1描绘了在旋转圆盘工作电极的表面上电解质的层流。

[0009] 图2描绘了具有PVB涂料的基板的开路电势的示例性数据，PVB涂料具有0% (wt/wt)、0.5% (wt/wt)或5% (wt/wt) DMcT。

[0010] 图3A描绘了DMcT和不含酸催化剂的PVB树脂中的化合物(II) (Vanlube 829)含硫缓蚀剂的计时电流法的示例性数据。

[0011] 图3B描绘了DMcT和含有酸催化剂的PVB树脂中的化合物(II) (Vanlube 829)含硫缓蚀剂的计时电流法的示例性数据。

[0012] 图3C描绘了DMcT和不含酸催化剂的PVB树脂中的化合物(II) (Vanlube 829)含硫缓蚀剂的计时电流法的示例性数据，其中基板在分析之前被刻有1"X。

[0013] 图3D描绘了具有酸催化剂的PVB树脂中的0.5% (wt/wt) Cu(DMcT)₂含硫缓蚀剂的计时电流法的示例性数据。

[0014] 图3E描绘了PVB树脂中的0.5% (wt/wt) PANI含硫缓蚀剂的计时电流法的示例性数据。

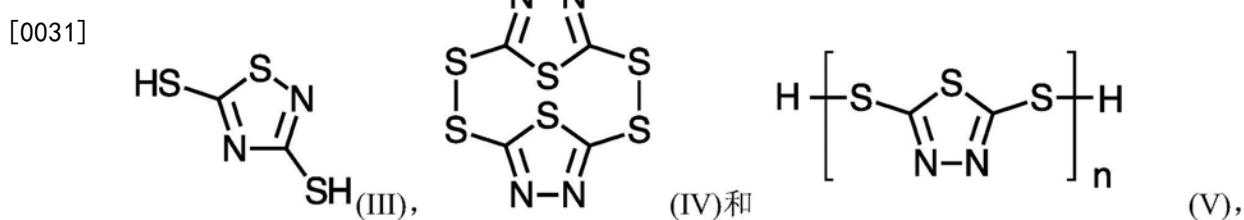
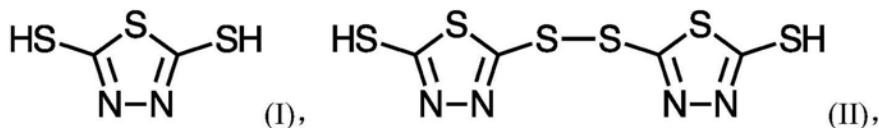
具体实施方式

- [0015] 首先定义了某些术语。另外的术语遍及说明书被定义。
- [0016] 本文使用的术语旨在作为“开放”术语。如本文所使用，开放术语，比如“包含 (comprise)”、“包括 (include)”和“具有”遍及说明书可互换地使用。
- [0017] 如本文所使用，“包含 (comprise)”、“具有”和“包括 (include)”的动词形式具有相同的含义。同样地，如本文所使用，“描述”、“公开”和“提供”的动词形式具有相同的含义。
- [0018] 如本文所使用，冠词“一 (a)”、“一 (an)”和“该 (the)”指一个或多于一个(例如，至少一个)冠词的语法对象。因此，单数形式“一 (a)”、“一 (an)”和“该 (the)”包括复数指示物，除非上下文以其他方式清楚地指示。
- [0019] “大约 (about)”和“近似(approximately)”通常表示给出测量值的本质或精度的测量的数量的可接受程度的误差。误差的示例性程度为给定值或值的范围的百分之25 (%), 典型地在10%以内, 和更典型地在5%以内。
- [0020] 如本文所使用，本文使用“或”意指术语“和/或”，并且与术语“和/或”可以互换地使用，除非上下文以其他方式清楚地指示。在本文的一些地方术语“和/或”的使用意思不是术语“或”的使用与“和/或”不是可互换的，除非上下文以其他方式清楚地指示。
- [0021] 所有语言比如“从 (from)”、“至 (to)”、“高至 (up to)”、“至少”、“大于”、“小于”等，包括列举的数值，并且指随后可以细分为作为上下文依据的子范围的范围。
- [0022] 范围包括每个单个的构件。因此，例如，具有1-3个构件的组指具有1、2或3个构件的组。类似地，具有6个构件的组指具有1、2、3、4、5或6个构件的组，以此类推。
- [0023] 短语“净制剂”指由指定组分的限定组合物组成的制剂，其中限定组合物的指定组分的总量总计100重量百分数。本领域普通技术人员将认识到，不是所有的制剂是“净制剂”，因为制剂可包括指定组分的限定组合物，其中限定组合物的指定组分的总量总计小于100重量百分数并且制剂的剩余物包括其他组分，其中限定组合物的指定组分和剩余物的总量总计100重量百分数。本文公开的制剂总计为指定组分和其他组分的总量的100重量百分数。
- [0024] 本文描述的化学结构根据IUPAC命名规则命名并且在适当的地方包括本领域公认的常用名称和缩写。IUPAC命名可以用化学结构绘图软件程序导出，比如ChemDraw[®] (PerkinElmer, Inc.)、ChemDoodle[®] (iChemLabs, LLC) 和Marvin (ChemAxon Ltd.)。除了表5中描绘的金属噻二唑的预测的化学结构以外，在本公开内容中化学结构控制至IUPAC名称被误称或以其他方式与本文公开的化学结构冲突的程度。
- [0025] 呈现标题，例如(a)、(b)、(i)等仅用于容易理解说明书和权利要求书。说明书或权利要求书中标题的使用不需要步骤或元素以字母或数字顺序或它们所呈现的顺序进行。
- [0026] 本公开内容涉及开发和实施该技术以通过识别和限定 (qualifying) 用于底漆、转化涂料 (conversion coating) 和密封剂的非六价铬替代物来消除六价铬 (Cr⁶⁺)。描述了抑制氧还原反应的包括单体、二聚体、聚合物和金属盐的新的电活性阴极硫系统的合成。这些缓蚀剂系统配制成简单的树脂系统，比如可作为涂料施加至铝板的聚(乙烯醇缩丁醛) (PVB)。
- [0027] 缓蚀制剂
- [0028] 在第一方面中，提供了缓蚀制剂。缓蚀制剂包括 (a) 至少一种树脂，(b) 至少一种布

朗斯台德酸和(c)至少一种含硫缓蚀剂。在一些方面中,至少一种树脂包括热塑性树脂,例如,聚乙烯聚合物、聚氨基甲酸酯聚合物、丙烯酸酯聚合物、苯乙烯聚合物或其组合。在这些方面中,热塑性树脂选自聚乙烯聚合物、聚氨基甲酸酯聚合物、丙烯酸酯聚合物和苯乙烯聚合物、或其组合。在一些方面中,热塑性树脂包括聚乙烯聚合物。在一些方面中,聚乙烯聚合物选自聚乙烯醇缩乙醛聚合物、聚乙烯醇缩丁醛聚合物和聚乙烯醇缩甲醛聚合物、或其组合。在一些方面中,聚乙烯聚合物包括聚乙烯醇缩丁醛聚合物。

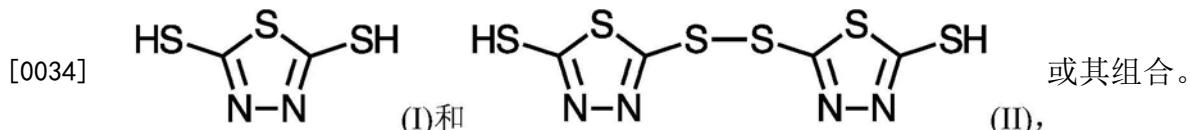
[0029] 在一些方面中,至少一种布朗斯台德酸选自 H_3PO_4 ; H_2SO_4 ; HX,其中X是Cl、Br或F; 和 HN_3 ; 或其组合。在一些方面中,至少一种布朗斯台德酸包括 H_3PO_4 。

[0030] 在一些方面中,至少一种含硫缓蚀剂包括噻二唑化合物。在这些方面的一些中,噻二唑化合物选自结构(I)-(V):

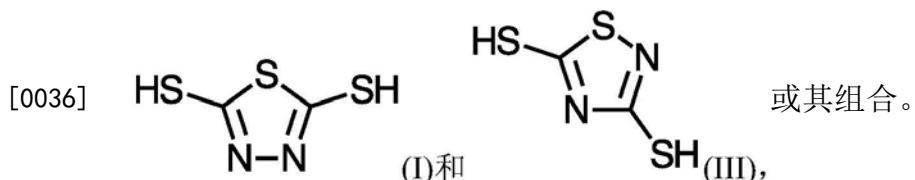


[0032] 或其组合,其中结构(V)的n等于或大于2。

[0033] 在这些方面的一些中,噻二唑化合物选自:



[0035] 在这些方面的一些中,噻二唑化合物选自:



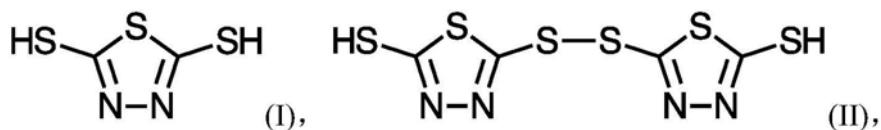
[0037] 在一些方面中,至少一种含硫缓蚀剂包括含有金属的噻二唑化合物。在这些方面的一些中,含有金属的噻二唑化合物选自:2,5-二巯基-1,3,4-噻二唑,二钾盐;聚[Zn:2,5-二巯基-1,3,4-噻二唑(1:1)];[Al:2,5-二巯基-1,3,4-噻二唑(1:3)];[Al:2,5-二巯基-1,3,4-噻二唑(3:1)];聚[Zn:(双-(2,5-二硫-1,3,4-噻二唑)(1:1))];聚[Fe:2,5-二巯基-1,3,4-噻二唑(1:1)];聚[Al:2,5-二巯基-1,3,4-噻二唑(1:1)];和聚[Cu:2,5-二巯基-1,3,4-噻二唑(1:1)];或其组合。在这些方面的一些中,含有金属的噻二唑化合物是聚[Zn:2,5-二巯基-1,3,4-噻二唑(1:1)]。

[0038] 在一些方面中,缓蚀制剂包括具体比例(例如,% (wt/wt))的至少一种树脂、至少一种布朗斯台德酸和至少一种含硫缓蚀剂。在一方面,至少一种树脂以范围从约8% (wt/wt)至约99% (wt/wt)的量存在,包括从约10% (wt/wt)至约99% (wt/wt)、从约15% (wt/wt)

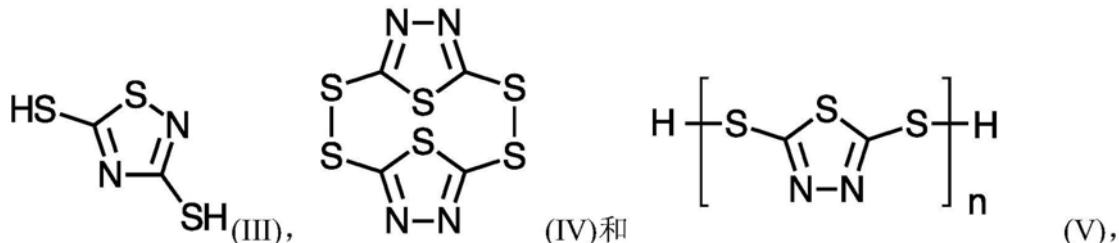
至约99% (wt/wt)、从约25% (wt/wt) 至约99% (wt/wt)、和从约50% (wt/wt) 至约99% (wt/wt) 的子范围。至少一种布朗斯台德酸以范围从约1% (wt/wt) 至约10% (wt/wt) 的量存在，包括从约2% (wt/wt) 至约10% (wt/wt)、从约3% (wt/wt) 至约10% (wt/wt)、从约5% (wt/wt) 至约10% (wt/wt)、从约6% (wt/wt) 至约10% (wt/wt)、和从约8% (wt/wt) 至约10% (wt/wt) 的子范围。至少一种含硫缓蚀剂以范围从约0.01% (wt/wt) 至约30% (wt/wt) 的量存在，包括从约0.01% (wt/wt) 至约30% (wt/wt)、从约0.05% (wt/wt) 至约30% (wt/wt)、从约0.10% (wt/wt) 至约30% (wt/wt)、从约0.20% (wt/wt) 至约30% (wt/wt)、从约0.40% (wt/wt) 至约30% (wt/wt)、从约1% (wt/wt) 至约30% (wt/wt)、从约2% (wt/wt) 至约30% (wt/wt)、从约5% (wt/wt) 至约30% (wt/wt)、从约10% (wt/wt) 至约30% (wt/wt)、从约15% (wt/wt) 至约30% (wt/wt)、从约20% (wt/wt) 至约30% (wt/wt)、和从约25% (wt/wt) 至约30% (wt/wt) 的子范围。在这些范围和子范围内考虑组分的具体量。例如，至少一种树脂可以以约8.2% (wt/wt)、约10% (wt/wt)、约15% (wt/wt)、约20% (wt/wt)、约25% (wt/wt)、约30% (wt/wt)、约40% (wt/wt)、约50% (wt/wt)、约60% (wt/wt)、约70% (wt/wt)、约80% (wt/wt)、90% (wt/wt)、约95% (wt/wt) 和约99% (wt/wt) 的量存在。至少一种布朗斯台德酸可以以约1% (wt/wt)、约2% (wt/wt)、约3.2% (wt/wt)、约4% (wt/wt)、约5% (wt/wt)、约6% (wt/wt)、约8% (wt/wt) 和约10% (wt/wt) 的量存在。至少一种含硫缓蚀剂以约0.01% (wt/wt)、约0.02% (wt/wt)、约0.05% (wt/wt)、约0.1% (wt/wt)、约0.2% (wt/wt)、约0.4% (wt/wt)、约1% (wt/wt)、约2% (wt/wt)、约5% (wt/wt)、约10% (wt/wt)、约15% (wt/wt)、约20% (wt/wt)、约25% (wt/wt) 和约30% (wt/wt) 的量存在。

[0039] 这些和其他组分可以包括在缓蚀制剂中，条件是所有组分的累积量不超过100% (wt/wt)。其他组分的实例包括用于悬浮或溶解上述的至少一种树脂、至少一种布朗斯台德酸和至少一种含硫缓蚀剂的溶剂和流体。示例性溶剂和流体包括水、乙醇、丙酮、2-丁氧基乙醇、醋酸正丁酯、正丁醇、正丁基丙酸酯、环己酮、二丙酮醇、二甲基酯、N,N-二甲基乙酰胺、N,N-二甲基甲酰胺、二甲基亚砜、乙酸乙酯、二氯乙烯、异佛尔酮、异丙基乙酸酯、异丙醇、乙酸甲酯、甲基戊基酮、甲乙酮、甲基异戊基酮、甲基异丁基酮、甲基丙基酮、甲基丙基酮、二氯甲烷、N-甲基2-吡咯烷酮、丙酸丙酯、二氯丙烯、四氢呋喃、1,1,1-三氯乙烷，等等，包括其组合。

[0040] 在这些范围内，考虑组分的具体类型。在这点上，例如，至少一种树脂包括聚乙烯醇缩丁醛；并且至少一种布朗斯台德酸包括H₃PO₄。在具体制剂考虑这些具体树脂和布朗斯台德酸组分的地方，具体制剂包括选自下列的至少一种含硫缓蚀剂：



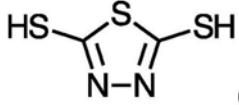
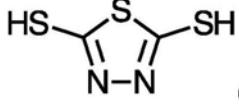
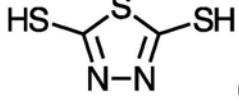
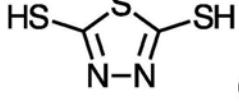
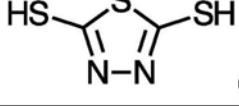
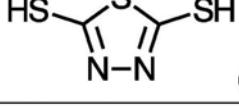
[0041]



[0042] 或其组合,其中结构(V)的n等于或大于2。

[0043] 在一些方面中,缓蚀制剂包括至少一种树脂——其为聚乙烯醇缩丁醛,至少一种布朗斯台德酸——其为H₃PO₄,和选自化合物(I)-(V)中的一种的至少一种的含硫缓蚀剂。符合这些组分标准的示例性缓蚀制剂包括表1中显示的制剂(1)-(140)中的至少一种。

[0044] 表1.示例性缓蚀制剂

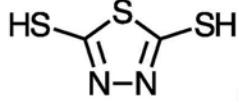
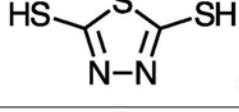
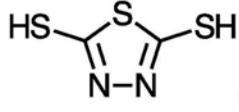
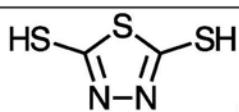
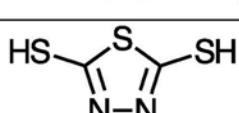
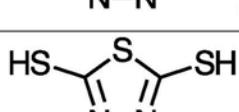
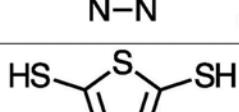
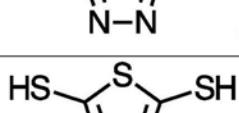
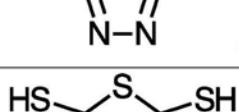
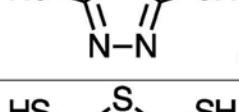
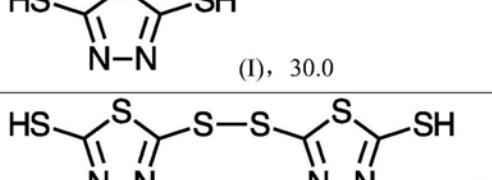
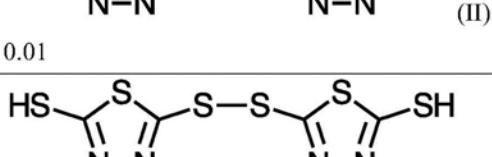
制剂	聚乙烯醇缩丁醛 (%wt/wt)	含硫缓蚀剂 (%wt/wt)	H ₃ PO ₄ (%wt/wt)
1	74.99	 (I), 0.01	10.0
2	79.99	 (I), 0.01	6.0
3	89.99	 (I), 0.01	4.0
4	98.99	 (I), 0.01	1.0
5	74.9	 (I), 0.1	10.0
6	79.9	 (I), 0.1	6.0

[0045]

[0046]

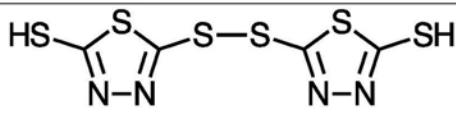
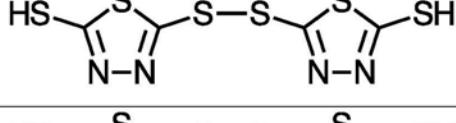
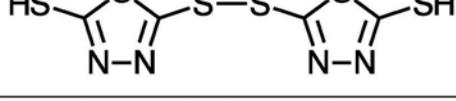
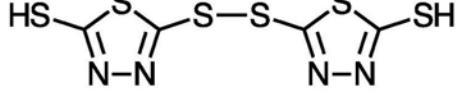
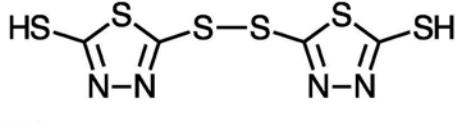
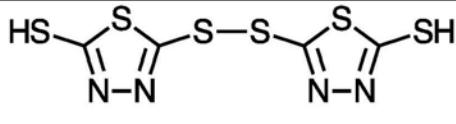
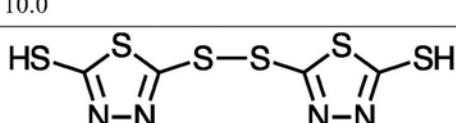
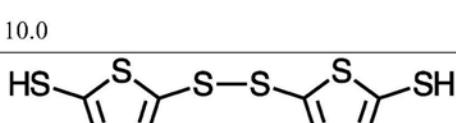
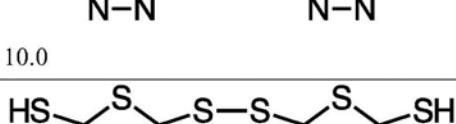
制剂	聚乙烯醇缩丁醛 (%wt/wt)	含硫缓蚀剂 (%wt/wt)	H ₃ PO ₄ (%wt/wt)
7	89.9	 (I), 0.1	4.0
8	98.9	 (I), 0.1	1.0
9	74.6	 (I), 0.4	10.0
10	50.0	 (I), 0.4	6.0
11	8.2	 (I), 0.4	3.2
12	20.6	 (I), 0.4	1.0
13	70.0	 (I), 5.0	10.0
14	74.4	 (I), 5.0	6.0
15	85.0	 (I), 5.0	4.0
16	94.0	 (I), 5.0	1.0
17	65.0	 (I), 10.0	10.0
18	75.0	 (I), 10.0	6.0

[0047]

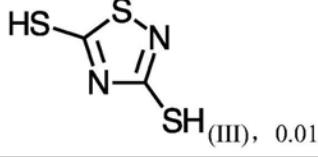
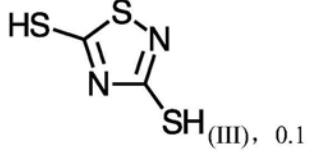
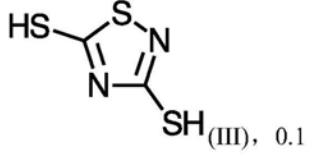
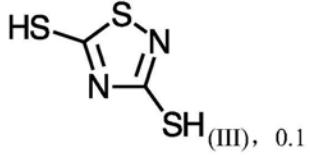
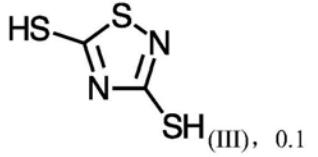
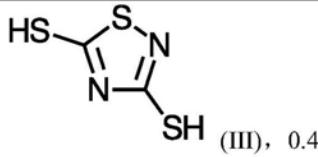
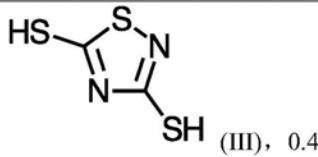
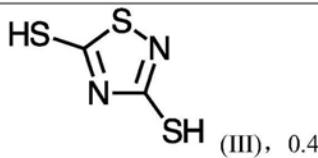
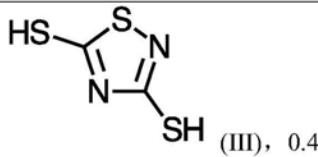
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19	80.0	 (I), 10.0	4.0
20	89.0	 (I), 10.0	1.0
21	55.0	 (I), 20.0	10.0
22	65.0	 (I), 20.0	6.0
23	70.0	 (I), 20.0	4.0
24	79.0	 (I), 20.0	1.0
25	50.0	 (I), 30.0	10.0
26	55.0	 (I), 30.0	6.0
27	60.0	 (I), 30.0	4.0
28	69.0	 (I), 30.0	1.0
29	74.99	 0.01 (II),	10.0
30	84.99	 (II),	6.0

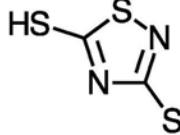
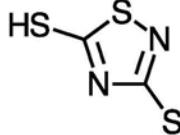
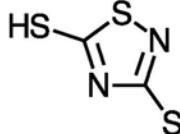
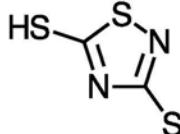
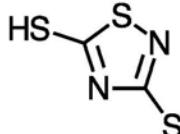
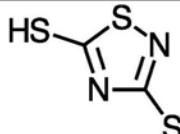
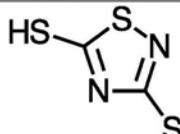
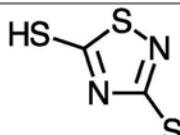
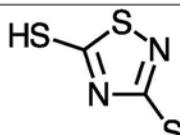
[0048]

制剂	聚乙烯醇缩丁醛 (%wt/wt)	含硫缓蚀剂 (%wt/wt)	H_3PO_4 (%wt/wt)
		0.01	
31	89.99	(II), 0.01	4.0
32	98.99	(II), 0.01	1.0
33	74.9	(II), 0.1	10.0
34	84.9	(II), 0.1	6.0
35	89.9	(II), 0.1	4.0
36	98.9	(II), 0.1	1.0
37	74.6	(II), 0.4	10.0
38	50.0	(II), 0.4	6.0
39	8.2	(II), 0.4	3.2
40	20.6	(II), 0.4	1.0

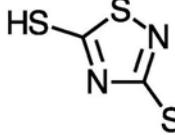
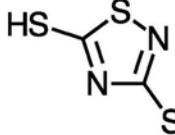
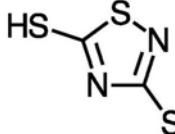
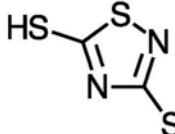
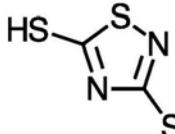
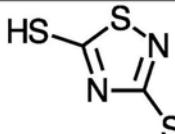
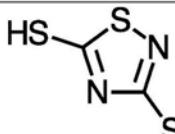
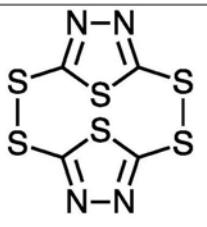
制剂	聚乙烯醇缩丁醛 (%wt/wt)	含硫缓蚀剂 (%wt/wt)	H ₃ PO ₄ (%wt/wt)
41	70.0	 (II), 5.0	10.0
42	74.4	 (II), 5.0	6.0
43	85.0	 (II), 5.0	4.0
44	94.0	 (II), 5.0	1.0
[0049]	45	 10.0 (II),	10.0
	46	 10.0 (II),	6.0
	47	 10.0 (II),	4.0
	48	 10.0 (II),	1.0
	49	 20.0 (II),	10.0
	50	 20.0 (II),	6.0

制剂	聚乙烯醇缩丁醛 (%wt/wt)	含硫缓蚀剂 (%wt/wt)	H ₃ PO ₄ (%wt/wt)
51	70.0	 20.0	4.0
52	79.0	 20.0	1.0
53	50.0	 30.0	10.0
54	55.0	 30.0	6.0
[0050]	55	 30.0	4.0
	56	 30.0	1.0
	57	 (III), 0.01	10.0
	58	 (III), 0.01	6.0
	59	 (III), 0.01	4.0

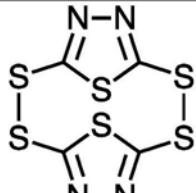
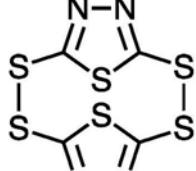
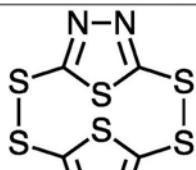
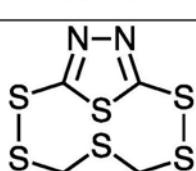
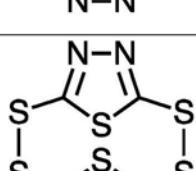
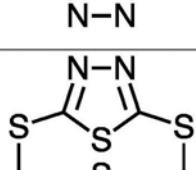
制剂	聚乙烯醇缩丁醛 (%wt/wt)	含硫缓蚀剂 (%wt/wt)	H ₃ PO ₄ (%wt/wt)
60	98.99		1.0
61	74.9		10.0
62	84.9		6.0
63	89.9		4.0
[0051]	64		1.0
	65		10.0
	66		6.0
	67		3.2
	68		1.0

制剂	聚乙烯醇缩丁醛 (%wt/wt)	含硫缓蚀剂 (%wt/wt)	H ₃ PO ₄ (%wt/wt)
69	70.0	 HS-C(=S)-NH-C(=S)-SH _(III) , 5.0	10.0
70	74.4	 HS-C(=S)-NH-C(=S)-SH _(III) , 5.0	6.0
71	85.0	 HS-C(=S)-NH-C(=S)-SH _(III) , 5.0	4.0
72	94.0	 HS-C(=S)-NH-C(=S)-SH _(III) , 5.0	1.0
[0052]	73	 HS-C(=S)-NH-C(=S)-SH _(III) , 10.0	10.0
	74	 HS-C(=S)-NH-C(=S)-SH _(III) , 10.0	6.0
	75	 HS-C(=S)-NH-C(=S)-SH _(III) , 10.0	4.0
	76	 HS-C(=S)-NH-C(=S)-SH _(III) , 10.0	1.0
	77	 HS-C(=S)-NH-C(=S)-SH _(III) , 20.0	10.0

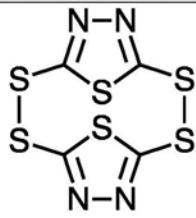
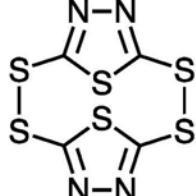
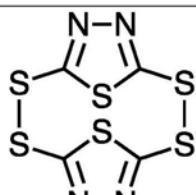
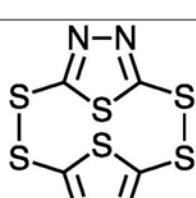
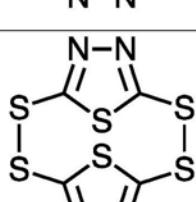
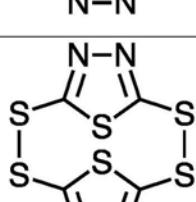
[0053]

制剂	聚乙烯醇缩丁醛 (%wt/wt)	含硫缓蚀剂 (%wt/wt)	H ₃ PO ₄ (%wt/wt)
78	60.0	 (III), 20.0	6.0
79	70.0	 (III), 20.0	4.0
80	79.0	 (III), 20.0	1.0
81	50.0	 (III), 30.0	10.0
82	55.0	 (III), 30.0	6.0
83	60.0	 (III), 30.0	4.0
84	69.0	 (III), 30.0	1.0
85	74.99	 (IV) 0.01	10.0

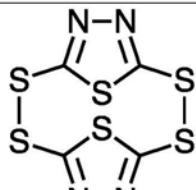
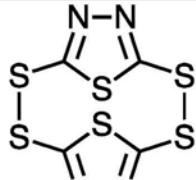
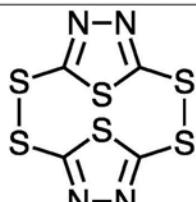
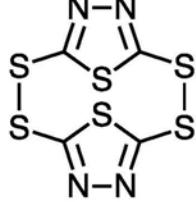
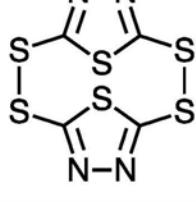
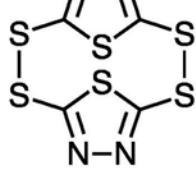
[0054]

制剂	聚乙烯醇缩丁醛 (%wt/wt)	含硫缓蚀剂 (%wt/wt)	H ₃ PO ₄ (%wt/wt)
86	84.99	 (IV) 0.01	6.0
87	89.99	 (IV), 0.01	4.0
88	98.99	 (IV), 0.01	1.0
89	74.9	 (IV), 0.1	10.0
90	84.9	 (IV), 0.1	6.0
91	89.9	 (IV), 0.1	4.0

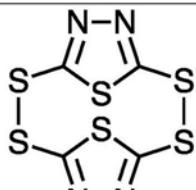
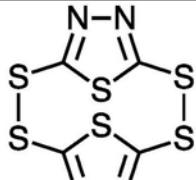
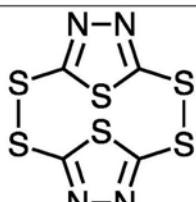
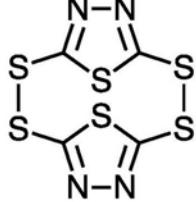
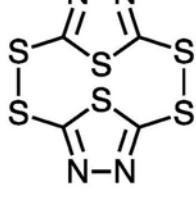
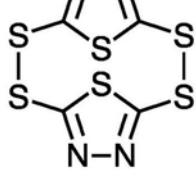
[0055]

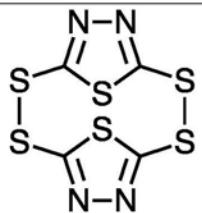
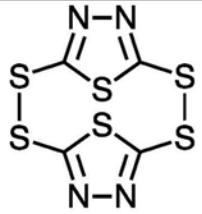
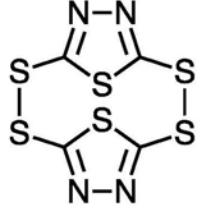
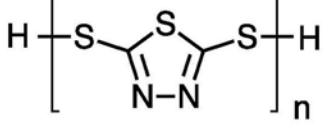
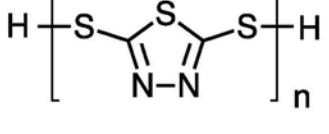
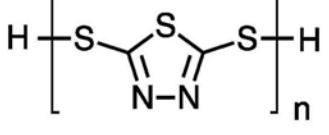
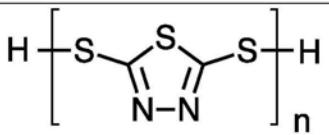
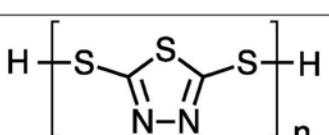
制剂	聚乙烯醇缩丁醛 (%wt/wt)	含硫缓蚀剂 (%wt/wt)	H ₃ PO ₄ (%wt/wt)
92	98.9	 (IV), 0.1	1.0
93	74.6	 (IV), 0.4	10.0
94	50.0	 (IV), 0.4	6.0
95	8.2	 (IV), 0.4	3.2
96	20.6	 (IV), 0.4	1.0
97	70.0	 (IV), 5.0	10.0

[0056]

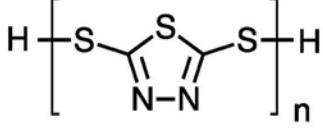
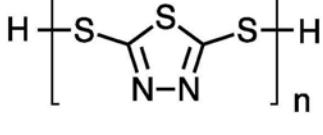
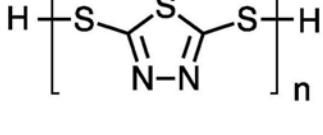
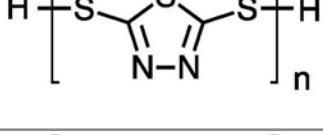
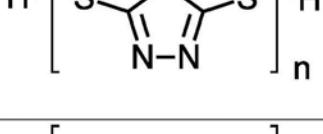
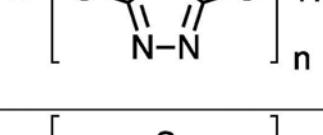
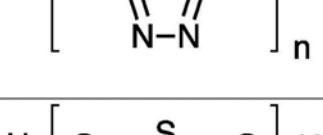
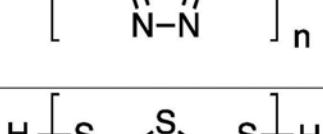
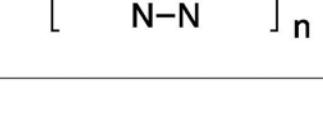
制剂	聚乙烯醇缩丁醛 (%wt/wt)	含硫缓蚀剂 (%wt/wt)	H_3PO_4 (%wt/wt)
98	74.4	 (IV), 5.0	6.0
99	85.0	 (IV), 5.0	4.0
100	94.0	 (IV), 5.0	1.0
101	65.0	 (IV), 10.0	10.0
102	70.0	 (IV), 10.0	6.0
103	80.0	 (IV), 10.0	4.0

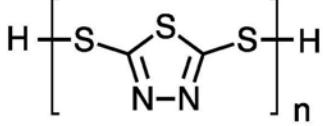
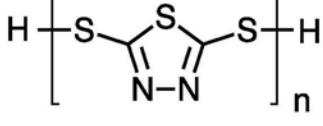
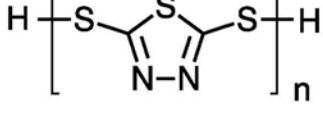
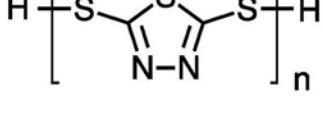
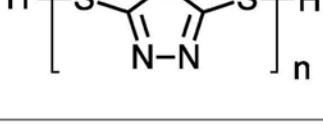
[0057]

制剂	聚乙烯醇缩丁醛 (%wt/wt)	含硫缓蚀剂 (%wt/wt)	H_3PO_4 (%wt/wt)
104	89.0	 (IV), 10.0	1.0
105	55.0	 (IV), 20.0	10.0
106	60.0	 (IV), 20.0	6.0
107	70.0	 (IV), 20.0	4.0
108	79.0	 (IV), 20.0	1.0
109	50.0	 (IV), 30.0	10.0

制剂	聚乙烯醇缩丁醛 (%wt/wt)	含硫缓蚀剂 (%wt/wt)	H_3PO_4 (%wt/wt)
[0058]	110	55.0  (IV), 30.0	6.0
	111	60.0  (IV), 30.0	4.0
	112	69.0  (IV), 30.0	1.0
	113	74.99  (V), 0.01	10.0
	114	84.99  (V), 0.01	6.0
	115	89.99  (V), 0.01	4.0
	116	98.99  (V), 0.01	1.0
	117	74.9  (V), 0.1	10.0

制剂	聚乙稀醇缩丁醛 (%wt/wt)	含硫缓蚀剂 (%wt/wt)	H ₃ PO ₄ (%wt/wt)	
[0059]	118	84.9	$\text{H}-\left[\begin{array}{c} \text{S} \\ \\ \text{S}-\text{C}=\text{N}-\text{C}=\text{N}-\text{S} \\ \\ \text{H} \end{array}\right]_n\text{H}$ <p style="text-align: center;">(V), 0.1</p>	6.0
	119	89.9	$\text{H}-\left[\begin{array}{c} \text{S} \\ \\ \text{S}-\text{C}=\text{N}-\text{C}=\text{N}-\text{S} \\ \\ \text{H} \end{array}\right]_n\text{H}$ <p style="text-align: center;">(V), 0.1</p>	4.0
	120	98.9	$\text{H}-\left[\begin{array}{c} \text{S} \\ \\ \text{S}-\text{C}=\text{N}-\text{C}=\text{N}-\text{S} \\ \\ \text{H} \end{array}\right]_n\text{H}$ <p style="text-align: center;">(V), 0.1</p>	1.0
	121	74.6	$\text{H}-\left[\begin{array}{c} \text{S} \\ \\ \text{S}-\text{C}=\text{N}-\text{C}=\text{N}-\text{S} \\ \\ \text{H} \end{array}\right]_n\text{H}$ <p style="text-align: center;">(V), 0.4</p>	10.0
	122	50.0	$\text{H}-\left[\begin{array}{c} \text{S} \\ \\ \text{S}-\text{C}=\text{N}-\text{C}=\text{N}-\text{S} \\ \\ \text{H} \end{array}\right]_n\text{H}$ <p style="text-align: center;">(V), 0.4</p>	6.0
	123	8.2	$\text{H}-\left[\begin{array}{c} \text{S} \\ \\ \text{S}-\text{C}=\text{N}-\text{C}=\text{N}-\text{S} \\ \\ \text{H} \end{array}\right]_n\text{H}$ <p style="text-align: center;">(V), 0.4</p>	3.2
	124	20.6	$\text{H}-\left[\begin{array}{c} \text{S} \\ \\ \text{S}-\text{C}=\text{N}-\text{C}=\text{N}-\text{S} \\ \\ \text{H} \end{array}\right]_n\text{H}$ <p style="text-align: center;">(V), 0.4</p>	1.0
	125	70.0	$\text{H}-\left[\begin{array}{c} \text{S} \\ \\ \text{S}-\text{C}=\text{N}-\text{C}=\text{N}-\text{S} \\ \\ \text{H} \end{array}\right]_n\text{H}$ <p style="text-align: center;">(V), 5.0</p>	10.0
	126	74.4	$\text{H}-\left[\begin{array}{c} \text{S} \\ \\ \text{S}-\text{C}=\text{N}-\text{C}=\text{N}-\text{S} \\ \\ \text{H} \end{array}\right]_n\text{H}$ <p style="text-align: center;">(V), 5.0</p>	6.0

制剂	聚乙烯醇缩丁醛 (%wt/wt)	含硫缓蚀剂 (%wt/wt)	H ₃ PO ₄ (%wt/wt)
127	85.0	 (V), 5.0	4.0
128	94.0	 (V), 5.0	1.0
129	65.0	 (V), 10.0	10.0
130	70.0	 (V), 10.0	6.0
[0060]	131	 (V), 10.0	4.0
	132	 (V), 10.0	1.0
	133	 (V), 20.0	10.0
	134	 (V), 20.0	6.0
	135	 (V), 20.0	4.0

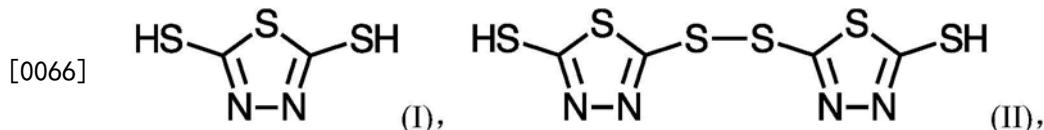
制剂	聚乙烯醇缩丁醛 (%wt/wt)	含硫缓蚀剂 (%wt/wt)	H ₃ PO ₄ (%wt/wt)	
[0061]	136	79.0	 (V), 20.0	1.0
	137	50.0	 (V), 30.0	10.0
	138	55.0	 (V), 30.0	6.0
	139	60.0	 (V), 30.0	4.0
	140	69.0	 (V), 30.0	1.0

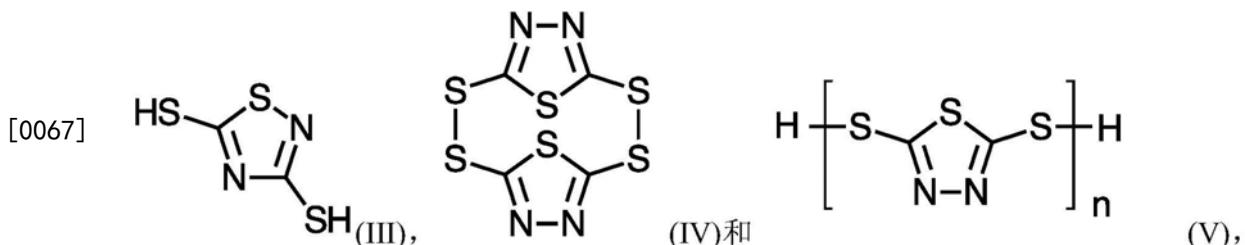
[0062] 基底涂料

[0063] 在第二方面中,提供了包括缓蚀制剂的基底涂料。缓蚀制剂包括:(a)至少一种树脂,(b)至少一种布朗斯台德酸和(c)至少一种含硫缓蚀剂。在一些方面中,至少一种树脂包括热塑性树脂。在这些方面中,热塑性树脂选自聚乙烯聚合物、聚氨基甲酸酯聚合物、丙烯酸酯聚合物和苯乙烯聚合物、或其组合。在这些方面的一些中,热塑性树脂包括聚乙烯聚合物。在这些方面的一些中,聚乙烯聚合物选自聚乙烯醇缩乙醛聚合物、聚乙烯醇缩丁醛聚合物和聚乙烯醇缩甲醛聚合物、或其组合。在一些方面中,聚乙烯聚合物包括聚乙烯醇缩丁醛聚合物。

[0064] 在一些方面中,至少一种布朗斯台德酸选自H₃PO₄;H₂SO₄;HX,其中X是Cl、Br或F;和HNO₃;或其组合。在这些方面的一些中,至少一种布朗斯台德酸包括H₃PO₄。

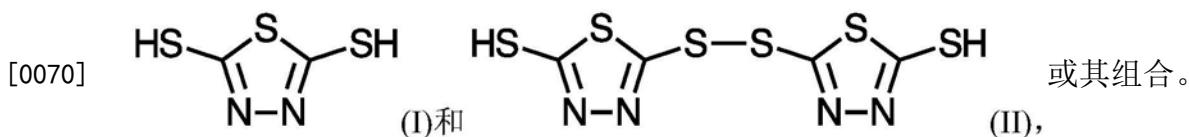
[0065] 在一些方面中,至少一种含硫缓蚀剂包括噻二唑化合物。在这些方面的一些中,噻二唑化合物选自结构(I)-(V) :



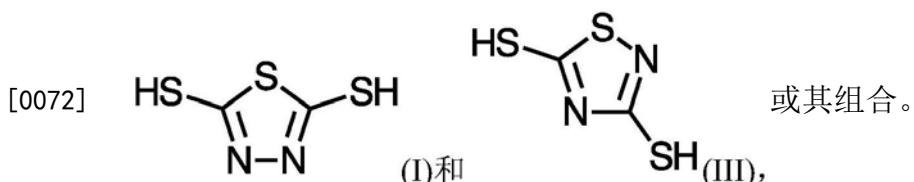


[0068] 或其组合,其中结构(V)的n等于或大于2。

[0069] 在这些方面的一些中,噻二唑化合物选自:



[0071] 在这些方面的一些中,噻二唑化合物选自:



[0073] 在一些方面中,至少一种含硫缓蚀剂包括含有金属的噻二唑化合物。在这些方面的一些中,含有金属的噻二唑化合物选自:2,5-二巯基-1,3,4-噻二唑,二钾盐;聚[Zn:2,5-二巯基-1,3,4-噻二唑(1:1)];[Al:2,5-二巯基-1,3,4-噻二唑(1:3)];[Al:2,5-二巯基-1,3,4-噻二唑(3:1)];聚[Zn:(双-(2,5-二硫-1,3,4-噻二唑)(1:1))];聚[Fe:2,5-二巯基-1,3,4-噻二唑(1:1)];聚[Al:2,5-二巯基-1,3,4-噻二唑(1:1)];和聚[Cu:2,5-二巯基-1,3,4-噻二唑(1:1)];或其组合。在这些方面的一些中,含有金属的噻二唑化合物是聚[Zn:2,5-二巯基-1,3,4-噻二唑(1:1)]。

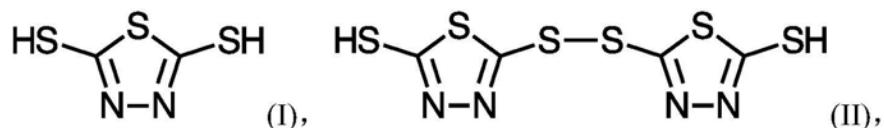
[0074] 在一些方面中,基底涂料包括具有具体比例的至少一种树脂、至少一种布朗斯台德酸和至少一种含硫缓蚀剂(例如,wt/wt)的缓蚀制剂。在一方面,至少一种树脂以范围从约8% (wt/wt)至约99% (wt/wt)的量存在,包括从约10% (wt/wt)至约99% (wt/wt)、从约15% (wt/wt)至约99% (wt/wt)、从约25% (wt/wt)至约99% (wt/wt)、和从约50% (wt/wt)至约99% (wt/wt)的子范围。至少一种布朗斯台德酸以范围从约1% (wt/wt)至约10% (wt/wt)的量存在,包括从约2% (wt/wt)至约10% (wt/wt)、从约3% (wt/wt)至约10% (wt/wt)、从约5% (wt/wt)至约10% (wt/wt)、从约6% (wt/wt)至约10% (wt/wt)、和从约8% (wt/wt)至约10% (wt/wt)的子范围。至少一种含硫缓蚀剂以范围从约0.01% (wt/wt)至约30% (wt/wt)的量存在,包括从约0.01% (wt/wt)至约30% (wt/wt)、从约0.05% (wt/wt)至约30% (wt/wt)、从约0.10% (wt/wt)至约30% (wt/wt)、从约0.20% (wt/wt)至约30% (wt/wt)、从约0.40% (wt/wt)至约30% (wt/wt)、从约1% (wt/wt)至约30% (wt/wt)、从约2% (wt/wt)至约30% (wt/wt)、从约5% (wt/wt)至约30% (wt/wt)、从约10% (wt/wt)至约30% (wt/wt)、从约15% (wt/wt)至约30% (wt/wt)、从约20% (wt/wt)至约30% (wt/wt)、和从约25% (wt/wt)至约30% (wt/wt)的子范围。在这些范围和子范围内,考虑组分的具体量。例如,至少一种树脂可以以约8.2% (wt/wt)、约10% (wt/wt)、约15% (wt/wt)、约20% (wt/wt)、约25% (wt/wt)、约30% (wt/wt)、约40% (wt/wt)、约50% (wt/wt)、约60% (wt/wt)、约70% (wt/wt)、约80%

(wt/wt)、90% (wt/wt)、约95% (wt/wt)、和约99% (wt/wt)的量存在。至少一种布朗斯台德酸可以以约1% (wt/wt)、约2% (wt/wt)、约3.2% (wt/wt)、约4% (wt/wt)、约5% (wt/wt)、约6% (wt/wt)、约8% (wt/wt) 和约10% (wt/wt) 的量存在。至少一种含硫缓蚀剂以约0.01% (wt/wt)、约0.02% (wt/wt)、约0.05% (wt/wt)、约0.1% (wt/wt)、约0.2% (wt/wt)、约0.4% (wt/wt)、约1% (wt/wt)、约2% (wt/wt)、约5% (wt/wt)、约10% (wt/wt)、约15% (wt/wt)、约20% (wt/wt)、约25% (wt/wt) 和约30% (wt/wt) 的量存在。

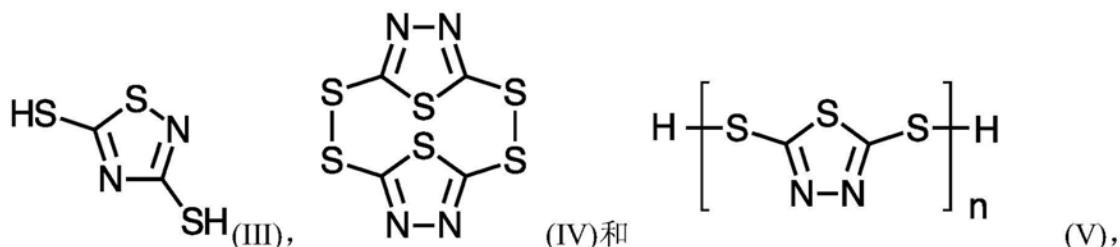
[0075] 这些和其他组分可以包括在具有缓蚀制剂的基底涂料中,条件是所有组分的累积量不超过100% (wt/wt)。其他组分的实例包括用于悬浮或溶解上述的至少一种树脂、至少一种布朗斯台德酸和至少一种含硫缓蚀剂的溶剂和流体。示例性溶剂和流体包括水、乙醇、丙酮、2-丁氧基乙醇、醋酸正丁酯、正丁醇、正丁基丙酸酯、环己酮、二丙酮醇、二甲基酯、N,N-二甲基乙酰胺、N,N-二甲基甲酰胺、二甲基亚砜、乙酸乙酯、二氯乙烯、异佛尔酮、异丙基乙酸酯、异丙醇、乙酸甲酯、甲基戊基酮、甲乙酮、甲基异戊基酮、甲基异丁基酮、甲基丙基酮、甲基丙基酮、二氯甲烷、N-甲基2-吡咯烷酮、丙酸丙酯、二氯丙烯、四氢呋喃、1,1,1-三氯乙烷,等等,包括其组合。

[0076] 其他组分可以包括在基底涂料中,诸如例如,染料、着色剂、颜料等。

[0077] 在这些范围内，考虑组分的具体类型。在这点上，基底涂料包括缓蚀制剂，缓蚀制剂具有至少一种树脂——其为聚乙烯醇缩丁醛——和至少一种布朗斯台德酸——其为 H_3PO_4 。在基底涂料包括考虑这些具体树脂和布朗斯台德酸组分的具体制剂的地方，具体制剂包括选自下列的至少一种含硫缓蚀剂：



〔0078〕



[0079] 或其组合,其中结构(V)的n等于或大于2。

[0080] 在一些方面中，具有缓蚀制剂的基底涂料包括至少一种树脂——其为聚乙烯醇缩丁醛，至少一种布朗斯台德酸——其为 H_3PO_4 ，和至少一种含硫缓蚀剂——其选自化合物(I) - (V)。符合这些组分标准的示例性基底涂料包括选自上文表1中显示的制剂(1) - (140)中的至少一种的缓蚀制剂。

[0081] 在第三方面中,公开了在基底上施加缓蚀制剂的方法。该方法包括两个步骤。第一步骤包括在基底上涂布缓蚀制剂。缓蚀制剂包括(a)至少一种树脂,(b)至少一种布朗斯台德酸和(c)至少一种含硫缓蚀剂。第二步骤包括固化涂料。在一些方面中,将涂料布置在基底上的步骤包括下列至少一种:浸渍、刷涂、流涂、丝网印刷、狭缝式模头挤出涂布(slot diecoating)、凹版涂布、粉末涂布、喷涂和旋转涂布涂料至基底上。在一些方面中固化涂料的步骤包括使涂料经历范围从约65°F至约160°F的温度。

[0082] 电活性阴极硫系统的合成。

[0083] 本公开内容的含硫缓蚀剂是电活性阴极硫化合物。某些含硫缓蚀剂包括选自结构(I) - (III) 和 (VI) 的商业上可得的噻二唑化合物,如表2中所显示。

[0084] 表2.作为缓蚀剂的示例性商业上可得的噻二唑化合物。

化合物	结构	IUPAC 名称[CAS 号]
[0085]		1,3,4-噻二唑-2,5-二硫酚 [1072-71-5]
		5,5'-二硫代双(1,3,4-噻二唑-2(3H)-硫酮) [72676-55-2]
		1,2,4-噻二唑-3,5-二硫酚 [20939-17-7]
		1,3,4-噻二唑-2,5-二硫酚, 二钾盐 [4628-94-8]

[0086] Vanlube 829表示化合物(II)的商用润滑剂添加剂(Vanderbilt Chemicals,LLC (Norwalk, CT (US)))。

[0087] 下述含硫缓蚀剂包括已知的噻二唑化合物(IV)和(V),其可在适当的条件下由化合物(I)的氧化而合成,如表3中显示。

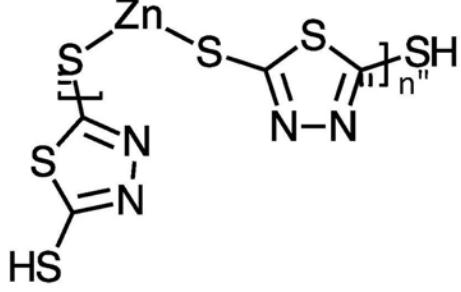
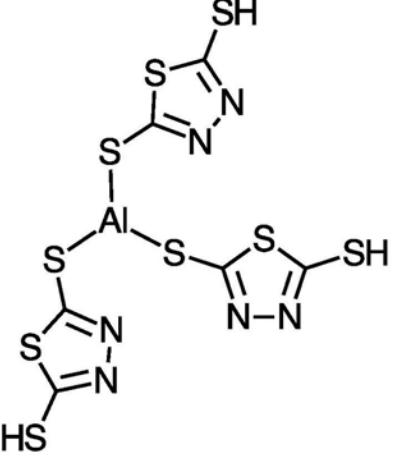
[0088] 表3.作为缓蚀剂的示例性噻二唑化合物。

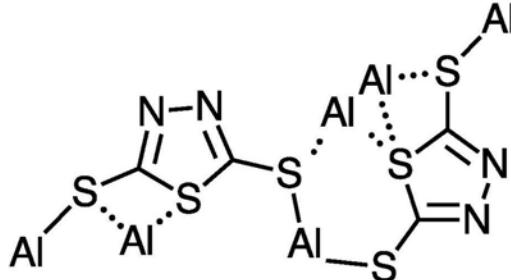
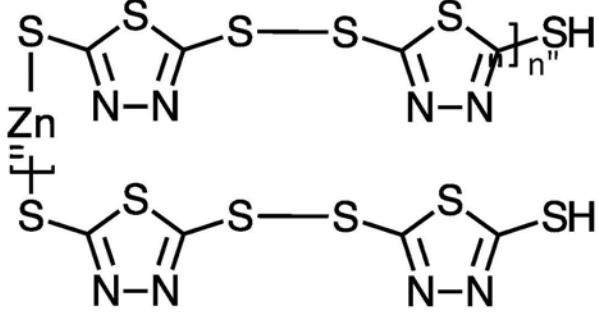
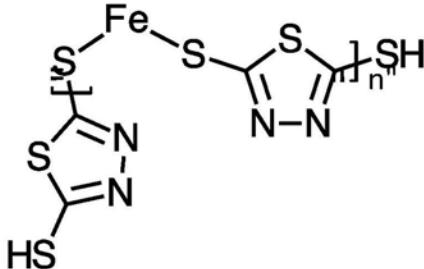
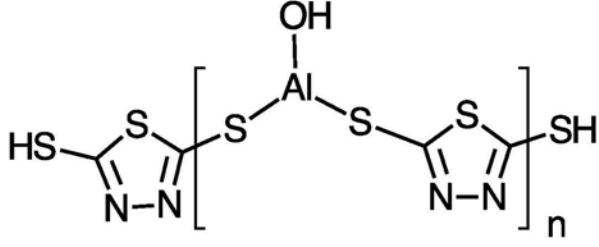
化合物	结构和 IUPAC 名	合成的引用
IV		Hugo 等 US4599425A (1986) (也见实施例 1)
V		E. Ziegele, J. Prakt. Chem. 60:40 (1899) (也见实施例 2)

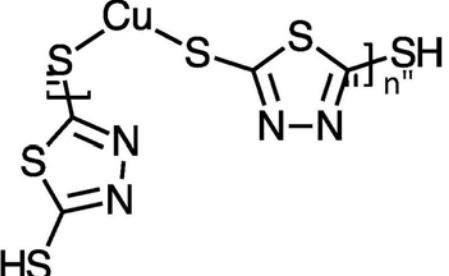
[0091] 下述含硫缓蚀剂包括新的金属噻二唑化合物(VII) - (XIII),其可根据本文公开的

具体实施例合成,如表4中显示。

[0092] 表4.作为含硫缓蚀剂的示例性金属噻二唑

化合物	预测的结构 ^a 和 IUPAC 名	合成实施例
VII	 聚[Zn:2,5-二巯基-1,3,4-噻二唑(1:1)], (n ≥ 2)	实施例 3
[0093]	 [Al:2,5-二巯基-1,3,4-噻二唑(1:3)]	实施例 4

化合物	预测的结构 ^a 和 IUPAC 名	合成实施例
IX	 <p>[Al:2,5-二巯基-1,3,4-噻二唑(3:1)], (n ≥ 2)</p>	实施例 5
X [0094]	 <p>聚[Zn:(双-(2,5-二硫代-1,3,4-噻二唑)(1:1))], (n ≥ 2)</p>	实施例 6
XI	 <p>聚[Fe:2,5-二巯基-1,3,4-噻二唑(1:1)], (n ≥ 2)</p>	实施例 7
XII	 <p>聚[Al:2,5-二巯基-1,3,4-噻二唑(1:1)], (n ≥ 2)</p>	实施例 8

化合物	预测的结构 ^a 和 IUPAC 名	合成实施例
[0095] XIII	 聚[Cu:2,5-二巯基-1,3,4-噻二唑(1:1)], (n ≥ 2)	实施例 9

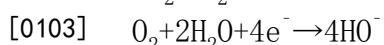
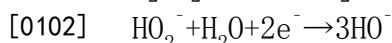
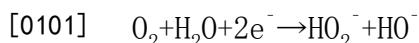
[0096] ^a预测的结构是基于合成试剂的摩尔比的考虑,而不是基于合成所得产物的分析特征。

[0097] 表征示例性含硫缓蚀剂的电活性阴极硫化合物活性。金属的腐蚀归因于下述氧化反应(方案I) :



[0099] (方案I)

[0100] 电活性阴极硫化合物通过根据下述氧还原反应进行氧的还原来抑制腐蚀(方案II) :



[0104] (方案II)

[0105] 线性扫描伏安法(LSV)和计时电流法用于评估含硫缓蚀剂作为电活性阴极硫化合物的性能。用旋转圆盘电极(RDE)进行LSV实验。旋转圆盘电极技术提供了测量灵敏度的某些益处,因为技术指示在稳定状态下在电极上具有动力学流(kinetic flow)的电流而不是在溶液中的静态测量(图1)。

[0106] 使用旋转圆盘电极,基于化合物抑制电解质中氧还原反应的能力测量缓蚀剂性能。如果电流值接近零,那么缓蚀剂视为是适当的,因为作为指示腐蚀的氧还原反应被隔离(sequestered)或停止。已知浓度的溶液(例如,包含10ppm缓蚀剂)用作比较缓蚀剂。使用方程式1(I_E 校正不由缓蚀剂(例如,电解质)引起的贡献)计算缓蚀剂效率(I_E)。

[0107] 缓蚀剂效率 = $(i_{\text{缓蚀剂}} - i_{\text{空白}}) / i_{\text{空白}}$ (方程式1)

[0108] 通过测量在-800mV的电流值(A)下评估不同缓蚀剂(10ppm溶液)的性能并且确定缓蚀剂效率,其结果显示在表5中。

[0109] 表5.示例性含硫缓蚀剂的性能

化合物 ^a	化合物 ^b	n	电流 (A) @800mV	电流 (A) S.D.	I_E
1,2,4DMcT	III	10	-1.53×10^{-4}	-9.14×10^{-5}	0.70
ZnDMcT	VII	4	-2.13×10^{-4}	-5.08×10^{-5}	0.58
1:3AlDMcT	VIII	4	-2.25×10^{-4}	-9.41×10^{-5}	0.55
3:1AlDMcT	IX	4	-2.59×10^{-4}	-1.05×10^{-5}	0.49

Vanlube 829	II	3	-2.68×10^{-4}	-1.62×10^{-5}	0.47
1:3AlDMcT(酸)	VIII	3	-2.83×10^{-4}	-7.95×10^{-5}	0.44
BDTD	IV	3	-3.00×10^{-4}	-4.01×10^{-5}	0.40
聚Zn(双-DMcT)	X	2	-3.12×10^{-4}	-1.32×10^{-5}	0.38
Fe(II) DMcT	XI	3	-3.23×10^{-4}	-8.65×10^{-6}	0.36
PDTD	V	1	-3.11×10^{-4}	NA	0.34
1:1AlDMcT	XII	3	-3.51×10^{-4}	-1.96×10^{-5}	0.30
Cu(II) DMcT	XIII	3	-4.01×10^{-4}	-2.36×10^{-5}	0.20
无(空白)		8	-5.03×10^{-4}	-1.19×10^{-4}	0.00

[0111] ^a化合物缩写如下:1,2,4DMcT=1,2,4-噻二唑-3,5-二硫酚(III);ZnDMcT=聚[Zn:2,5-二巯基-1,3,4-噻二唑(1:1)],(n≥2);1:3AlDMcT=[Al:2,5-二巯基-1,3,4-噻二唑(1:3)];3:1AlDMcT=Al:2,5-二巯基-1,3,4-噻二唑(3:1);Vanlube 829=5,5'-二硫代双(1,3,4-噻二唑-2(3H)-硫酮);1:3AlDMcT(酸)=[Al:2,5-二巯基-1,3,4-噻二唑(1:3)](酸);BDTD=双-[2,5-二硫-1,3,4-噻二唑];聚Zn(双-DMcT)=聚[Zn:双-(2,5-二硫-1,3,4-噻二唑)(1:1)],(n≥2);Fe(II) DMcT=聚[Fe:2,5-二巯基-1,3,4-噻二唑](1:1),(n≥2);PDTD=聚(2,5-二硫-1,3,4-噻二唑);1:1AlDMcT=聚[Al:2,5-二巯基-1,3,4-噻二唑(1:1)],(n≥2);和Cu(II) DMcT=聚[Cu:2,5-二巯基-1,3,4-噻二唑(1:1)],(n≥2)。

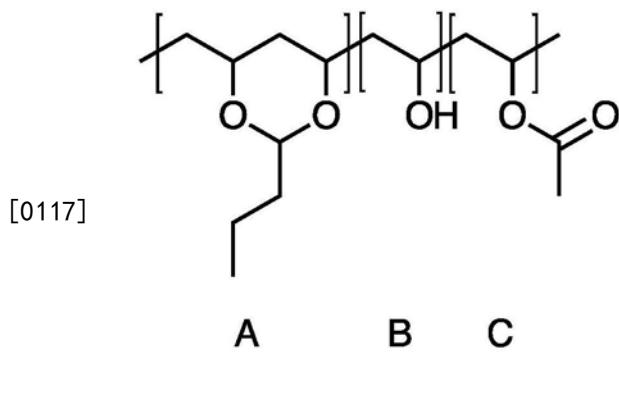
[0112] ^b化合物命名描述在表2-4中。

[0113] 缓蚀剂的溶解度与其在水溶液(未显示)中的性能相关性较低。在电解质中的溶解度和测量的缓蚀剂性能之间的相关性指示溶解度影响性能。由于该原因,优选地在树脂系统中而不是在电解质中评估缓蚀剂的性能。

[0114] 缓蚀制剂和涂料的制备。

[0115] 将缓蚀剂并入树脂允许在正常使用条件下性能评估,与在水性或有机溶剂中相比。基于2,3-二巯基1,3,4-噻二唑(DMcT)的缓蚀剂化合物已知与通常用于航空航天底漆的环氧树脂具有反应性。已知DMcT使胺治疗剂(curative)质子化并且打破环氧树脂环,以形成强的C-S键。

[0116] 选择聚乙烯醇缩丁醛(PVB)树脂系统作为用于并入缓蚀剂的示例性树脂系统,因为其是相对非反应性的、具有好的粘合,并且不溶于水,以允许电化学测试和性能评估。PVB树脂通常用作表面涂布之前金属表面上的透明的“磷化底漆”。聚乙烯醇缩丁醛是热塑性树脂,使用热其与痕量金属酸交联。在该具体的方面中,磷酸用作催化剂。PVB(XIV)由聚乙烯醇(PVOH)和丁醛之间的反应形成,酸作为催化剂。



[0118] 加括号的部分A、B和C沿着PVB聚合物分子随机分布。

[0119] 有机缓蚀剂一般需要更高的载荷,因为与常规的缓蚀颜料——比如铬酸锶和铬酸锌——相比,它们具有更高的颜料吸收值。示例性DMcT和Vanlube 829吸油量值在铬酸锶的相同的相对范围内,允许对包含铬酸锶的MIL C 8514制剂非常小的修饰。

[0120] 开路电势 (OCP) 测量两个半电池反应在平衡时的组合电势 (Jones, 1996; 方案 III)。

[0121] $M \rightarrow M^{2+} + 2e^-$

[0122] $2H^+ + 2e^- \rightarrow H_2$

[0123] (方案III)

[0124] 在具有PVB树脂的板上收集OCP测量,所述PVB树脂具有0%、0.5%和5% (wt/wt) 的DMcT装载,使用填充有用磷酸盐缓冲盐水 (PBS) 缓冲的5% (wt/wt) NaCl电解质夹钳电池 (clamp cell) 和铂参比电极。金属板是这些测量中的工作电极。随着时间测量OCP,直到电势值达到稳定状态。

[0125] 观察了达到稳定状态的时间和缓蚀剂装载之间的相关性。5% DMcT板达到稳定状态需要最长的时间,约100ks (28h),而没有缓蚀剂或具有0.5%缓蚀剂的板达到稳定状态需要的时间较短,25ks和50ks (7h和14h) (图2)。该相关性提供了板上缓蚀剂的性能的强健测量,其比用包含缓蚀剂溶液的LSV实验更灵敏。

[0126] 在具有示例性缓蚀涂料施加至它们的表面上的基板进行计时电流法(图3A-E)。与缺少含硫缓蚀剂的树脂涂料相比,包括酸催化剂的涂料的表现比缺少酸催化剂的那些更好(比较图3A和3B)。涂布之后对基板划线增强了包含含硫抑制涂料的基板的计时电流性能与缺少含硫缓蚀剂的涂料相比的观察的差异(图3C)。在LSV实验中,化合物(XIII) (Cu (II) DMcT) 的表现比对照溶液更好(表5,上文)。但是,与缺少缓蚀剂的制剂相比,该化合物是涂布在基板上的缓蚀制剂中无效的缓蚀剂(图3D)。当与缺少缓蚀剂的制剂相比时,PANI涂料制剂作为缓蚀制剂在它们的性能上不同(图3E)。使用来自计时电流法的结果(图3A-E),方程式2用于计算每种缓蚀剂的效率(I.E.):

$$[0127] \text{缓蚀剂效率 (I.E.)} = 1 - \frac{i_I}{i_0} \quad (\text{方程式 2})$$

[0128] 其中 i_I =具有缓蚀剂的涂料平衡时的电流 (μA),和 i_0 =无缓蚀剂的涂料平衡时的电流 (μA)。表6总结了示例性缓蚀制剂和涂料的数据。

[0129] 表6.示例性缓蚀制剂和涂料的缓蚀剂效率。

涂料 ¹	i_t (mA)	缓蚀剂效率(%) ²
实验 1:		
PVB (无缓蚀剂)	-546.8	0.0
0.5% Vanlube 829-无催化剂	-641.3	-17.3
0.5% DMcT-无催化剂	-595.0	-8.8
5% DMcT-无催化剂	-559.4	-2.3
实验 2:		
PVB (无缓蚀剂)	-550.1	0.0
0.5% Vanlube 829	-385.6	29.9
0.5% DMcT	-383.1	30.4
5% DMcT	-343.4	37.6
5% Vanlube 829	-340.5	38.1
[0130] 实验 3:		
PVB (无缓蚀剂)-划线的	-661.4	0.0
0.5% Vanlube 829-划线的	-500	24.4
0.5% DMcT-划线的	-500	24.4
5% Vanlube 829-划线的	-433.1	34.5
5% DMcT-划线的	-67.7	89.8
实验 4:		
PVB (无缓蚀剂)	-547.4	0.0
0.5% PANI DMcT	-448.9	10.7
5% PANI DMcT	-505.6	7.6
5% PANI HCl	-622.6	-13.7
0.5% PANI HCl	-639.9	-16.9
[0131]		
涂料 ¹	i_t (mA)	缓蚀剂效率(%) ²
5% PANI 碱	-597.5	-9.2
0.5% PANI 碱	-678.3	-23.9
实验 5:		
0.5% Cu(DMcT) ₂	-612.1	-11.8

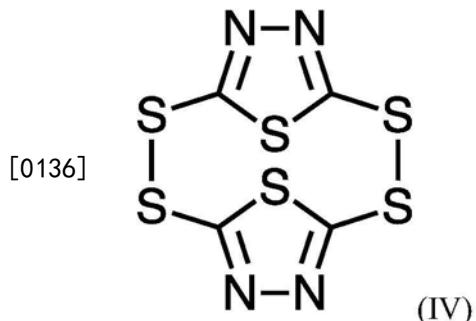
[0132] ¹缓蚀剂效率(I.E.)是根据方程式2计算。

[0133] 当与对照树脂(例如,PVB)相比时,表6中呈现的缓蚀剂效率的正值反映了作为涂料的有效的缓蚀制剂。当与对照树脂(例如,缺少缓蚀剂的PVB)相比时,表6中呈现的缓蚀剂

效率的负值反映了作为涂料无效的缓蚀制剂。

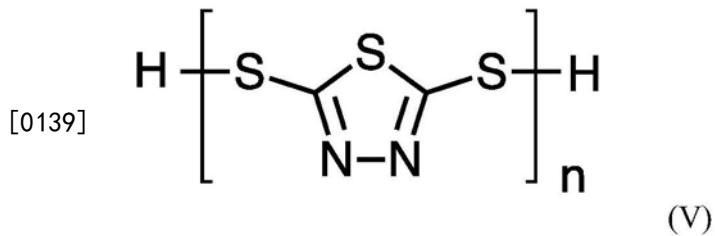
[0134] 实施例

[0135] 实施例1. 双-[2,5-二硫-1,3,4-噻二唑] (IV) 的合成



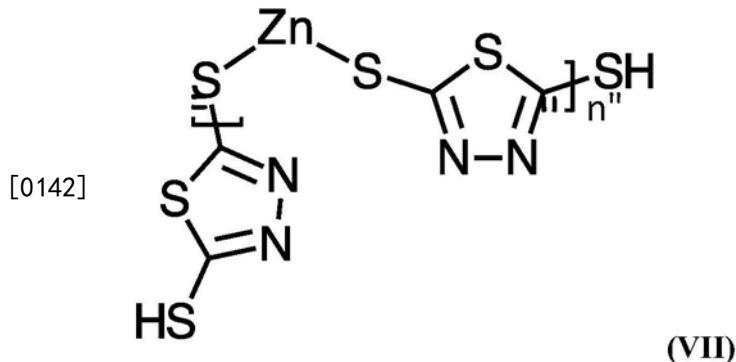
[0137] 将十五克粉末形式的DMcT (0.1摩尔) 悬浮在0℃的200ml的水中。在强力搅拌悬浮液的同时,以缓慢的速度(使用蠕动泵)逐滴添加30%过氧化氢溶液(14g (0.1摩尔)),使得反应温度不超过50℃。在添加过氧化物之后一个小时,过滤出BDTD产物,用去离子水冲洗三次,并且在50℃下干燥12小时。

[0138] 实施例2. 聚(2,5-二硫-1,3,4-噻二唑) (V) 的合成



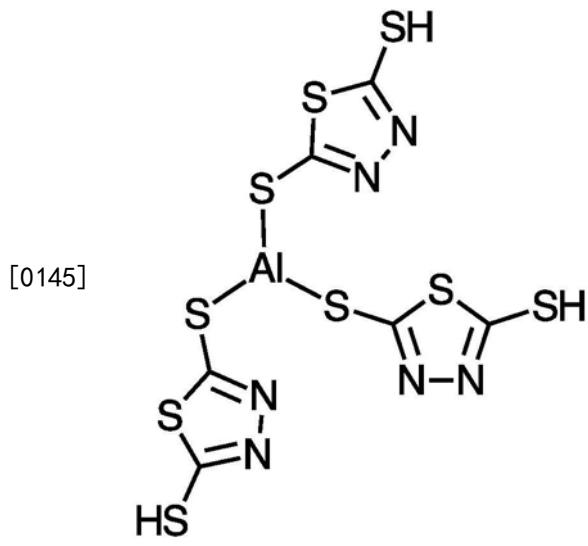
[0140] 在20℃下,将二十二克的1,3,4-噻二唑-2,5-二硫二钾(KDMcT) (0.1摩尔)溶于200ml的水中。将过硫酸铵(25.1g)溶于120ml的水中。在强力搅拌KDMcT溶液的同时,在45分钟内,用蠕动泵,逐滴添加过硫酸盐溶液。另外搅拌溶液1小时(在该时间期间形成固体)。用水冲洗所得PDTD产物4×200ml。将固体转移至Waring®搅拌机,分散在200ml水中并且用0.1M HCl酸化,使得pH至2.0。用水(6×250ml)再次冲洗产物并且在真空干燥器中干燥。

[0141] 实施例3. 聚[Zn:2,5-二巯基-1,3,4-噻二唑(1:1)], (n≥2) (VII) 的合成



[0143] 在20℃下,将十五克的DMcT (0.1摩尔) 分散在250ml的水中。伴随搅拌缓慢添加一百克的8%氢氧化钠。形成了透明黄色溶液。将氯化锌(13.6克 (0.1摩尔))溶于100ml水中并且缓慢添加至黄色DMcT溶液。在室温下,搅拌所得溶液一个小时。形成了白色沉淀。用蒸馏水冲洗沉淀并且在80℃下真空干燥16个小时。

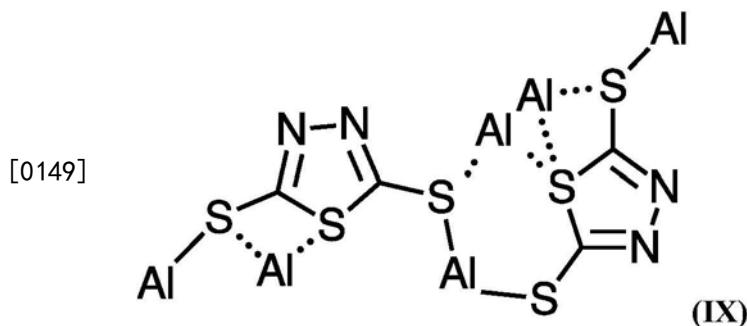
[0144] 实施例4.[Al:2,5-二巯基-1,3,4-噻二唑(1:3)](VIII)的合成



[0146] 对于[Al:2,5-二巯基-1,3,4-噻二唑(1:3)]，将75g的DMcT(0.5摩尔)溶于1升的1.0N NaOH(1摩尔)中。所有溶解的DMcT产生透明的琥珀-黄色溶液。伴随搅拌将硝酸铝九水合物(62.5g(0.167摩尔))缓慢添加至DMcT溶液，此时立即开始形成浅黄色沉淀。缓慢搅拌其中DMcT与铝的摩尔比是3:1的所得混合物4小时。使用玻璃电极测量的浆料的pH被测定为5.44。使用真空过滤，通过Whatman[®] 1001 125定性滤纸过滤浆料并且用250ml部分的MilliQ[®]水冲洗3次。风干之后，回收18.4克黄色粉末(产物1)。无色滤液的pH是5.49(体积=1.25升)。将50ml的3.8M H₂SO₄添加至滤液，以使得pH下降至1.26。在添加酸期间，形成浑浊沉淀。检测到了轻微的“硫”气味。真空过滤该沉淀并且用100ml MilliQ[®]水冲洗4次并且空气干燥。回收13.2g浅黄色产物(产物2)。

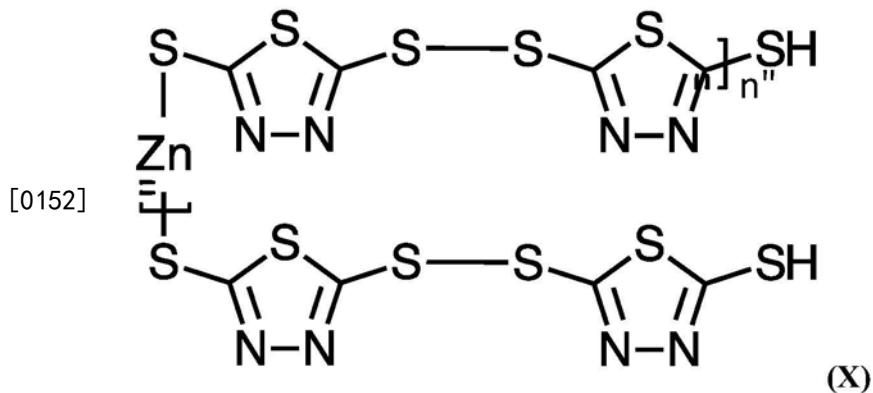
[0147] 以相同的方式制备[Al:2,5-二巯基-1,3,4-噻二唑(1:3)](酸)形式，除了省略了将75g的DMcT(0.5摩尔)溶于1升1.0N NaOH(1摩尔)的初始步骤。而是，将75g的DMcT(0.5摩尔)溶于1升水并且如上述与62.5g(0.167摩尔)的硝酸铝九水合物反应。

[0148] 实施例5.[Al:2,5-二巯基-1,3,4-噻二唑(3:1)](IX)的合成。



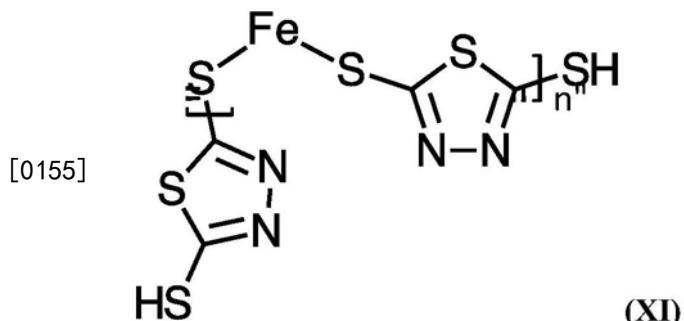
[0150] 在20℃下，将十五克(0.1摩尔)的DMcT分散在250ml的水中。伴随搅拌缓慢添加一百克的8%氢氧化钠。形成了透明黄色溶液。将硝酸铝九水合物(112.54克(0.3摩尔))溶于100ml的水并且缓慢添加至黄色DMcT溶液。在室温下搅拌所得溶液一个小时。用去离子水冲洗形成的固体沉淀3次。

[0151] 实施例6.聚[Zn:(双-(2,5-二巯基-1,3,4-噻二唑)(1:1)],(n≥2)(X)的合成



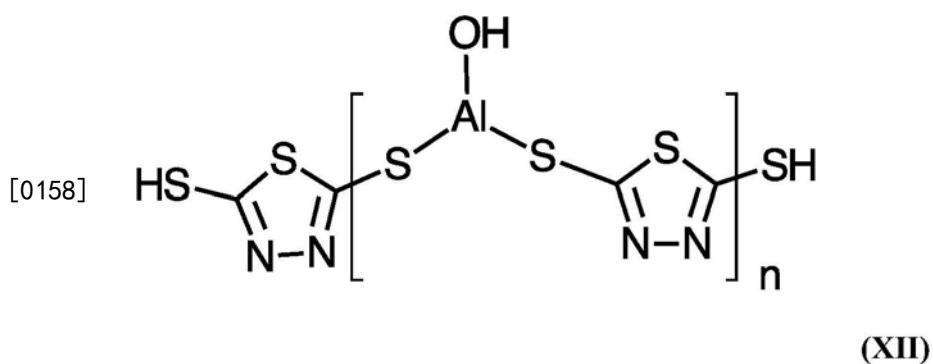
[0153] 在环境温度下,伴随着N₂鼓泡,将Vanlube 829DMcT二聚体(化合物(II))(59.6g(0.2摩尔))分散在400ml的1.0M NaOH中。形成了浑浊黄色浆料。将27.2克(0.2摩尔)固体氯化锌溶于200ml的蒸馏水中。将氯化锌溶液缓慢添加至浑浊黄色浆料。立即形成淡黄色浆料。在室温下,伴随着N₂鼓泡,搅拌浆料过夜。使用真空过滤,通过具有0.45μm孔的尼龙过滤器膜过滤浆料。用100ml的蒸馏水冲洗沉淀Zn(双-DMcT)3次并且空气干燥,然后放入真空干燥器过夜至完全干燥。

[0154] 实施例7.聚[Fe:2,5-二巯基-1,3,4-噻二唑](1:1), (n≥2) (XI) 的合成。



[0156] 在20℃下,将十五克(0.1摩尔)的DMcT分散在250ml的水中。伴随搅拌缓慢添加一百克的8%氢氧化钠。形成了透明黄色溶液。将二十七克(0.1摩尔)硫酸亚铁七水合物(FW=278.02)溶于100ml水中并且缓慢添加至黄色NaDMcT溶液。在室温下,将所得溶液搅拌一个小时。形成了细小黑色沉淀。用100ml的蒸馏水冲洗沉淀3次并且在80℃下真空干燥。

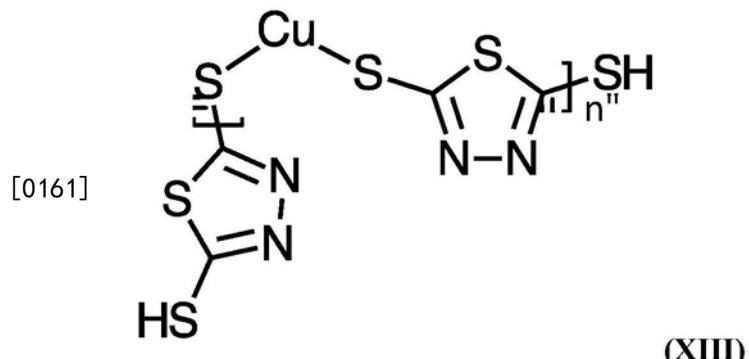
[0157] 实施例8.聚[Al:2,5-二巯基-1,3,4-噻二唑](1:1), (n≥2) (XII) 的合成。



[0159] 在20℃下,将十五克(0.1摩尔)的DMcT分散在250ml的水中。伴随搅拌缓慢添加一百克的8%氢氧化钠。形成了透明黄色溶液。将硝酸铝九水合物(37.5g(0.1摩尔))溶于100ml的水中并且缓慢添加至黄色DMcT溶液。在室温下,搅拌所得溶液一个小时。用去离子

水冲洗形成的固体沉淀3次并且空气干燥,以产生粉末。

[0160] 实施例9.聚[Cu:2,5-二巯基-1,3,4-噻二唑(1:1)]_n(XIII)的合成。



[0162] 在20℃下,将十五克(0.1摩尔)的DMcT分散在250ml的水中。伴随搅拌缓慢添加一百克的8%氢氧化钠。形成了透明黄色溶液。将氯化铜(II)二水合物(17.0g(0.1摩尔))溶于100ml的水中并且缓慢添加至黄色DMcT溶液。在室温下,搅拌所得溶液一个小时。形成了白色沉淀。用蒸馏水冲洗沉淀并且在80℃下真空干燥16个小时。

[0163] 实施例10.通过线性扫描伏安法和计时电流法表征含硫缓蚀剂。

[0164] 电解质系统。调查了用于研究水溶液中缓蚀剂的数个电解质,并且总结在下面表7中。示出了所有这些溶液的离子和离子浓度以及pH。稀释的Harrison溶液经常用于电化学阻抗频谱(EIS)实验。下面也显示了基于航空器搭接接头中出现的溶液的“搭接接头模拟溶液”(LJSS)的特性(Ferrer, 2002)。也呈现了用于中性盐雾试验(ASTM B 117)的标准5%NaCl溶液。

[0165] 表7. 用于含硫缓蚀剂的电化学表征的示例性电解质

[0166]

电解质系统 ¹	A	B	C	D	E	F
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[0167]

电解质系统 ¹	A	B	C	D	E	F
pH	7.0	7.0	7.4	4.5	4.5	9.0
盐	% (wt/wt) [M (mol/L)]					
总离子	6.0 [1.05]	5.0 [0.90]	1.0 [0.15]	4.0 [0.36]	0.4 [0.14]	0.2 [0.03]
NaCl	5.8 [1.04]	5 [0.90]	0.8 [0.14]	0.5 [0.09]	0.05 [0.07]	0.1 [0.02]
(NH ₄) ₂ SO ₄	N/A	N/A	N/A	3.5 [0.28]	0.35 [0.07]	N/A
KCl	0.02 [0.0027]	N/A	0.02 [0.0027]	N/A	N/A	N/A
Na ₃ PO ₄	0.2 [0.01]	N/A	0.2 [0.01]	N/A	N/A	N/A
NaNO ₂	N/A	N/A	N/A	N/A	N/A	0.03 [0.004]
NaHCO ₃	N/A	N/A	N/A	N/A	N/A	0.03 [0.004]
NaF	N/A	N/A	N/A	N/A	N/A	0.01 [0.002]
H ₂ O	94.0	95.0	99.0	96.0	99.6	99.9

[0168] ¹电解质系统如下:A是5%NaCl-磷酸盐缓冲盐水(PBS);B是5%NaCl-中性盐雾室;C是PBS;D是Harrison溶液(电化学电解质);E是稀释的Harrison溶液(EIS);并且F是搭接接头模拟溶液(LJSS)。表中的“N/A”反映盐组分未包括在指定的电解质系统中。

[0169] 选择5% (wt/wt) 氯化钠溶液(即,表7的电解质系统A) 模拟高度腐蚀性环境并且潜在地加速腐蚀。缓冲电解质,以消除pH的改变,而影响缓蚀剂性能测量。选择7的pH是因为其与海水类似。

[0170] 通过添加试剂级氯化钠<18M • cm电阻率至去离子水(将52.6克NaCl添加至1升水),产生5% (wt/wt) (0.9M) 氯化钠电介质溶液。然后,用来自Sigma Aldrich- (P4417-100TAB) 的磷酸盐缓冲盐水片剂使溶液缓冲至中性pH 7,每200ml溶液1片。将缓蚀剂溶于用磷酸盐缓冲盐水缓冲的5%氯化钠电解质,以维持pH为7。通过取具有更高已知缓蚀剂浓度的溶液的等分试样并且稀释制备10ppm溶液来产生百万分之十份(10ppm) 溶液。在大部分情况下,较高浓度目标是50ppm。通过在一升容量瓶中,在5%NaCl缓冲的电解质中添加0.050克的缓蚀剂产生初始溶液。并不是所有的缓蚀剂都被溶解,所以过滤溶液,以计算溶解度和实际浓度。用搅拌棒搅拌溶液过夜并且然后使用预称重的、4.7cm直径、1.0微米孔尺寸玻璃纤维过滤器(Whatman Grade GF/B 1821-047) 和Millipore玻璃过滤漏斗过滤。玻璃过滤器和夹钳漏斗(clamp funnel) 是对之前使用Buchner漏斗和纸过滤器的过滤方法的一种改进。在收集滤液之后,用去离子水充分冲洗漏斗和滤纸,以确保没有电解质盐陷入过滤器中并且收集过滤器漏斗一侧的残留的固体。在约120°C的烘箱中使带有固体的过滤器干燥过夜,允许干燥器中达到室温,并且称重。基于溶解的实际缓蚀剂计算实际的溶液浓度。浓度计算也考虑有时仍存在在于过滤器中的残留的盐。通过进行空白对照测量这些。取50ppm溶液的等分试样并且产生最后的10ppm的溶液。

[0171] 线性扫描伏安法和计时电流法实验。使用1000rpm的EG&G Princeton Applied

Research模型636旋转圆盘电极(RDE)转子——其具有Series G-750稳压器,750微安型号(PCI4G750-47062),使用铂对电极和玻璃甘汞Ag/AgCl参比电极(图6),进行溶液中各种缓蚀剂的线性扫描伏安法(LSV)。使用Gamry Framework软件。使用读数之间抛光的铜圆盘(1cm^2)工作电极。确认99%+纯铜圆盘的纯度是99。使用Baird DV4电弧/火花光谱仪(optical emission spectrometer)。

[0172] 为了测量LSV,在-0.3和-1伏特之间进行电势扫描,扫描速度是10mV/s。确定了在-0.800V下平台上的电流值是缓蚀剂功能的指示。通过重复地扫描测量稳定状态下的LSV值,直到随着时间该值停止变化。

[0173] 为了测量计时电流法,电势保持在-0.800V,并且随着时间测量电流,直到获得稳定的状态值。

[0174] 实施例11.缓蚀制剂和涂料的制备。

[0175] PVB树脂中缓蚀剂的装载基于使用用于通过Gardner-Coleman方法的颜料的吸油量的ASTM D 1483-95标准测试方法测定的临界颜料体积浓度。用于计算的颜料密度和比重值见于文献(Koleske (1995);Vanderbilt Chemicals,LLC (2012))中。DMcT和Vanlube 829作为代表性DMcT基材料被测试。基于由吸油量值计算的临界颜料体积浓度以涂料中每种含硫缓蚀剂的两种浓度——5%和0.5%——为目标。

[0176] 为了制备表1中的示例性缓蚀制剂和涂料,制备了下述材料:树脂、酸催化剂和含硫缓蚀剂。

[0177] 树脂.如下制备示例性树脂。使用高剪切气动混合器将五十九克(59g)聚乙烯醇缩丁醛Butvar-76溶于405g乙醇和131g正丁醇中,混合过夜,以提供10%的树脂(wt/wt)溶液。

[0178] 酸催化剂.如下制备示例性酸催化剂溶液。将二十克(20g)磷酸与17g去离子水和73g乙醇结合以提供18.2%的酸催化剂(wt/wt)溶液。

[0179] 为了制备包括0.4% (wt/wt)含硫缓蚀剂的制剂或涂料,比如由表1中的制剂11、39、67、95和123描述的那些,将61.7g的树脂(10% (wt/wt))溶液添加至高剪切THINKYTM混合器中配备的THINKYTM混合杯并且将0.316g的含硫缓蚀剂添加至树脂溶液。在2000RPM下混合21min之后,将13.1g的酸催化剂(18.2% (wt/wt))溶液添加至混合杯,并且将所得的混合物混合1min。所得的缓蚀制剂包括8.2% (wt/wt)的树脂、3.2% (wt/wt)的酸催化剂和0.4% (wt/wt)的含硫缓蚀剂。

[0180] 另外的示例性制剂和基底涂料

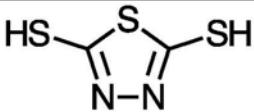
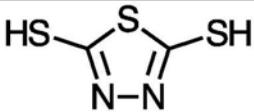
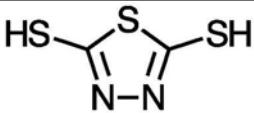
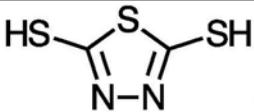
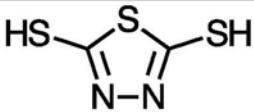
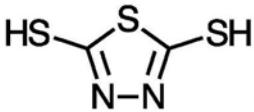
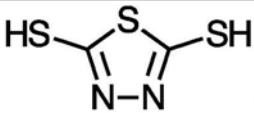
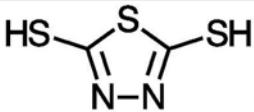
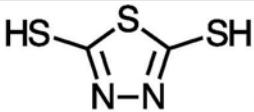
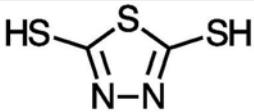
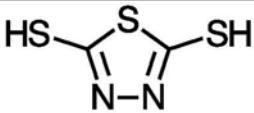
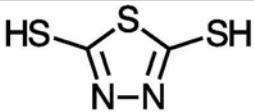
[0181] 如下制备包括除制剂11、39、67、95和123以外的含硫缓蚀制剂的表1中余下的制剂。参考表8中的组合物,将指定量的树脂添加至高剪切THINKYTM混合器中配备的THINKYTM混合杯,并且将指定量的含硫缓蚀剂添加至树脂。在2000RPM下混合21min之后,将提供100克混合物的最终重量的指定量的酸催化剂溶液和足够量的溶剂(无水乙醇)添加至混合杯,并且将所得的100克混合物混合1min。表8中的每种指定组合物提供指定用于除上文描述的制剂11、39、67、95和123以外的表1中的每种对应制剂的必需组分。

[0182] 表8.示例性组合物和基底涂料

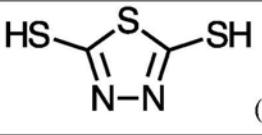
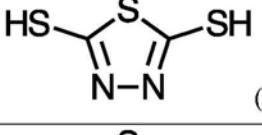
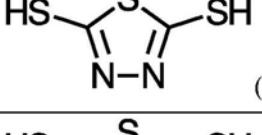
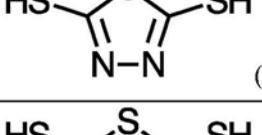
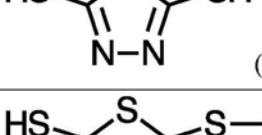
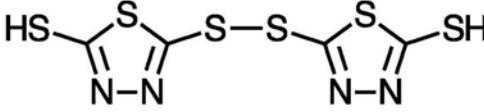
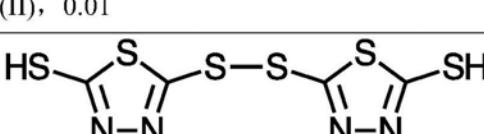
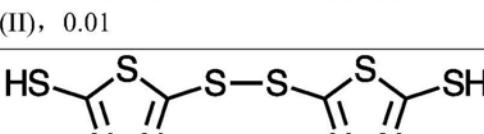
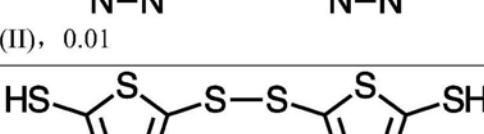
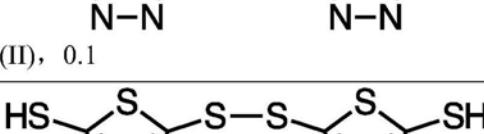
[0183]

组合物	PVB ^a (g)	含硫缓蚀剂 (g)	H ₃ PO ₄ (g)	溶剂 ^b (g)
1	74.99	 (I), 0.01	10.0	15.0
2	79.99	 (I), 0.01	6.0	14.0
3	89.99	 (I), 0.01	4.0	6.0
4	98.99	 (I), 0.01	1.0	N/A ^c
5	74.9	 (I), 0.1	10.0	15.0
6	79.9	 (I), 0.1	6.0	14.0
7	89.9	 (I), 0.1	4.0	6.0
8	98.9	 (I), 0.1	1.0	N/A ^c
9	74.6	 (I), 0.4	10.0	15.0
10	50.0	 (I), 0.4	6.0	43.6

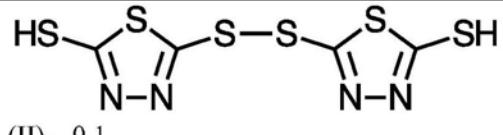
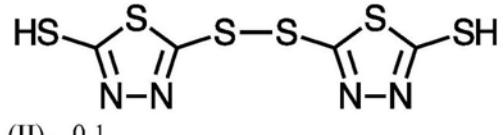
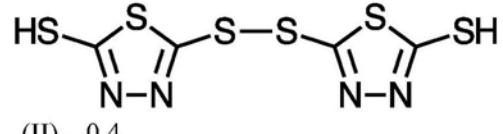
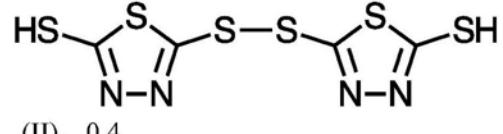
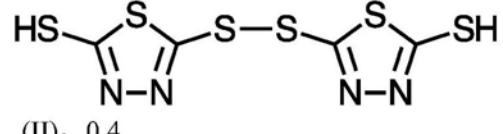
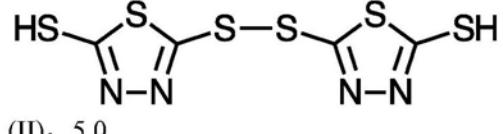
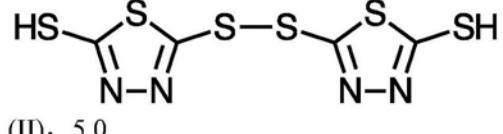
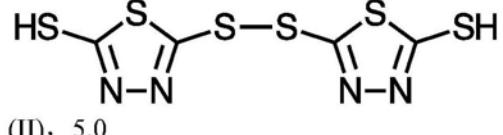
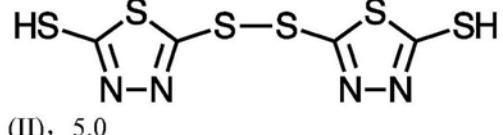
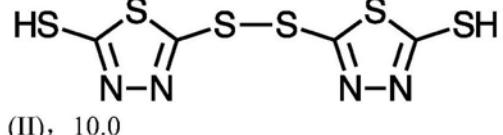
[0184]

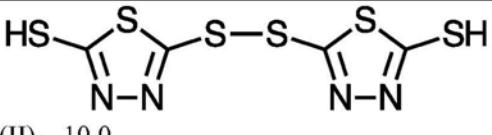
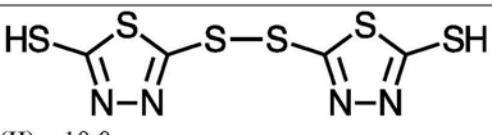
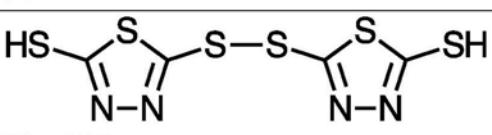
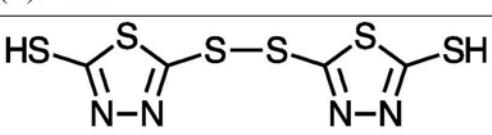
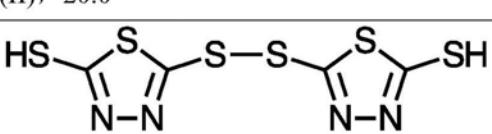
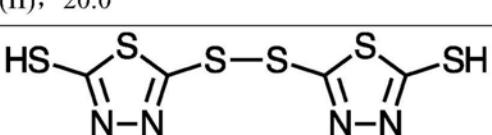
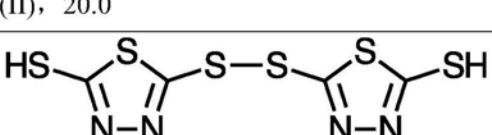
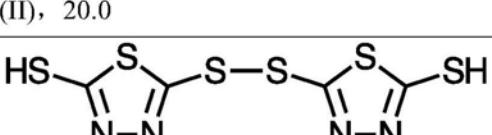
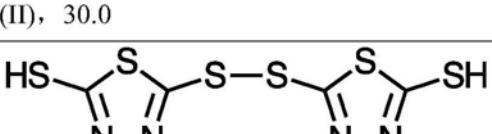
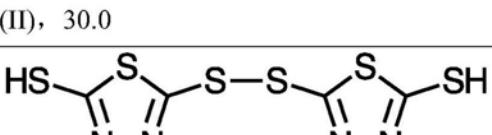
组合物	PVB ^a (g)	含硫缓蚀剂 (g)	H ₃ PO ₄ (g)	溶剂 ^b (g)
12	20.6	 (I), 0.4	1.0	78.0
13	70.0	 (I), 5.0	10.0	15.0
14	74.4	 (I), 5.0	6.0	14.6
15	85.0	 (I), 5.0	4.0	6.0
16	94.0	 (I), 5.0	1.0	N/A ^c
17	65.0	 (I), 10.0	10.0	15.0
18	75.0	 (I), 10.0	6.0	9.0
19	80.0	 (I), 10.0	4.0	6.0
20	89.0	 (I), 10.0	1.0	N/A ^c
21	55.0	 (I), 20.0	10.0	15.0
22	65.0	 (I), 20.0	6.0	9.0
23	70.0	 (I), 20.0	4.0	6.0

[0185]

组合物	PVB ^a (g)	含硫缓蚀剂 (g)	H ₃ PO ₄ (g)	溶剂 ^b (g)
24	79.0	 (I), 20.0	1.0	N/A ^c
25	50.0	 (I), 30.0	10.0	10.0
26	55.0	 (I), 30.0	6.0	9.0
27	60.0	 (I), 30.0	4.0	6.0
28	69.0	 (I), 30.0	1.0	N/A ^c
29	74.99	 (II), 0.01	10.0	15.0
30	84.99	 (II), 0.01	6.0	9.0
31	89.99	 (II), 0.01	4.0	6.0
32	98.99	 (II), 0.01	1.0	N/A ^c
33	74.9	 (II), 0.1	10.0	15.0
34	84.9	 (II), 0.1	6.0	9.0

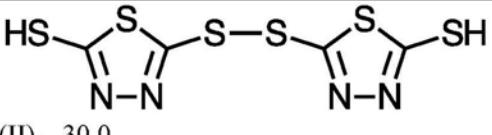
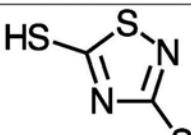
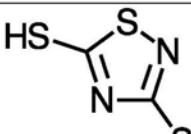
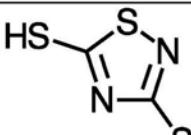
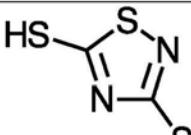
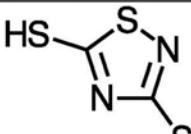
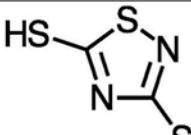
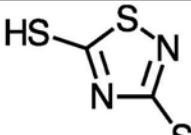
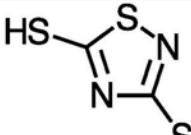
[0186]

组合物	PVB ^a (g)	含硫缓蚀剂 (g)	H ₃ PO ₄ (g)	溶剂 ^b (g)
35	89.9	 (II), 0.1	4.0	6.0
36	98.9	 (II), 0.1	1.0	N/A ^c
37	74.6	 (II), 0.4	10.0	15.0
38	50.0	 (II), 0.4	6.0	43.6
40	20.6	 (II), 0.4	1.0	78.0
41	70.0	 (II), 5.0	10.0	15.0
42	74.4	 (II), 5.0	6.0	14.6
43	85.0	 (II), 5.0	4.0	6.0
44	94.0	 (II), 5.0	1.0	N/A ^c
45	65.0	 (II), 10.0	10.0	15.0

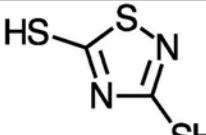
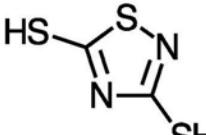
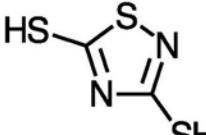
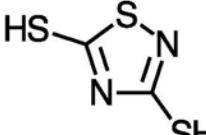
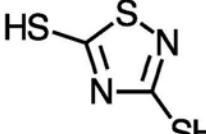
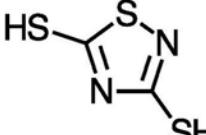
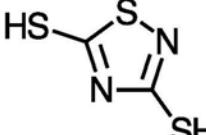
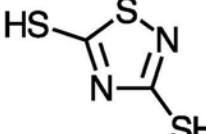
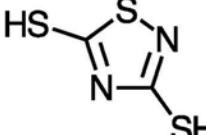
组合物	PVB ^a (g)	含硫缓蚀剂 (g)	H ₃ PO ₄ (g)	溶剂 ^b (g)
46	70.0	 (II), 10.0	6.0	14.0
47	80.0	 (II), 10.0	4.0	6.0
48	89.0	 (II), 10.0	1.0	N/A ^c
49	55.0	 (II), 20.0	10.0	15.0
50	60.0	 (II), 20.0	6.0	14.0
51	70.0	 (II), 20.0	4.0	6.0
52	79.0	 (II), 20.0	1.0	N/A ^c
53	50.0	 (II), 30.0	10.0	10.0
54	55.0	 (II), 30.0	6.0	9.0
55	60.0	 (II), 30.0	4.0	6.0

[0187]

[0188]

组合物	PVB ^a (g)	含硫缓蚀剂 (g)	H ₃ PO ₄ (g)	溶剂 ^b (g)
56	69.0	 (II), 30.0	1.0	N/A ^c
57	74.99	 (III), 0.01	10.0	15.0
58	84.99	 (III), 0.01	6.0	9.0
59	89.99	 (III), 0.01	4.0	6.0
60	98.99	 (III), 0.01	1.0	N/A ^c
61	74.9	 (III), 0.1	10.0	15.0
62	84.9	 (III), 0.1	6.0	9.0
63	89.9	 (III), 0.1	4.0	6.0
64	98.9	 (III), 0.1	1.0	N/A ^c

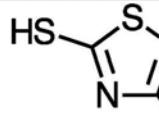
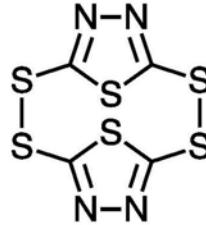
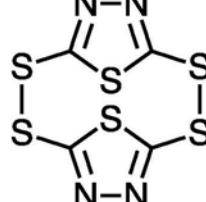
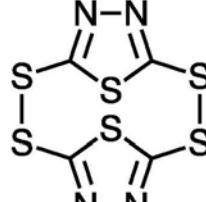
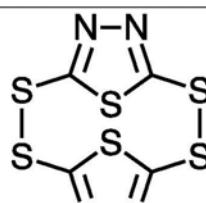
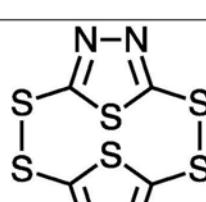
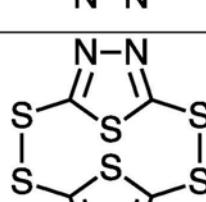
[0189]

组合物	PVB ^a (g)	含硫缓蚀剂 (g)	H ₃ PO ₄ (g)	溶剂 ^b (g)
65	74.6	 (III), 0.4	10.0	15.0
66	50.0	 (III), 0.4	6	43.6
68	20.6	 (III), 0.4	1.0	78.0
69	70.0	 (III), 5.0	10.0	15.0
70	74.4	 (III), 5.0	6.0	14.6
71	85.0	 (III), 5.0	4.0	6.0
72	94.0	 (III), 5.0	1.0	N/A ^c
73	65.0	 (III), 10.0	10.0	15.0
74	70.0	 (III), 10.0	6.0	14.0

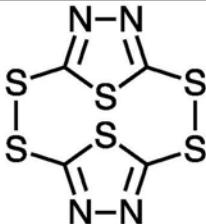
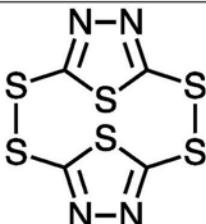
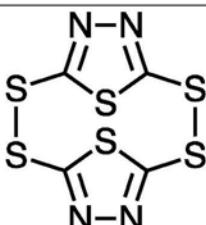
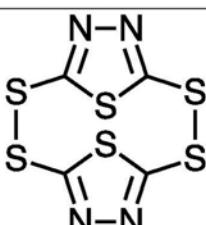
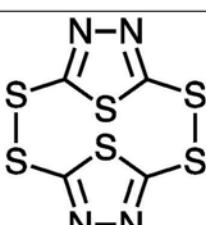
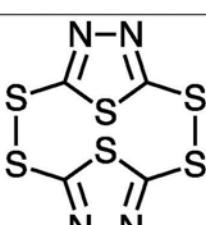
[0190]

组合物	PVB ^a (g)	含硫缓蚀剂 (g)	H ₃ PO ₄ (g)	溶剂 ^b (g)
75	80.0	 (III), 10.0	4.0	6.0
76	89.0	 (III), 10.0	1.0	N/A ^c
77	55.0	 (III), 20.0	10.0	15.0
78	60.0	 (III), 20.0	6.0	14.0
79	70.0	 (III), 20.0	4.0	6.0
80	79.0	 (III), 20.0	1.0	N/A ^c
81	50.0	 (III), 30.0	10.0	10.0
82	55.0	 (III), 30.0	6.0	9.0
83	60.0	 (III), 30.0	4.0	6.0

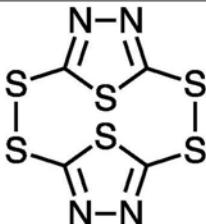
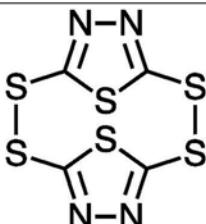
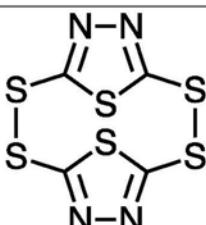
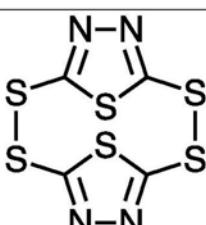
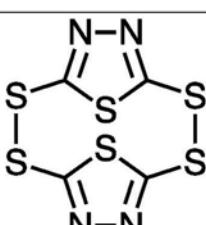
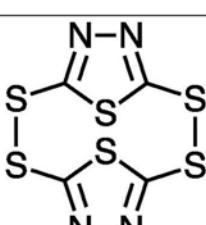
[0191]

组合物	PVB ^a (g)	含硫缓蚀剂 (g)	H ₃ PO ₄ (g)	溶剂 ^b (g)
84	69.0	 (III), 30.0	1.0	N/A ^c
85	74.99	 (IV) 0.01	10.0	15.0
86	84.99	 (IV) 0.01	6.0	9.0
87	89.99	 (IV), 0.01	4.0	6.0
88	98.99	 (IV), 0.01	1.0	N/A ^c
89	74.9	 (IV), 0.1	10.0	15.0
90	84.9	 (IV), 0.1	6.0	9.0

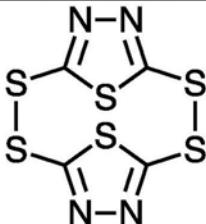
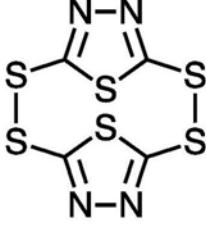
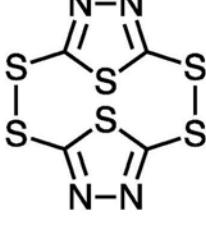
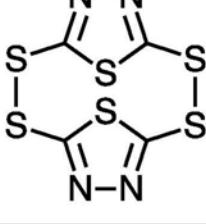
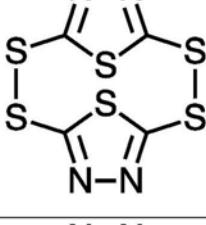
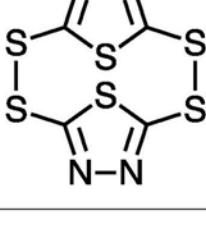
[0192]

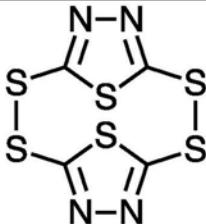
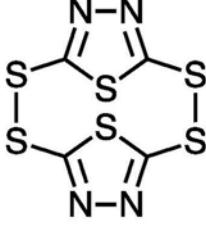
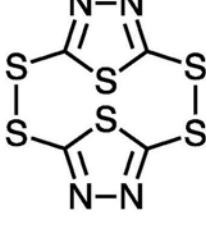
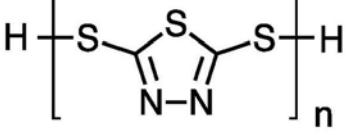
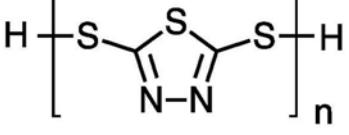
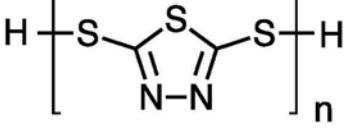
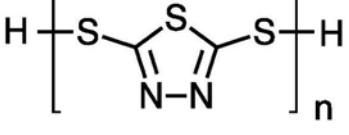
组合物	PVB ^a (g)	含硫缓蚀剂 (g)	H ₃ PO ₄ (g)	溶剂 ^b (g)
91	89.9	 (IV), 0.1	4.0	6.0
92	98.9	 (IV), 0.1	1.0	N/A ^c
93	74.6	 (IV), 0.4	10.0	15.0
94	50.0	 (IV), 0.4	6.0	43.6
96	20.6	 (IV), 0.4	1.0	78.0
97	70.0	 (IV), 5.0	10.0	15.0

[0193]

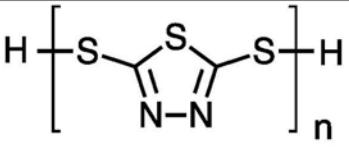
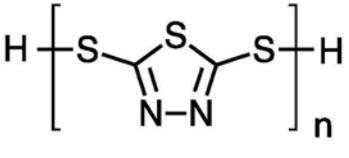
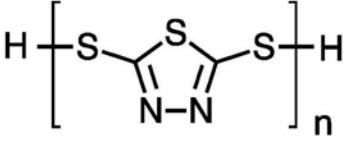
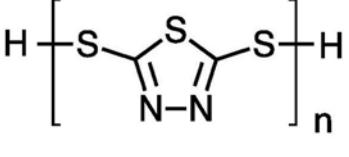
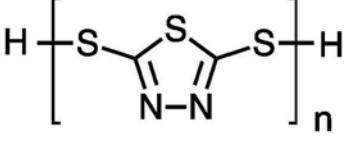
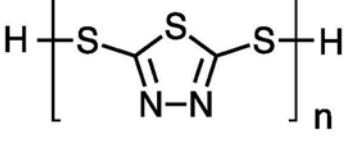
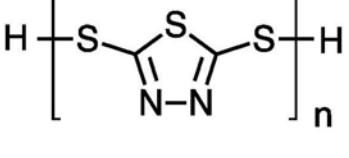
组合物	PVB ^a (g)	含硫缓蚀剂 (g)	H ₃ PO ₄ (g)	溶剂 ^b (g)
98	74.4	 (IV), 5.0	6.0	14.6
99	85.0	 (IV), 5.0	4.0	6.0
100	94.0	 (IV), 5.0	1.0	N/A ^c
101	65.0	 (IV), 10.0	10.0	15.0
102	70.0	 (IV), 10.0	6.0	14.0
103	80.0	 (IV), 10.0	4.0	6.0

[0194]

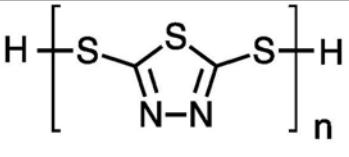
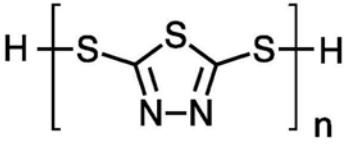
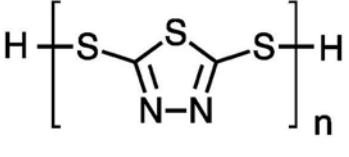
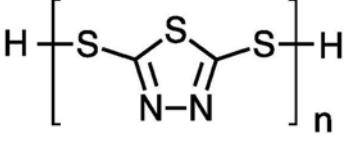
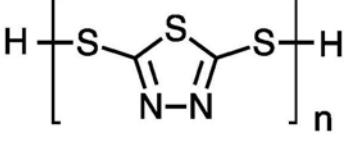
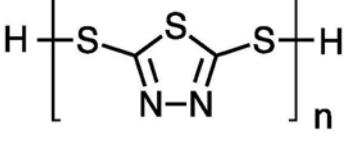
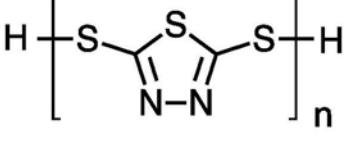
组合物	PVB ^a (g)	含硫缓蚀剂 (g)	H ₃ PO ₄ (g)	溶剂 ^b (g)
104	89.0	 (IV), 10.0	1.0	N/A ^c
105	55.0	 (IV), 20.0	10.0	15.0
106	60.0	 (IV), 20.0	6.0	14.0
107	70.0	 (IV), 20.0	4.0	6.0
108	79.0	 (IV), 20.0	1.0	N/A ^c
109	50.0	 (IV), 30.0	10.0	10.0

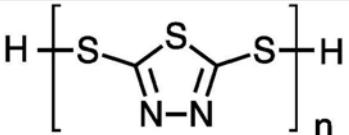
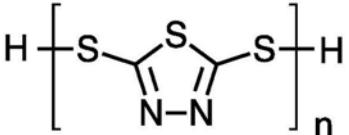
组合物	PVB ^a (g)	含硫缓蚀剂 (g)	H ₃ PO ₄ (g)	溶剂 ^b (g)
110	55.0	 (IV), 30.0	6.0	9.0
111	60.0	 (IV), 30.0	4.0	6.0
112	69.0	 (IV), 30.0	1.0	N/A ^c
[0195]	113	74.99  0.01 (V),	10.0	15.0
	114	84.99  0.01 (V),	6.0	9.0
	115	89.99  0.01 (V),	4.0	6.0
	116	98.99  0.01 (V),	1.0	N/A ^c

组合物	PVB ^a (g)	含硫缓蚀剂 (g)	H ₃ PO ₄ (g)	溶剂 ^b (g)
117	74.9		10.0	15.0
118	84.9		6.0	9.0
119	89.9		4.0	6.0
[0196]	120		1.0	N/A ^c
121	74.6		10.0	15.0
122	50.0		6.0	43.6
124	20.6		1.0	78.0

组合物	PVB ^a (g)	含硫缓蚀剂 (g)	H ₃ PO ₄ (g)	溶剂 ^b (g)	
[0197]	125	70.0 5.0	 (V),	10.0	15.0
	126	74.4 5.0	 (V),	6.0	14.6
	127	85.0 5.0	 (V),	4.0	6.0
	128	94.0 5.0	 (V),	1.0	N/A ^c
	129	65.0 10.0	 (V),	10.0	15.0
	130	70.0 10.0	 (V),	6.0	14.0
	131	80.0 10.0	 (V),	4.0	6.0

[0198]

组合物	PVB ^a (g)	含硫缓蚀剂 (g)	H ₃ PO ₄ (g)	溶剂 ^b (g)
132	89.0	 10.0 (V),	1.0	N/A ^c
133	55.0	 20.0 (V),	10.0	15.0
134	60.0	 20.0 (V),	6.0	14.0
135	70.0	 20.0 (V),	4.0	6.0
136	79.0	 20.0 (V),	1.0	N/A ^c
137	50.0	 30.0 (V),	10.0	10.0
138	55.0	 30.0 (V),	6.0	9.0

组合物	PVB ^a (g)	含硫缓蚀剂 (g)	H ₃ PO ₄ (g)	溶剂 ^b (g)
[0199]	139	60.0		4.0
		30.0	(V),	6.0
	140	69.0		1.0
		30.0	(V),	N/A ^c

[0200] ^aPVB, 获得自Eastman化学公司 (Kingsport, Tennessee (US)) 的聚乙烯醇缩丁醛。

[0201] ^b溶剂是乙醇。

[0202] ^cN/A, 不适用, 因为该混合物已经为100g (即, 100% (wt/wt))。

[0203] 实施例12. 通过线性扫描伏安法和计时电流法表征涂料制剂。

[0204] 基板制备. 选择用于施加树脂的基板是7075-T6裸铝, 因为该材料被广泛地用在航空器内部结构零件上, 其中可见包含六价铬的底漆。根据BAC5663, I型, 1类, B级制备铝板, 其需要溶剂清洁, 用红色Scotch-brite垫湿磨, 随后在Pace B-82与水1:7的溶液中冲洗。用自来水冲洗面板并且确认无水膜不破表面 (water break free surface)。喷射涂布的面板是4" × 6", 7075-T6裸合金。面板被溶剂清洁、湿磨并且用三种不同浓度的DMcT的PVB树脂涂布。制备另外的铝板 (7075-T6裸铝, 4" × 4" × 0.04") , 用于通过用甲乙酮溶剂冲洗面板旋转涂布; 用肥皂和水冲洗面板, 伴随磨损 (1:8PACE B-82:水, 手动砂磨机上的ScotchBrite垫) , 用水冲洗面板水并且风干面板。

[0205] 涂料施加和固化。在具有控制的温度和湿度的喷漆室中用Devilbiss EXL喷枪喷射PVB涂料。用丁醇溶剂稀释涂料以使得能够顺利地喷射出。涂料在约160°F下固化2小时, 随后在环境条件下固化7天。使用同位素探伤仪测量涂层的厚度。这些面板被用于中性盐雾暴露。使用喷射方法面板上的涂层厚度是不一致的并且必须被显著地稀释以使得能够使用喷枪。

[0206] 与喷射相比, 旋转涂布机提供表面上涂料的更均匀的分布。使用Chemat Technology KW-4A旋转涂布机旋转涂布随后的4" × 4" 面板。参数最初为500RPM, 10秒, 随后为2000rpm, 40秒。

[0207] 旋转涂布的面板在~250°F下固化2小时。

[0208] 涂料的开路电势-面板作为工作电极。测量具有喷射施加有0%、0.5% 和5% DMcT 装载的PVB涂料的面板的开路电势。圆形玻璃电池被夹在面板的表面, 并且填充有用磷酸缓冲液 (NaCl (5% (wt/wt) - 磷酸缓冲盐水 (PBS)) 缓冲的5% (wt/wt) NaCl电解质。工作电极连接头被连接至面板, 以便面板表现得像工作电极。Ag/AgCl甘汞参比电极和铂对电极被放置在电解质中。在这些实验之前不运行线性扫描伏安法或其他应用的电势实验以防止破坏涂层。

[0209] 线性扫描伏安法和计时电流法实验。线性扫描伏安法 (LSV) 和计时电流法——二者均使用旋转圆盘电极——用于分析涂料的缓蚀性能。

[0210] 使用夹钳电池构造使面板经受磷酸盐缓冲盐水 (5% (wt/wt) NaCl-PBS) 中 5% (wt/wt) 的氯化钠。使用 1000rpm 的 Pine Model AFMSRCE 旋转圆盘电极转子——其具有 Series G-750 稳压器, 750 微安型号 (PCI4G750-47062), 具有铂对电极、银/银氯化物参比电极和 99%+ 纯铜圆盘 (1cm^2) 旋转工作电极, 在 5 个涂布的面板上执行线性扫描伏安法 (LSV) 和计时电流法。平行试验是 EG&G Princeton Applied Research Model 636 旋转圆盘电极 (RDE) 转子——其具有 Series G-750 稳压器, 750 微安型号 (PCI4300-33026)。Gamry Framework 软件用作 LSV 和计时电流法的测量工具。

[0211] 使用在工作电极和参比电极之间施加的从 0.3 至 -1 伏特的电势扫描运行 LSV, 扫描速率为 10mV/s。通过使工作电极电势步进至 -0.8 伏特运行计时电流法, 并且测量所得的电极的电流, 1800 秒 (0.5 小时)。

[0212] LSV 和计时电流法在每个样品上重复 2-3 次, 在每次测量之间有 1 小时。在面板上面的 5% (wt/wt) NaCl/PBS 的导电性、溶解的氧和 pH 测量在所有的 LSV 和计时电流法重复之前和之后进行一次。

[0213] 通过参考并入

[0214] 本文提及的所有出版物、专利和专利申请在此通过引用以它们的整体并入, 如同每个单独的出版物、专利或专利申请明确地和单独地指示通过引用被并入。在冲突的情况下, 将参照包括本文的任何定义的本申请。

[0215] 本文使用的术语是为了仅描述具体实施方式的目的, 并且不旨在是限制性的。关于本文的基本上、任何复数和/或单数术语的使用, 本领域技术人员可以从适于上下文和/或申请的复数转换。为了清楚起见, 各种单数/复数置换可以在本文明确地阐释。

[0216] 虽然已经参考某些实施方式描述了本发明, 但是本领域技术人员将理解, 可以做出各种改变并且等价物可以被替换, 而不背离本发明的范围。另外, 可以做出许多改变以使具体情形或材料适应本发明的教导, 而不背离其范围。因此, 本发明不意欲被限于公开的具体实施方式或实施例, 但是本发明将包括落在所附权利要求的范围内的所有实施方式。

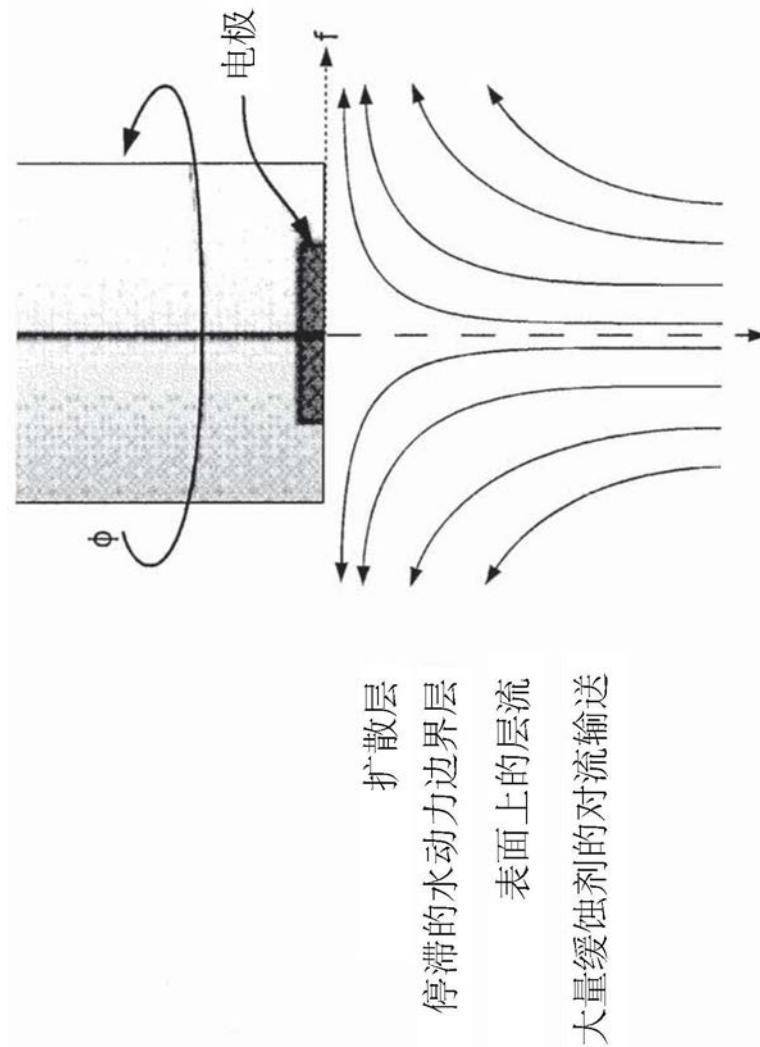
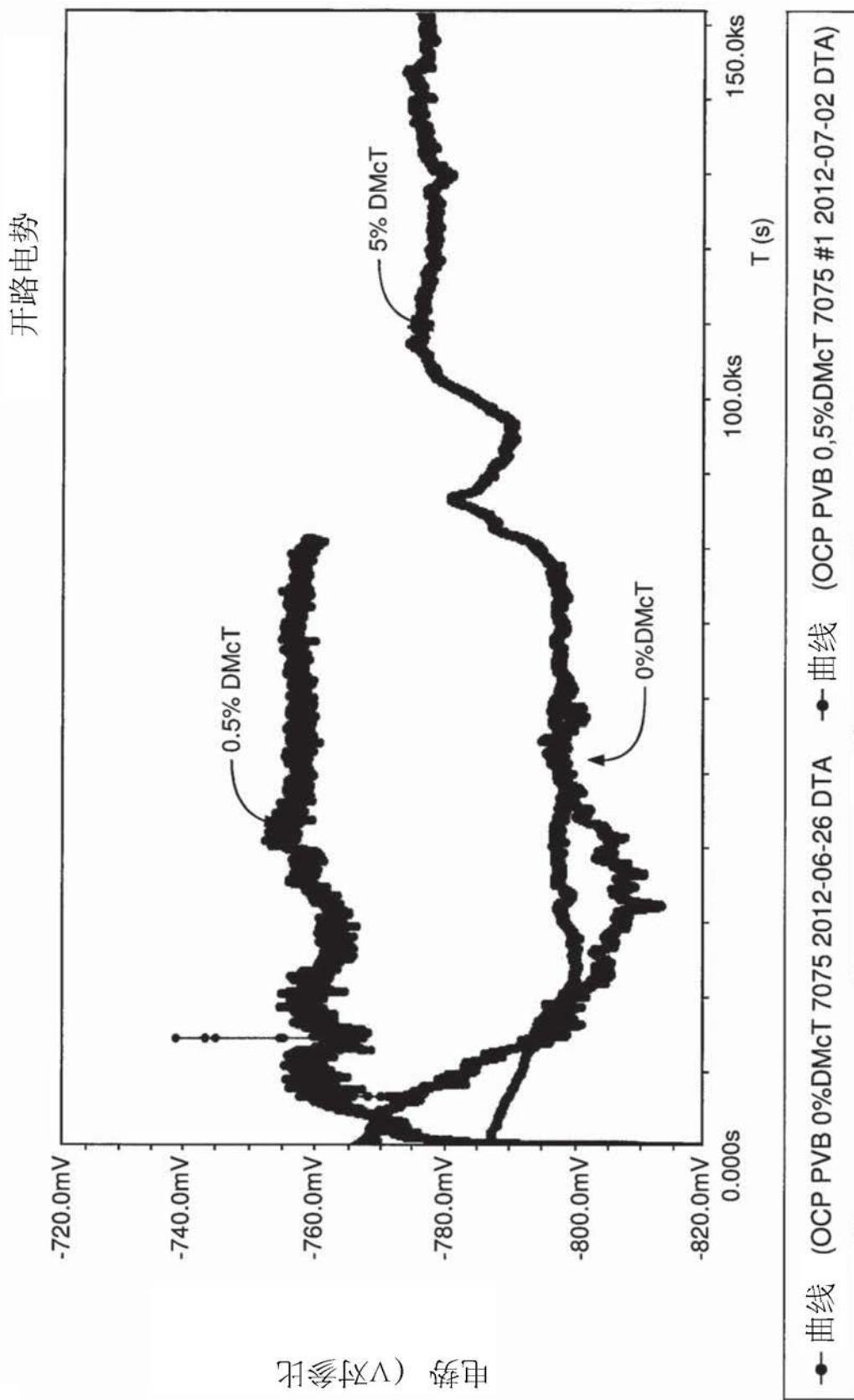


图1



计时电流法扫描

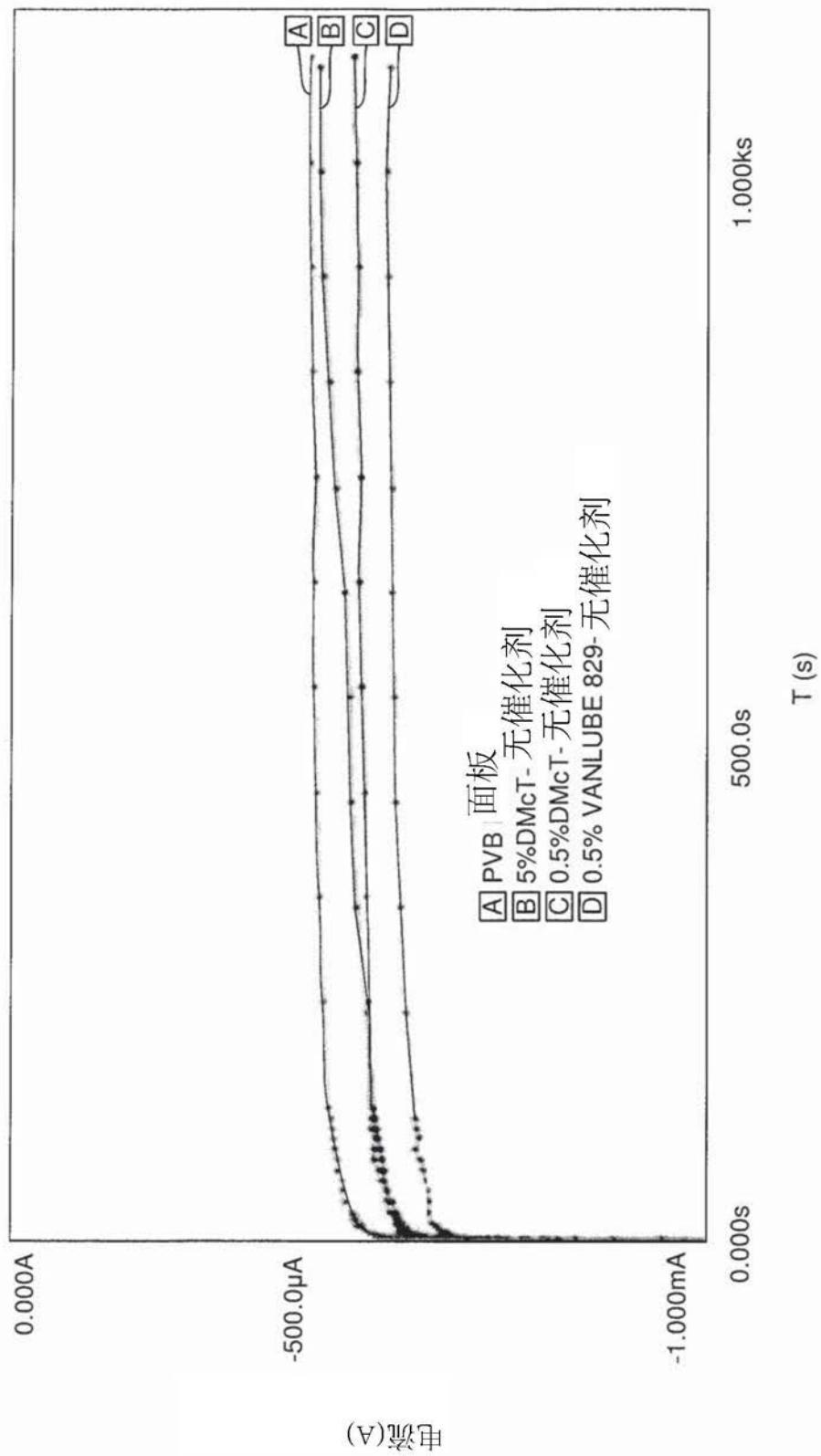


图3A

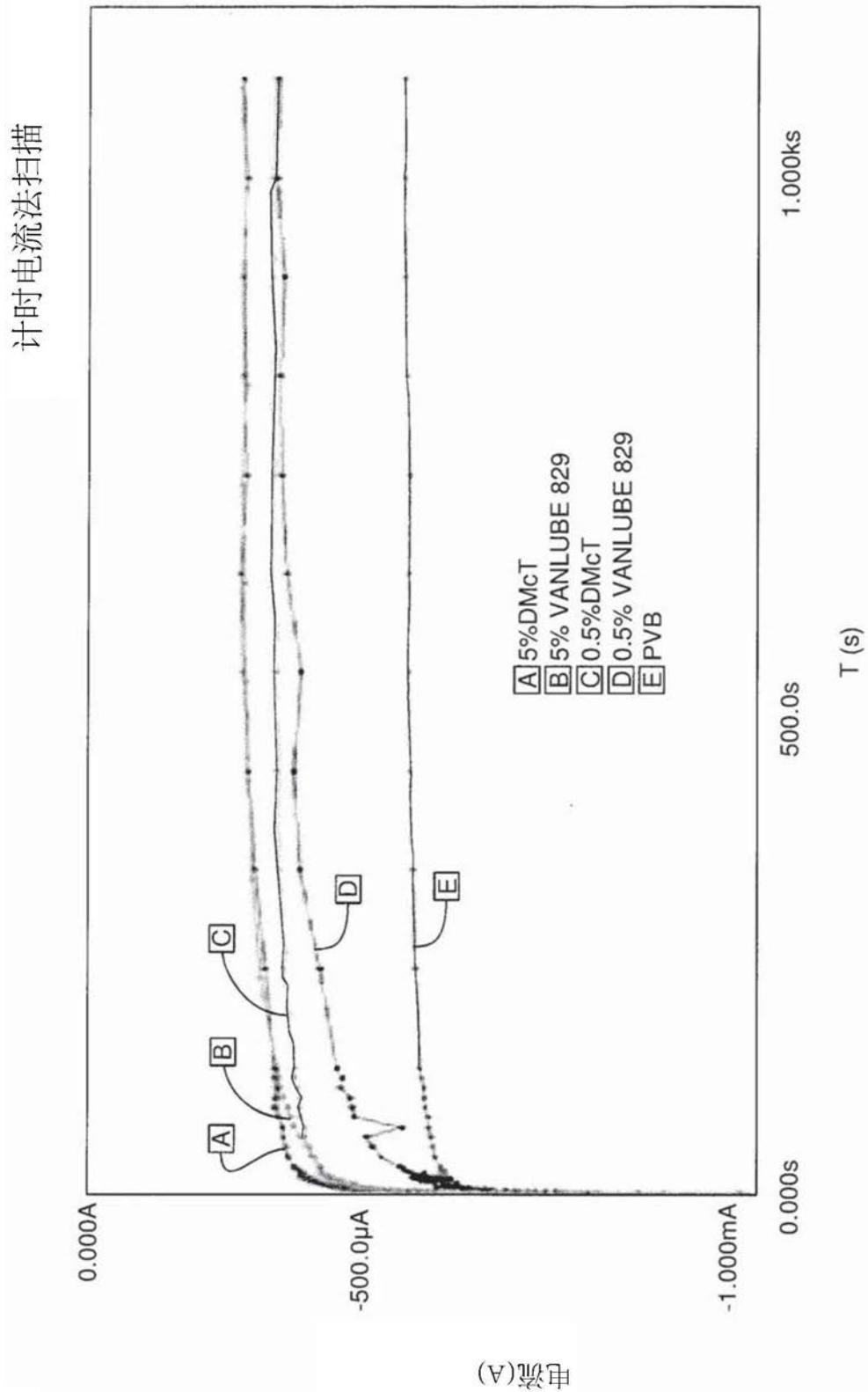


图3B

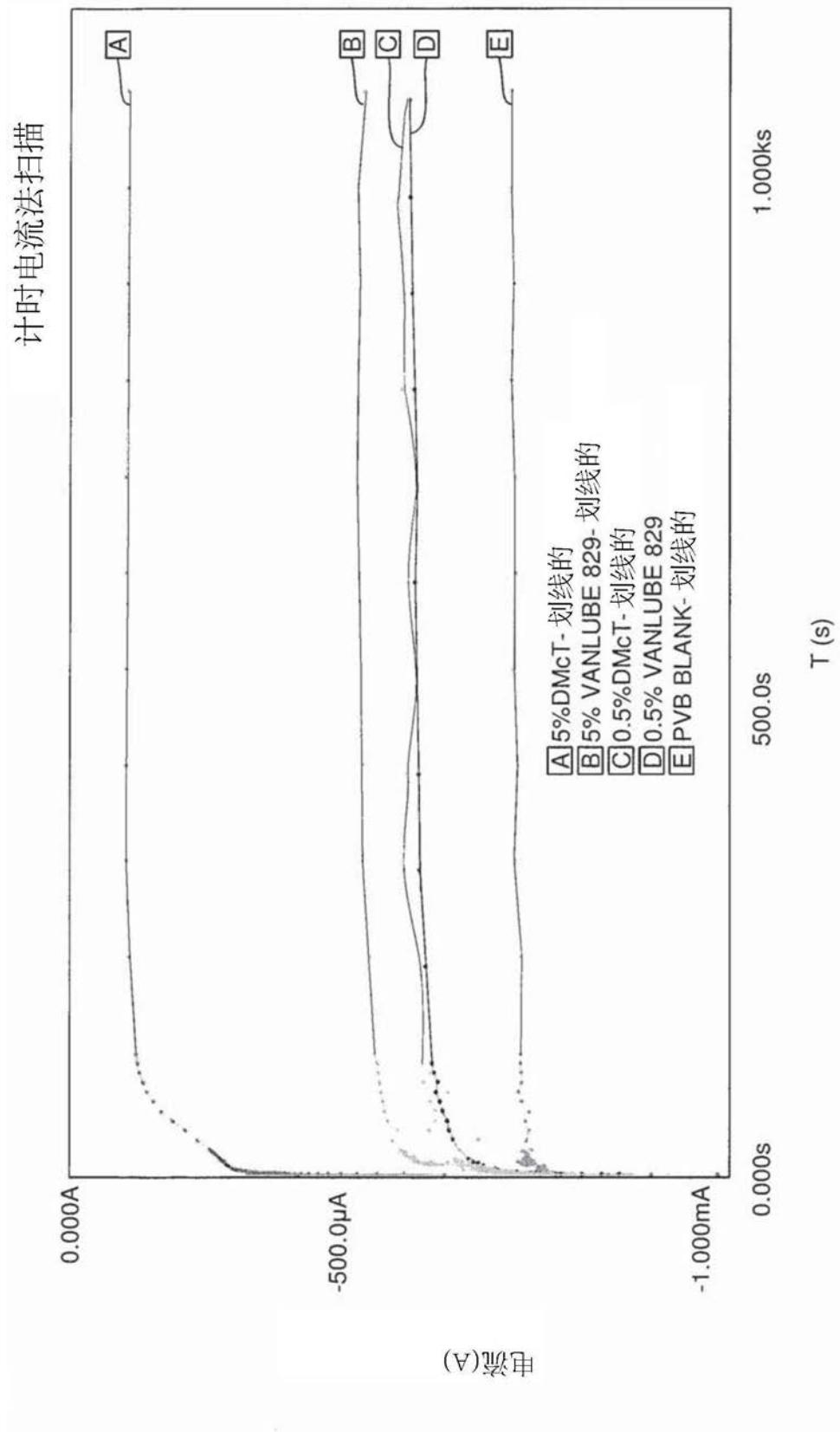


图3C

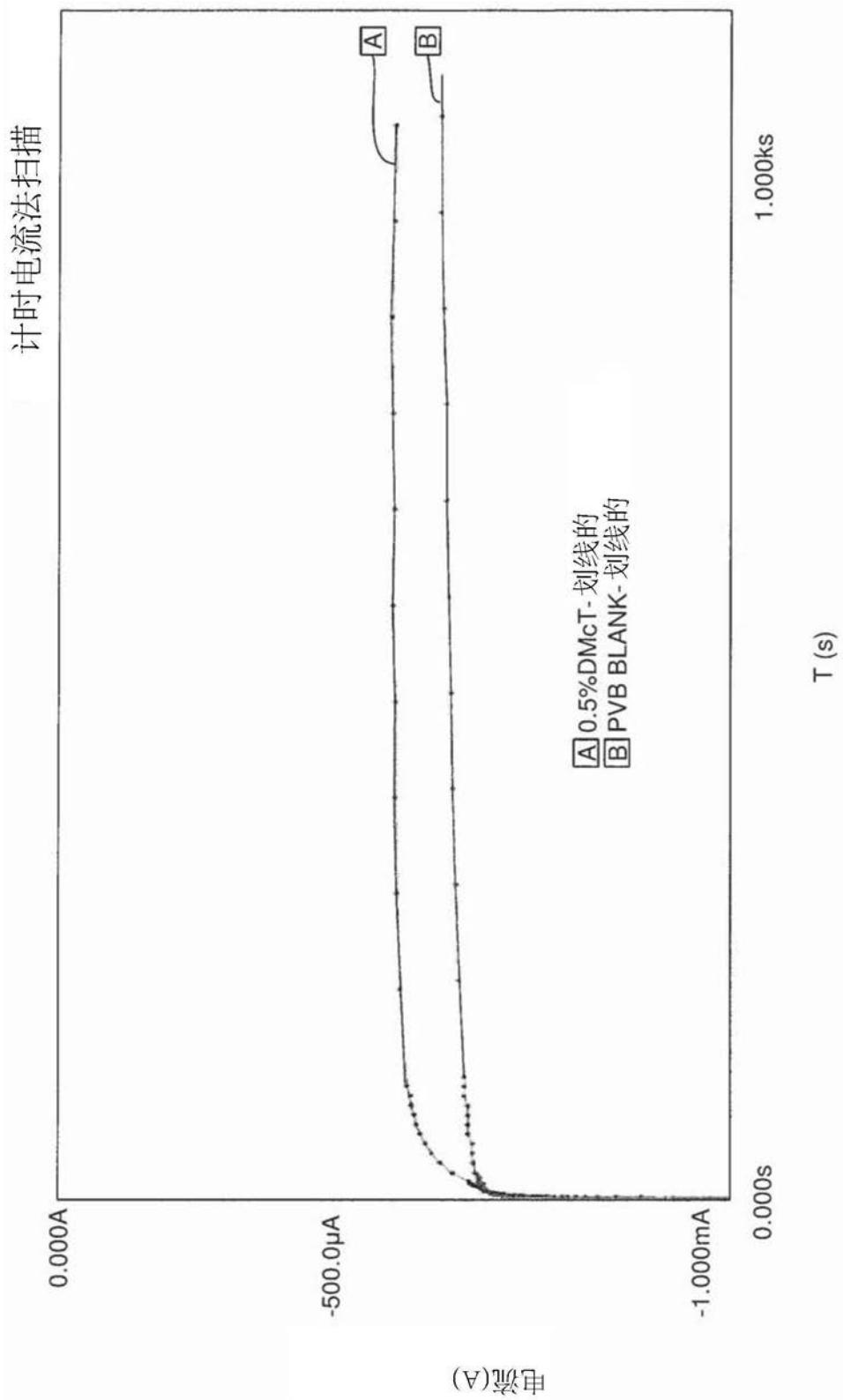


图3D

计时电流法扫描

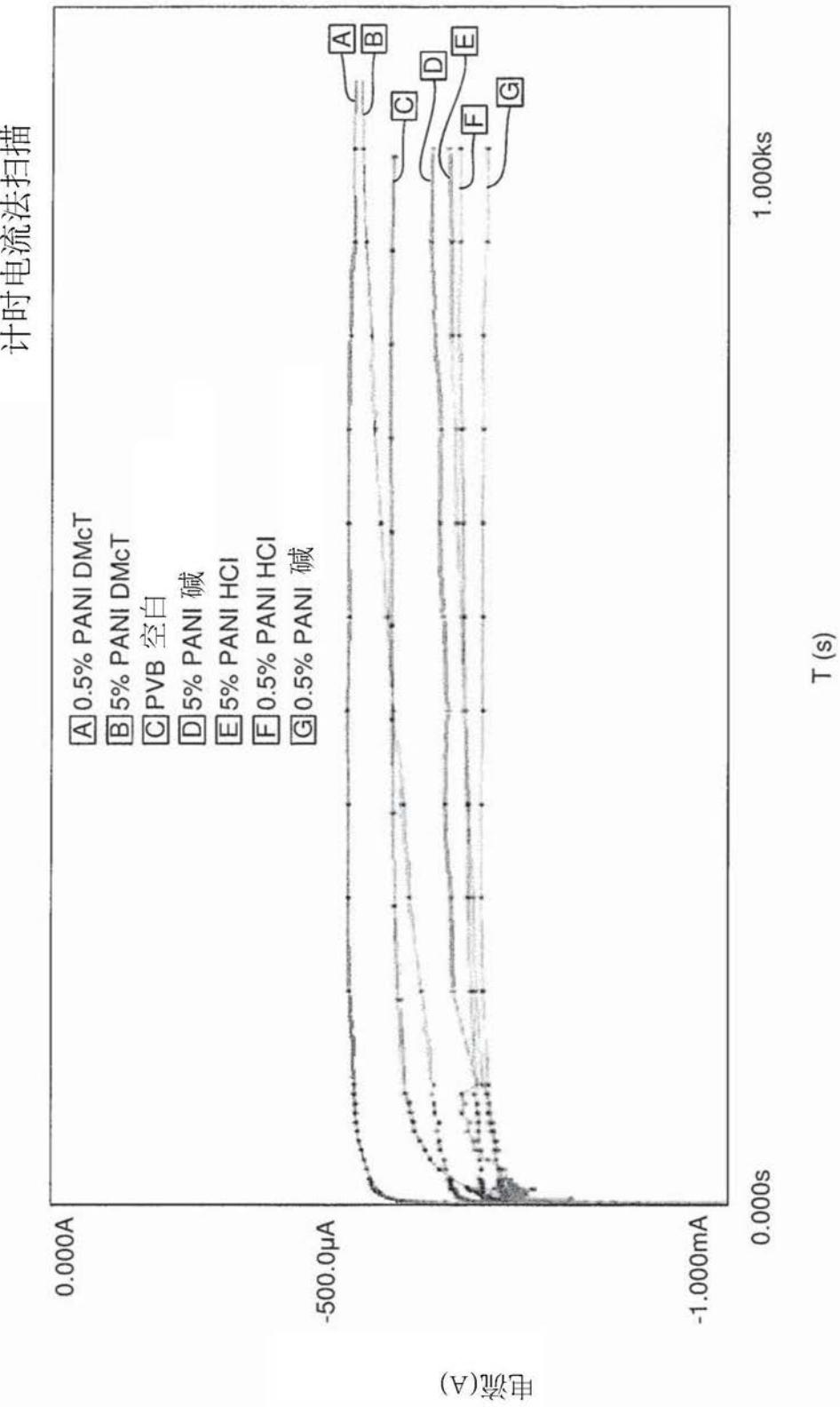


图3E