

## **Service Life Extension of Trivalent Chromium Based Passivations for Zinc**

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March 1994

The service life of trivalent blue passivations for zinc is limited mainly by the increase of dissolved iron during operation. The normally sky-blue passive layers get an increasing yellowish colour with increasing content of iron in the passivation bath. Depending on the desired quality of the zinc-plated and passivated parts, the upper limit of tolerable iron lies within 300 and 800 ppm.

Efficient control of the dissolution of iron and its effects will prolong the service life of blue passivations by several times. This *Technical Letter* presents actions which were proved in practice to extend the durability of passivation baths.

## **1 How does dissolved iron lead to yellowish passive films?**

During zinc passivation in solutions of trivalent chromium, a very thin layer of blue chromium(III)-zinc-oxide is deposited. In the presence of dissolved iron(III), the co-deposition of brown-yellow iron(III)-zinc-oxide takes place which discolours the passive layer to yellowish. Because this co-deposition is a competitive reaction, the intensity of the yellowish colour is not only determined by the absolute value of the iron concentration but also by its relation to the chromium concentration. Thus, a value of 400 ppm iron in low concentrated passivation baths leads to yellowish parts, while higher concentrated baths with the same iron content are still able to yield acceptable results.

For maximum service life, the trivalent passivation baths should not be too thin.

## **2 Where is iron dissolved from?**

In rack lines, the primary iron drag-in is produced by dissolution of parts fallen into the bath. Secondly, iron dissolves from zinc free areas of tubes or other parts with deep cavities, even during normal operation.

Barrel lines are not as sensitive as rack lines because barrels should (normally!) not loose parts and most cavities should be covered with zinc properly during barrel plating. Also, the drag-out is higher using barrels, thus the solution is "rejuvenated" regularly. But: passing back of rinse water to the bath, drag-in of poor quality rinse water with a high iron content and incompletely closing barrel doors, lead usually to a significant rise of iron concentration.

## **3 Actions against the dissolution of iron**

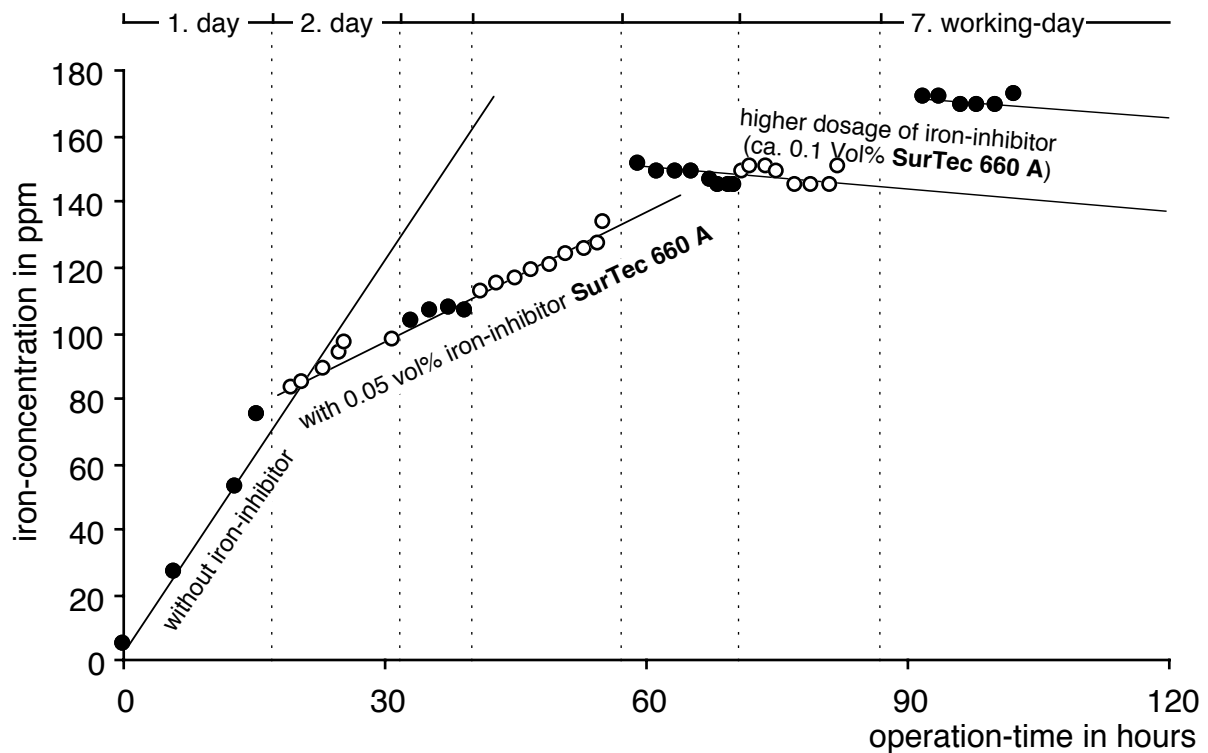
### **3.1 Maintenance of the Bath**

The main iron drag-in can be avoided by a thorough bath control. Parts fallen into the solution should be taken out immediately, at least once a shift. Good filtration of the zinc baths and meticulous rinsing are important to reduce the drag-in of iron hydroxide.

### **3.2 Use of Iron Inhibitor *SurTec 660 A***

In trivalent blue chromate solutions of *SurTec 660*, *661*, *662*, *664* or *667*, the corrosive iron dissolution of parts or uncovered areas is hindered effectively by addition of 0.05 - 0.2 Vol% iron inhibitor *SurTec 660 A* to the bath.

The diagram shows the rise of iron concentration in a rack bath with *SurTec 660* before and after addition of 0.05 Vol% iron inhibitor *SurTec 660 A*. The increase of iron after addition was 3 times slower!



**Diagram:** Iron content of a rack bath with *SurTec 660* (trivalent blue passivation of zinc); 5000 l bath of an acid zinc line in a job shop.

Further increase of the inhibitor *SurTec 660 A* hindered the iron dissolution so effectively that by build-in into the passive layer and drag-out at daytime, more iron was lost than dissolved, thus leading to a decrease of the iron content. During the night it increased again because parts fallen into the solution had not been taken out. This again illustrates the importance of a good bath care.

The inhibitor covers bare iron areas hindering the acidic attack. So it is dragged out of the solution and has to be maintained. Best and easiest way of dosage will be together with the chromium(III) concentrate, in the same relation as for bath make-up. If for example a bath was made-up with 7 Vol% *SurTec 660* chromium(III) concentrate and 0.07 Vol% *SurTec 660 A* iron inhibitor, with 1 litre concentrate 10 ml iron inhibitor has to be added.

For easier handling *SurTec 661* is available, which is the chromium(III) concentrate plus 1 % iron inhibitor. At a bath make-up with 5-10 Vol%, an inhibitor concentration of 0.05-0.1 Vol% is reached which should be sufficient for most purposes. If the solution was made-up thinner, or severe iron drag-in was expected, additional inhibitor *SurTec 660 A* is necessary and should be added before treating the critical parts.

### 3.3 Masking of the Iron Content by Citric Acid

Citric acid can be used to mask already dissolved iron in the passivation bath. Citric acid is a weak complexing agent hindering the co-deposition of iron in the passive layer (which would create the yellowish colour). In baths with *SurTec 660*, more than 800 ppm iron can be masked with citric acid without appearance of yellowish parts. 800 ppm iron without citric acid normally lead to intense yellowish passive layers.

As an overdosage of citric acid could accelerate the iron dissolution, ca. 100 ppm of unmasked iron has to be kept in the bath. For masking 100 ppm iron, 375 g citric acid is required per 1000 l bath (e.g. 1 l *SurTec 660 C*, an aqueous solution of 375 g/l citric acid). If citric acid was already added to the bath solution, this amount has to be subtracted.

At an iron concentration of x ppm,  $(x-100) \cdot 0.01$  l citric acid solution *SurTec 660 C* is required per  $(x-100)$  ppm for 1000 l bath volume.

**Example 1:** The iron content is 150 ppm, no citric acid was used up to now. So per each 1000 l bath volume,  $(150 - 100) \cdot 0.01$  l = 0.5 l *SurTec 660 C* should be added. By this way, 100 ppm iron remain unmasked, 50 ppm iron is masked by the addition of 0.5 l *SurTec 660 C* per 1000 l bath volume.

**Example 2:** 1.5 l *SurTec 660 C* per 1000 l bath has already been added, and the iron content is analysed as 350 ppm. For this amount of iron:  
 $(350 - 100) \cdot 0.01$  l = 2.5 l *SurTec 660 C* would be required. 1.5 l per each 1000 l are already in the solution, so only  $2.5$  l -  $1.5$  l = 1 l *SurTec 660 C* per 1000 l have to be added.

Please be advised that the addition of citric acid results in strange appearance with some trivalent blue passivations. Therefore, *SurTec* can recommend the use of citric acid or *SurTec 660 C* only for its own trivalent blue passivations *SurTec 660*, *661* and *662*. In the blue passivations *SurTec 664* and *667*, citric acid must **not** be applied.

## 4 Conclusion

By good bath control together with the use of the iron inhibitor *SurTec 660 A*, the service life of trivalent blue passivations can be extended significantly. With citric acid, it is possible in some baths to mask already dissolved iron substantially, leading to further service life prolongation. A guide to longer durability involve:

1. measuring the iron content with AAS or just semiquantitative with test stripes, e.g. Merckoquant Iron Test.
2. adapting the dosage of the iron inhibitor *SurTec 660 A* by tracing the iron concentration. If the rise is too fast a higher dosage must be applied.
3. masking already dissolved iron with citric acid. Keep 100 ppm unmasked!!
4. of course, removing parts fallen into the bath as soon as possible.

Following these guidelines, the service life of *SurTec 660* can be extended by 3 times minimum. "Champion" up to now is a 5000 l *SurTec 660* rack bath, 2 shifts/day, permanent operation, 50-60 % tubes and pipes, reaching a service life of more than 25 weeks.

# SurTec 66x

## Control of Trivalent Blue Chromates

### Make-Up

Concentration\*: (summer): \_\_\_\_\_ vol% at \_\_\_\_\_ °C

(winter): \_\_\_\_\_ vol% at \_\_\_\_\_ °C

pH-Value: **1.8** (adjust with nitric acid, see back side)

Immersion time: \_\_\_\_\_ s

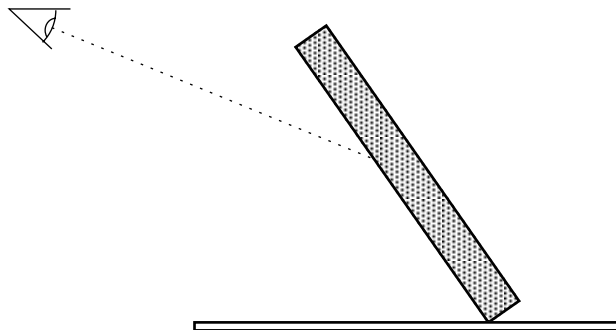
Transfer time: \_\_\_\_\_ s

\* During operation the nominal value decreases by 0.5-1 vol% on 5 g/l increasing zinc. It decreases on 5 °C increasing temperature or increases on 5 °C decreasing temperature by 0.5-1 vol%.

### Dosage by sight control of the parts

The iridescent colour of the chromate layer is an indication of its thickness and therefore is an excellent hint for adjusting the optimal operating conditions.

Place a part inclined on a white sheet of paper and look from an angled point of view down at the part.



Adjust the chromating bath in dependence on the colour effect according to the table.

Iridescent colour	Cause	Actions
golden	chromate layer much too thin	increase concentration <b>and</b> immersion time
reddish-golden	chromate layer too thin	increase concentration
reddish-blue	chromate layer little too thin	small increase of concentration <b>or</b> immersion time
<b>blue</b>	<b>chromating optimal</b>	<b>no actions</b>
greenish-blue	chromate layer little too thick	small decrease of immersion time
greenish	little overchromating	decrease of immersion time; 1. aid: pH-value may be temporarily decreased (but not beyond 1.65) while decreasing the concentration by working-out. dilute the bath, when not satisfied
greenish-yellow	heavy overchromating	dilute the bath

**IMPORTANT:** It is necessary to distinguish between the golden and the yellowish colour, therefore observe the parts very carefully in either case.

# SurTec 66x

## pH-Adjustment of Trivalent Blue Chromates

desired pH	1,6	1,7	1,8	1,9	2	2,1	2,2
meas. pH	amount of NaHCO <sub>3</sub> in kg per 1000 l bath						
1	6,29	6,72	7,07	7,34	7,56	7,73	7,87
1,1	4,56	5,00	5,34	5,62	5,83	6,01	6,14
1,2	3,19	3,62	3,97	4,24	4,46	4,63	4,77
1,3	2,10	2,53	2,88	3,15	3,37	3,54	3,68
1,4	1,23	1,67	2,01	2,29	2,50	2,68	2,81
1,5	0,55	0,98	1,33	1,60	1,82	1,99	2,13
1,6		0,43	0,78	1,05	1,27	1,44	1,58
1,7	0,46		0,34	0,62	0,84	1,01	1,15
1,8	0,83	0,37		0,27	0,49	0,66	0,80
1,9	1,12	0,66	0,29		0,22	0,39	0,53
2	1,35	0,89	0,52	0,23		0,17	0,31
2,1	1,54	1,08	0,71	0,42	0,18		0,14
2,2	1,68	1,22	0,85	0,56	0,33	0,15	
2,3	1,80	1,34	0,97	0,68	0,45	0,26	0,12
2,4	1,89	1,43	1,06	0,77	0,54	0,35	0,21
2,5	1,97	1,50	1,14	0,84	0,61	0,43	0,28
2,6	2,02	1,56	1,19	0,90	0,67	0,49	0,34
2,7	2,07	1,61	1,24	0,95	0,72	0,53	0,39
2,8	2,11	1,64	1,28	0,99	0,75	0,57	0,42
2,9	2,14	1,67	1,31	1,01	0,78	0,60	0,45
3	2,16	1,70	1,33	1,04	0,81	0,62	0,48
3,1	2,18	1,72	1,35	1,06	0,82	0,64	0,49
3,2	2,19	1,73	1,36	1,07	0,84	0,65	0,51
3,3	2,20	1,74	1,37	1,08	0,85	0,67	0,52
3,4	2,21	1,75	1,38	1,09	0,86	0,68	0,53
3,5	2,22	1,76	1,39	1,10	0,87	0,68	0,54
3,6	2,23	1,76	1,40	1,10	0,87	0,69	0,54
3,7	2,23	1,77	1,40	1,11	0,88	0,69	0,55
3,8	2,23	1,77	1,40	1,11	0,88	0,70	0,55
3,9	2,24	1,78	1,41	1,12	0,88	0,70	0,55
4	2,24	1,78	1,41	1,12	0,89	0,70	0,56

amount of 53 % HNO<sub>3</sub> in kg per 1000 l bath

Because of the buffering property of dissolved zinc, the actual amounts may be higher to a small extent than given in the table above.