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International Co-operative Programme on Effects on Materials, including Historic and Cultural Monuments

Evaluation of decay of painted systems for steel after 1 and 2 years of exposure (1997-1999)

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Contents

Page

Summary

International Co-operative Programme on Effects on Materials, including Historic and Cultural Monuments is a research project launched by the Executive Body for the Convention on Long-range Transboundary Air Pollution for studying the effect of airborne pollution on materials. The study is in its second phase and this report covers the results after one and two years of exposure of painted panels.

The paint system exposed has been steel panels coated with two layers alkyd paint (total 80 μm).

The damage of the paint system has been evaluated by using the well-established ASTM-standards on samples exposed.

Damage from the cut is observed at all test sites and after two years ASTM values from 9 to 6 are observed. A manual evaluation of the results compared to the environmental parameters seems to indicate that the damage is affected by air pollution like in the big cities. However the damage is also surprisingly high at rural sites particularly at sites, with high amount of rain.

Filiform corrosion, shown as thin whiskers under the paint film from the cut, are more dominated in the second phase of the programme. Surprisingly they turn up on all the new sites in the programme except for the mountain site Chaumont in Switzerland, but only for 1/3 of the sites from the first phase. For the time being we have no good explanation for these changes in the corrosion pattern. However, since we have a new batch of samples prepared by another company this time we can not be sure that the samples are completely comparable.

Cracking of the corrosion protection paint films has been observed on samples from the Tel Aviv site after two years but was never observed in the first phase of the programme.

A comparison between the results from the first and second phase shows that the damages are less severe this time. The same trend has earlier been shown for the air pollution parameters. The reduction is highest in the most polluted sites like Milan and Kopisty but is also substantial at the rural EMEP sites Birkenes, Aspvreten and Ähtäri in Scandinavia.

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1. Introduction

Airborne acidifying pollutants are known to be one major cause of corrosion of different materials including the extensive damage that has been observed on historic and cultural monuments. In order to fill some important gaps of knowledge in this field the Executive Body for the Convention on Long-range Transboundary Air Pollution decided to launch an international co-operative programme. The programme was started in September 1987 and has involved exposure at 39 test sites in 12 European countries and in the United States and Canada. The first phase of the exposure programme was finished in 1995. However, during the eight years where the exposure programme has been carried out, a large change in the pollution situation in Europe has been observed. The SO_2 concentrations have been drastically reduced, while the changes in the NO_2 and O_3 levels have been minor. This new pollution situation where the importance of NO_2 and O_3 were in focus, led to a proposal of a second phase of the programme. The new 4 years exposure project was launched in the fall 1997 with redefined environmental measuring programme, a better combination of test sites for field exposure and with several new countries as partners in the project (Swedish Corrosion Institute rev. 1993).

The aim of the new programme is to perform a quantitative evaluation of the effect of NO_x and other pollutants like ozone and sulphur pollutants in combination with climatic parameters on the atmospheric corrosion of important materials. For this purpose, measurements of gaseous pollutants, precipitation and climate parameters have been initiated at or nearby each test site, together with evaluation of corrosion of the exposed test materials at each site.

A Task Force is organising the programme with Sweden as lead country and Swedish Corrosion Institute serving as the Main Research Centre. Sub-centres in different countries have been appointed, each responsible for their own material group. The material groups are:

Structural metals:

- Steel and zinc for trend analyses (Sub-centre responsible for evaluation: SVUOM Praha as., Prague, Czech Republic).
- Zinc for 4 year's of exposure (EMPA Corrosion/Surface Protection, Dübendorf, Switzerland).
- Copper and cast bronze (Bayerisches Landesamt für Denkmalpflege, Munich, Germany).

Stone materials: Portland limestone (Building Research Establishment Ltd., Department of Environment, Waterford, United Kingdom).

Paint coatings: Steel with silicon alkyd paint (Norwegian Institute for Air Research, Kjeller, Norway).

Glass materials: Two types of glass M1 and M3 (Institute of Chemistry, Academy of Fine Arts, Vienna, Austria)

Norwegian Institute for Air Research has been the sub-centre for the environmental database through the whole programme.

The exposure programme has fewer materials than in the first phase, mainly because we have to use materials which are sensitive enough for having sufficient reaction within 4 years of exposure.

2. Materials

The paint system tested was steel panels coated with two layers of alkyd paint (total 80 μm). The edges were sealed with an extra thick coating to prevent corrosion from the edges.

3. Evaluation

The test panels have a horizontal cut on the front surface and are painted with alkyd on both sides. The painted panels are only freely exposed since the expected lifetime in sheltered position is much longer than 4 years.

The evaluation has been focused on the spread of damage around an artificial cut through the paint measured in mm and given as the ASTM rating numbers from RN = 10 to RN = 0 (ASTM 1987). Other forms of damages are only reported when the damages seem important for the total evaluation of the attack. The results of the evaluation for one and two years are given in Table 1.

4. Results

4.1 Damage located to the cut

Table 1 gives the results for 1 and 2 years of exposure.

Table 1: The results for spread from cut for the alkyd painted panels after one and two years of exposure.

			1997-98	1997-98	1997-99	1997-99
Site no	Country	Place	mm	ASTM D 1654-79a	mm	ASTM D 1654-79a
01	Czech Republic	Prague-Bech.	3	8	4	7
03	Czech Republic	Kopisty	4	7	6	6
05	Finland	Ähtari	3	8	4	7
07	Germany	Waldhof L.	3	8	4	7
09	Germany	Langenfeld	3	8	4	7
10	Germany	Bottrop	3	8	5	7
13	Italy	Rome	2.5	8	2.5	8
14	Italy	Casaccia	3	8	3	8
15	Italy	Milan	3	8	3	8
16	Italy	Venice	2	9	3	8
21	Norway	Oslo	2	9	2.5	8
23	Norway	Birkenes	4	7	6	6
24	Sweden	Stockholm	3	8	3	8
26	Sweden	Aspvreten	4	7	4.5	7
27	United Kingdom	Lincoln Cathedral	5	7	6	6
31	Spain	Madrid	1.5	9	2	9
33	Spain	Toledo	1.5	9	2	9
34	Russia	Moscow	3.5	7	3.5	7
35	Estonia	Lahemaa	3	8	5	7
36	Portugal	Lisbon	5	7	4	7
37	Canada	Dorset	3.5	7	3.5	7
40	France	Paris	1.5	9	3	8
41	Germany	Berlin	4	7	3	8
43	Israel	Tel Aviv	2.5	8	3	8
44	Norway	Svanvik	3	8	3.5	7
45	Switzerland	Chaumont	2	9	2.5	8
46	United Kingdom	London	5	7	4	7
47	USA	Los Angeles	2.5	8	2.5	8
49	Belgium	Antwerp	2.5	8	3	8

The spread from the cut in mm reported is the mean distance between the blisters above and below the cut. It seems to be a trend to more damage in the big cities and to the sites with more humid conditions. From Table 1 it is obvious that little have happened to the panels the second year. A closer analysis of the environmental impact to the paint damage will hopefully be easier to do after the next intake in 2001.

4.2 Filiform corrosion

While flaking and blistering were the dominating form for damage in the first phase of the programme, filiform attack occurs more frequently in the second phase. Figure 1 show a typical example of this type of attack taken from the two years of exposure at Lincoln Cathedral. Table 2 gives the results of filiform corrosion for the test sites and the evaluation technique used is illustrated in Figure 2.

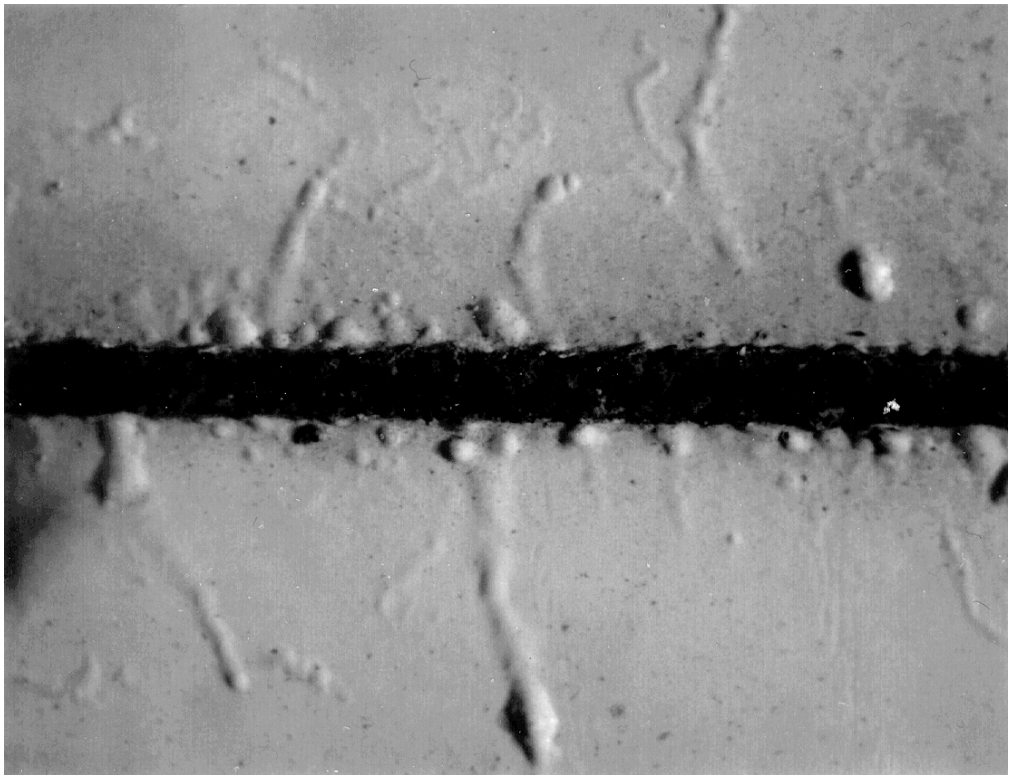

Figure 1: Filiform attack from the cut on alkyd painted panels at site Lincoln Cathedral.

Evaluation techniques for filiform corrosion are described in ISO standard 4623. In our evaluation we divide the results into four groups. First group is panels without any sign of filiform corrosion marked “none” in Table 2. Second group is panels where beginning sign of threads is observed in microscope, marked “slight” in Table 2. Third group is panels with filiform corrosion on one side of the cut. The spread from the cut of the longest thread is measured in millimeter in the same way as the measurement of m_1 in Figure 1. The value is given in Table 2 and marked with the exponent 1. The fourth group is illustrated in Figure 2. The longest thread in both directions is measured, m1 and m2. The mean value (M) given in Table 2 is marked with the exponent 2 and is calculated from the total spread of the longest thread in both directions (m) from the equation M=(m-1)/2 since the width of the cut, is 1 millimeter.

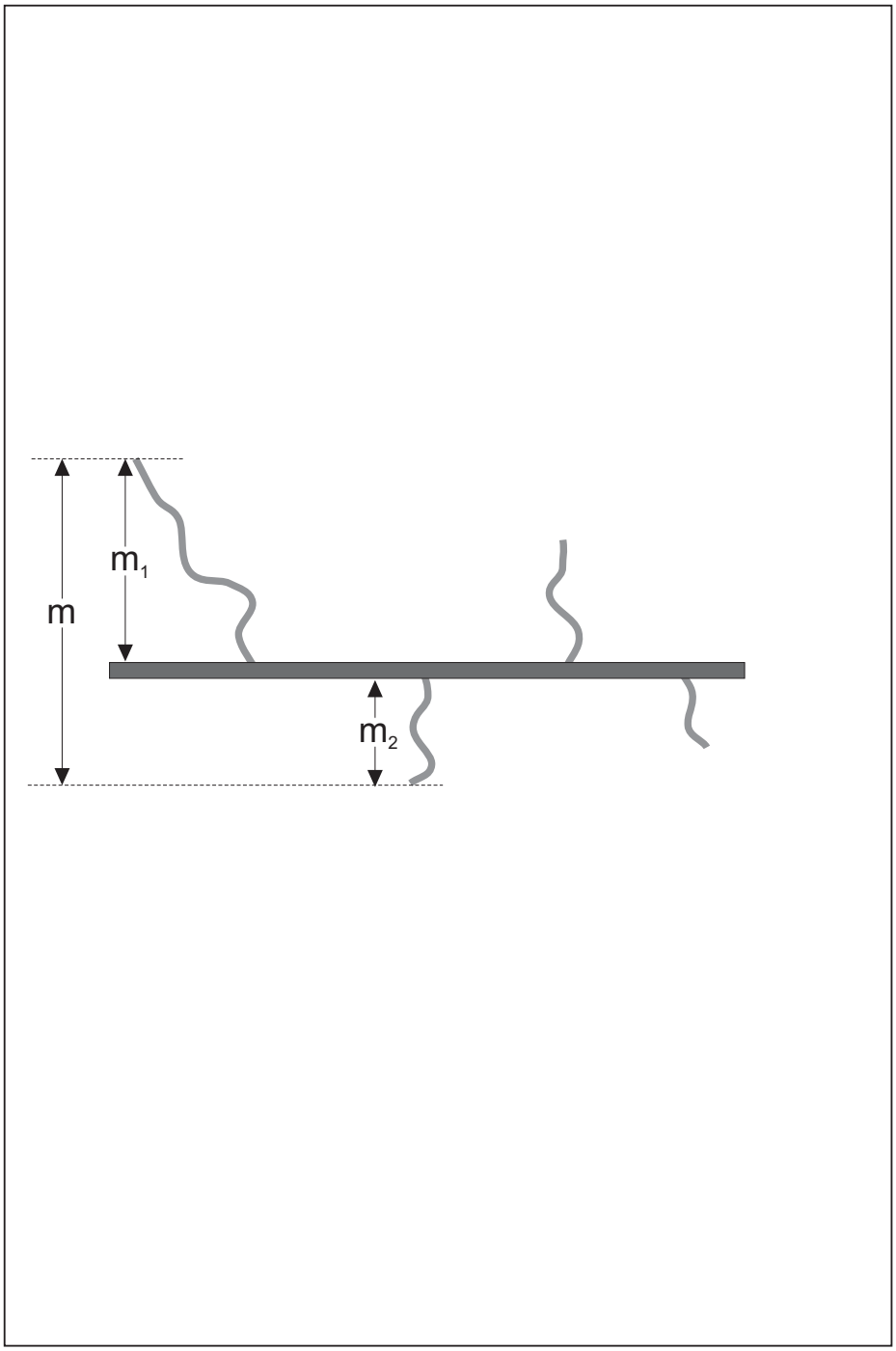

Figure 2: Illustration of evaluation of filiform corrosion on testpanel with cut.

Table 2: The results for filiform attack on the alkyd painted panels after one and two years of exposure.

			1997-98	1997-99
Site no	Country	Place	mm	mm
01	Czech Republic	Prague-Bech.	none	none
03	Czech Republic	Kopisty	none	none
05	Finland	Ähtari	2[1] (only one panel)	none
07	Germany	Waldhof L.	none	slight
09	Germany	Langenfeld	none	slight
10	Germany	Bottrop	none	5[1] (only one panel)
13	Italy	Rome	none	none
14	Italy	Casaccia	4-8[1] (only one panel)	8[1] (only one panel)
15	Italy	Milan	none	none
16	Italy	Venice	none	4[1] (only one panel)
21	Norway	Oslo	none	none
23	Norway	Birkenes	9[1] (only one panel)	none
24	Sweden	Stockholm	none	none
26	Sweden	Aspvreten	none	2.5[1](only one panel)
27	United Kingdom	Lincoln Cathedral	15[2]	20[2]
31	Spain	Madrid	none	none
33	Spain	Toledo	none	none
34	Russia	Moscow	7[1] (only one panel)	none
35	Estonia	Lahemaa	3[1]	none
36	Portugal	Lisbon	17-22[2]	5[2]
37	Canada	Dorset	none	none
40	France	Paris	16[2]	18[2]
41	Germany	Berlin	4[1] (only one panel)	10[2]
43	Israel	Tel Aviv	15[2](only one panel)	11[2]
44	Norway	Svanvik	6-21[2]	7[1] (only one panel)
45	Switzerland	Chaumont	none	none
46	United Kingdom	London	23[2]	20-25[2]
47	USA	Los Angeles	10[2]	6[2]
49	Belgium	Antwerp	15[2]	11[2]

Exponent 1= filiform corrosion on one side of the cut
Exponent 2= filiform corrosion on both sides of the cut

Filiform attack will reach further out from the cut than the blisters and is observed for 13 sites after two years for the second phase. Among the sites that are included in both periods, 3 had filiform attack in the first phase 1987-88, while 6 sites had that attack in the second phase. For the 8 new sites in added to the programme 7 of the sites had filiform corrosion both after one and two years. Filiform corrosion is complicated to evaluate since it is large deviation been the parallels. Further the distinctness of the filiform corrosion differed from one panel to the next. Often filiform corrosion may occur only on one of the three panels. This is marked in Table 2.

4.3 Dirt

Dirt has been observed on panels for several sites. The evaluation is a visual inspection and for some sites like Venice and some of the EMEP background sites the dirt is black fungus. At Kopisty soot is observed and for the cities, corroded steel particles may give a stain as spots to the surface.

4.4 Cracking

The alkyd paint has got severe general cracking of the paint film at the test site 43 Tel Aviv. This is a phenomena not observed at any of the sites during the first phase of the exposure programme.

5. Trends

In Table 3 the results of damage from cut from the test sites, which are included in both phases of the programme, are given. The results listed are the values from one and two years of exposure. The table can be used for comparison of trends for the different sites. The results from the first phase of the programme (1987-88) are earlier reported (Henriksen et al. 1998).

In Figure 3 a scatterplot showing the results after two years of exposure in the two phases of the programme is given.

Table 3: The results from the alkyd painted panels after one and two years of exposure in 1997-99 and 1987-89.

			1997-98	1987-88	1997-99	1987-89
Site no	Country	Place	mm	mm	mm	mm
01	Czech Republic	Prague-Bech.	3	5.5	4	9-12
03	Czech Republic	Kopisty	4	10-14	6	16-21
05	Finland	Ähtari	3	5-6	4	6-7.5
07	Germany	Waldhof L.	3	7	4	7-8
09	Germany	Langenfeld	3	4.5	4	5
10	Germany	Bottrop	3	5-6	5	7.5
13	Italy	Rome	2.5	2.5	2.5	2.5-3
14	Italy	Casaccia	3	3-5	3	4
15	Italy	Milan	3	8-9	3	10-12
16	Italy	Venice	2	5.5	3	5-7.5
21	Norway	Oslo	2	5	2.5	5-6
23	Norway	Birkenes	4	9	6	11-12
24	Sweden	Stockholm	3	5	3	5
26	Sweden	Aspvreten	4	6	4.5	6-10
27	United Kingdom	Lincoln Cathedral	5	5	6	5
31	Spain	Madrid	1.5	4	2	3.5-4
33	Spain	Toledo	1.5	2-3	2	2
34	Russia	Moscow	3.5	2-2.5	3.5	3
35	Estonia	Lahemaa	3	5-7	5	5.5-7
36	Portugal	Lisbon	5	3-4	4	3-4
37	Canada	Dorset	3.5	4-4.5	3.5	5

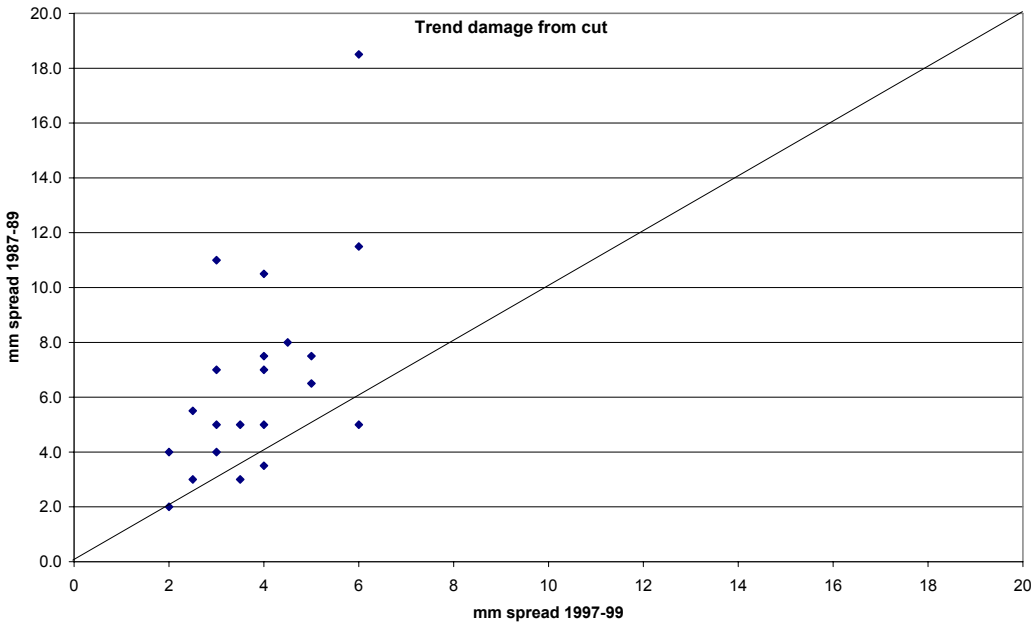

Figure 3: The spread in damage from cut after two years of exposure for the period 1987-89 against 1997-99

From the data in Table 3 and Figure 3 it is obvious that most sites have had a positive trend for the last ten years. A slight change to more corrosion is observed on the sites 27 Lincoln Cathedral, site 34 Moscow and site 36 Lisbon. Particularly the sites with high attack in the first phase have got the largest reduction.

6. Discussion

An evaluation of the deterioration of paint by use of ASTM standards has some limitations. Even if the deterioration processes themselves are irreversible, the evaluation techniques based on visual inspections of changes around a cut using simple tools are not able to record the processes correctly. A major problem is that the processes interact with each other and the environment can affect the resulting damages in different ways in different climate. An example is the new Tel Aviv site where the cracking of the paint occurs in a way never observed in the first phase of the programme.

For the statistical dose-response evaluation we have chosen the deterioration parameter damage from the cut since this was the parameter where the results were expected to develop first. It is also an irreversible process that is easy to follow. Damage from the cut is observed at all test sites and after two years ASTM values from 9 to 6 are observed. The highest damage of painted panels is observed in the big cities with high air pollution (Henriksen et al 1997 and 2000). However the damage is also surprisingly high at rural sites particularly at sites with high amount of rain.

Filiform corrosion, shown as thin whiskers under the paint film from the cut, are more dominating in the second phase of the programme. Surprisingly they turn up on all the new sites in the programme except for the mountain site Chaumont in Switzerland, but only for 1/3 of the sites from the first phase. For the time being we have no good explanation for these changes in the corrosion pattern. High humidity is described in the literature as an important factor for filiform corrosion and some of the results may support this observation, but the multipollution situation observed in big cities, may also be important. Another uncertainty for the evaluation is that we have a new badge of samples prepared by another company this time and we can not be sure that the samples are completely comparable.

Cracking of the corrosion protection paint film has been observed on samples from the Tel Aviv site after two years but was never observed in the first phase of the programme.

A comparison between the results from the first and second phase shows that the damages are less severe this time. The same trend has earlier been shown for the air pollution parameters. The reduction is highest in the most polluted sites like Milan and Kopisty but is also substantial at the rural EMEP sites Birkenes, Aspvreten and Ähtäri in Scandinavia. It is therefore most likely that the reduced level of air pollution causes the reduced corrosion of painted panels. The dose-response equations reported at the end of phase one tried to define the lifetime before maintenance was needed, ASTM $\leq$ 5 (Henriksen et al 1998). To run a new statistical treatment we need more data with high corrosion and this evaluation will therefore not be done before after the intake of the four years exposure.

7. Conclusions

The damage of the paint system has been evaluated by using the well-established ASTM-standards on the samples exposed. The results show that the damage from the cut is less dominating in the second phase of the programme. This follows the trends also observed for the pollution parameters.

The development of the damages is still too low for estimating a lifetime for the paint system in different environments.

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ABSTRACT

The paint steel panels coated with two layers alkyd paint (total 80 µm) have been exposed for 1 and 2 years. The damage of the paint system has been evaluated by using the well-established ASTM-standards.
Damage from the cut is observed at all test sites, and after two years. ASTM values from 9 to 6 are observed. Comparing the results with the environmental parameters seems to indicate that the damage is affected by air pollution like in the big cities. However, the damage is also surprisingly high at rural sites, particularly at sites with high amount of rain.

Filiform corrosion, shown as thin whiskers under the paint film from the cut, is more dominated in the second phase of the programme than in first phase 1987-1989.Cracking of the corrosion protection paint films has been observed on samples from the Tel Aviv site after two years, but was never observed in the first phase of the programme.

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ABSTRACT (in Norwegian)

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