International Paint & Printing Ink Council

DE 53, Agenda item 7
Cargo Oil Tank Coating and Corrosion Protection

Information on coating test development

IPPIC PSPC Work Group

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1. Introduction

The paint industry, as members of the Industry Joint Working Group JWG/COTCPS, has been involved in the drafting of the IMO PSPC/COT test method since 2007. Since the establishment of IPPIC's PSPC Work group in April 2008, the work has been carried out by this group. The paint industry had reservations regarding the first test protocol submitted by JWG/COTSPC (DE 51/19/1). A trial run of the test was carried out by IPPIC and presented at a JWG/COTCPS meeting in Busan in October 2008. The conclusion of this trial run was that test protocol could not be recommended and IPPIC offered to continue the further development.

IPPIC decided to establish a new Joint Working Group in January-February 2009. The JWG was established with representatives from class societies, ship owner organizations, shipyards, testing labs and paint industry (list of members in Annex I). At DE 52 in March 2009 the Joint Working Group chaired by IPPIC was requested to continue the development of test protocol with the view of finalizing it at DE 53. The work should be carried out as part of TOR 2 for the Correspondence Group that DE 52 formed under the chairmanship of Mr. Masanori Yoshida, Japan.

Two JWG meetings, one in May 2009 and one in October 2009, were held. During the first meeting, agreement was made to test using a model oil proposed by INTERTANKO. This artificial medium was a model for a "reasonable worse case" crude oil. At the second JWG meeting the three months results of this test series were presented. The JWG did not reach full consensus and further discussion would take place based on six months of testing. At this meeting it was also concluded that further investigation into the test method was required. Therefore, in November 2009, IPPIC started a second test program based on an experimental design, focusing on the immersion liquid constituents.

In this report, the six-month results of the first series are presented, together with the two-month results of the experimental design test series.

2. First test series

2.1 Test set up agreed at the JWG in May 2009.

The test was carried out in two laboratories, one in Japan and one in the Netherlands. Coated panels, both pure and modified epoxies applied over both blasted steel and shop-primed substrates, were supplied by seven manufacturers. Panels were exposed to a vapor test at 60°C and immersion tests at 40°C and 60°C.

The conditions for the vapor tests were set as below:

- Modified ISO 3231 at 60°C
- Gastight cabinet flushed periodically with gas mixture
  (N_2 (83±2%), CO_2 (13±2%), O_2 (4±1%))
- Additions of SO_2 (300ppm) and H_2S (200 ppm)

- Water; periodically added/refreshed to maintain humidity at 95±5%
- Total test duration 6 months
- First assessment after 3 months
- Evaluation by rust (ISO 4628-3) and blistering (ISO 4628-2)

The conditions for the immersion test were set as below:

- Immersion at 40°C and 60°C (panels fully immersed)
- Immersion liquid based upon distillate marine fuel, DMA grade (density : 0.849 kg -0.880 kg/L, viscosity : 2.98 mm2/s (5 CSt)[1] or equivalent)
- Naphthenic acid (1-Methylcyclohexanecarboxylic acid to provide an acid number of 2.5 mg KOH/g)
- Benzene/Toluene (1:1) 8% w/w
- H_2S 5 ppm
- Seawater 5% w/w
- Total test duration 6 months
- First assessment after 3 months
- Evaluation by rust (ISO 4628-3) and blistering (ISO 4628-2)

2.2 Results of first series

The results for the two tests are summarized in the tables below.

2.2.1 Vapor test

None of the panels showed rust. Insignificant blister formation was seen on two panels after three months and six months on panels tested in Japan. The blister formation is regarded as insignificant as blisters only occur on the edge of panels. The vinyl reference panel failed the vapor test.

2.2.2 Immersion test

The failure mode was blister formation, both in the results of the test laboratories in Japan and in Europe.

Discrimination between systems was observed at 40°C as well as at 60°C.

Failures were observed for pure epoxy (PE) as well as modified epoxy (ME) and also for abrasive blast cleaned panels (BL) and zinc silicate shop primed panels (SP).

The vinyl system which was included as an indicator for a system that should not pass the test did in fact fail after three months in both the vapor test and the immersion test and further testing was discontinued. The coal tar epoxy coating passed the test, irrespective of test condition.

[1] This mixture was supplied by Saybolt Netherlands

30th September,'09

Summary of COT tests(3months)

		Vapour Test				40 deg. Immersion				60 deg. Immersion			
		PE		ME		PE		ME		PE		ME	
		BL	SP	BL	SP	BL	SP	BL	SP	BL	SP	BL	SP
	1	OK	OK	OK	OK	OK	OK	B	B	OK	OK	B	OK
E	2	OK	OK	OK	OK	OK	OK	OK	OK	OK	B	B	OK
	3	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
U	4	OK	-	OK	-	-	OK	-	OK	OK	OK	-	-
	5	OK	OK	OK	OK	OK	OK	B	B	OK	OK	-	B
	6	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	B	OK
	7	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
	Vinyl	-	-	B	B	-	-	B	B	-	-	B	B
	TE	-	-	OK	OK	-	-	OK	OK	-	-	OK	OK

		Vapour Test				40 deg. Immersion				60 deg. Immersion			
		PE		ME		PE		ME		PE		ME	
		BL	SP	BL	SP	BL	SP	BL	SP	BL	SP	BL	SP
J	1	OK	B*	OK	B*	OK	OK	OK	B	OK	OK	B	B
A	2	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
P	3	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
A	4	OK	OK	OK	OK	OK	-	-	-	OK	B	OK	OK
N	5	OK	OK	OK	OK	OK	OK	B	B	OK	OK	B	B
	6	OK	OK	OK	OK	OK	OK	OK	OK	OK	B	OK	OK
	7	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
	Vinyl	-	-	B	B	-	-	B	B	-	-	B	B
	TE	-	-	OK	OK	-	-	OK	OK	-	-	OK	OK

B : Blisters

B*: Blisters on edge only

12th January,'10

Summary of COT tests(6months)

		Vapour Test				40 deg. Immersion				60 deg. Immersion			
		PE		ME		PE		ME		PE		ME	
		BL	SP	BL	SP	BL	SP	BL	SP	BL	SP	BL	SP
	1	OK	OK	OK	OK	OK	OK	B	B	OK	OK	B	OK
E	2	OK	OK	OK	OK	OK	OK	OK	OK	OK	B	B	B
	3	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
U	4	OK	-	OK	-	-	OK	-	OK	OK	OK	-	-
	5	OK	OK	OK	OK	OK	OK	B	B	OK	OK	-	B
	6	OK	OK	OK	OK	OK	OK	OK	OK	B	B	B	OK
	7	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
	Vinyl	-	-	-	-	-	-	-	-	-	-	-	-
	TE	-	-	OK	OK	-	-	OK	OK	-	-	OK	OK

		Vapour Test				40 deg. Immersion				60 deg. Immersion			
		PE		ME		PE		ME		PE		ME	
		BL	SP	BL	SP	BL	SP	BL	SP	BL	SP	BL	SP
J	1	OK	B*	OK	B*	OK	OK	OK	B	OK	OK	B	B
A	2	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	B	OK
P	3	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	B
A	4	OK	OK	OK	OK	OK	-	-	-	OK	B	OK	OK
N	5	OK	OK	OK	OK	OK	B*	B	B	OK	OK	B	B
	6	OK	OK	OK	OK	OK	OK	OK	OK	OK	B	OK	B
	7	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	B	OK
	Vinyl												
	TE												

B : Blisters

B*: Blisters on edge only

Figure 1, tables with the results of the first test series (agreed in May 2009)

2.3 Conclusions from test results

- Reproducibility between the European and Japanese laboratory results is considered good, with some more spread in the immersion at 60°C results for the modified epoxies.
- All systems passed the vapor test, even after six months exposure, except for the vinyl reference system.
- Comparing the six months results with the three months results, some more systems show failure at six months.
- No significant difference can be concluded between blasted or shop primed substrates.
- Modified epoxy, in general, shows inferior performance compared to pure epoxy when immersed at 60°C.

3 Second test series (experimental design series)

3.1 Test set up and experimental design

In order to examine the key influencing factors in the immersion liquid in more detail and find any possible interaction between these factors, an experimental design test was set up using DOE 7 Statease software. For this test, 15 different test liquids with a composition around the previously (JWG) agreed immersion test liquid were prepared (see clause 2.1 for description). A further test liquid, where the benzene was replaced by xylene was also included (solution 17). This latter test was performed to investigate if the very toxic/ carcinogenic benzene could be replaced by xylene without affecting the experimental results.

A total number of 204 panels have been tested. Below is the composition of the tests liquids and the number of paint systems tested in each variant.

	Factor 1	Factor 2	Factor 3				
Run	A:acid nr	B:BT	C:H2S				
	mg KOH/g	%	ppm	Pure blasted	Pure shopprimed	Modified blasted	Modified shopprimed
1	2,5	5,0	10,0	4	2	4	2
2	2,5	0,0	5,0	4	2	4	2
3	5,0	10,0	0,0	4	2	4	2
4	5,0	5,0	5,0	4	2	4	2
5	0,0	5,0	5,0	4	2	4	2
6	2,5	10,0	5,0	4	2	4	2
7	2,5	5,0	5,0	4	2	4	2
8	2,5	4,0	5,0	4	2	4	2
9	0,0	0,0	0,0	4	2	4	2
10	2,5	5,0	0,0	4	2	4	2
11	2,5	5,0	5,0	4	2	4	2
12	0,0	10,0	10,0	4	2	4	2
13	2,5	4,0	5,0	4	2	4	2
14	2,5	5,0	5,0	4	2	4	2
15	5,0	0,0	10,0	4	2	4	2
17	2,5	4 XT	5,0	7	5	7	5

Table 1, composition of test liquids and panels tested (Run 16 was by mistake denoted Run 17)

3.2 Results of experimental design series

Tests panel evaluation was executed at the COT laboratory in Haarlem, Holland. The experimental design test commenced on December 4th 2009 and panels were evaluated on February 5th 2010. A further evaluation of the panels will be made after three months exposure to verify initial results and conclusions.

	Factor 1	Factor 2	Factor 3	1 p s		1 p b		1 m s		1 m b		2 p s		2 p b		2 m s		2 m b		3 p b		3 m b		4 p b		4 m b	
Run	A:acid nr	B:BT	C:H2S	W	O	W	O	W	O	W	O	W	O	W	O	W	O	W	O	W	O	W	O	W	O	W	O
	mg KOH/g	%	ppm																								
1	2,5	5,0	10,0	4	4	10	10	10	10	10	10	5	2	9	10	6	8	7	10	10	10	10	10	10	10	10	10
2	2,5	0,0	5,0	8	10	6	5	10	10	5	7	5	2	9	10	10	8	6	10	10	10	10	10	10	10	10	10
3	5,0	10,0	0,0	7	0	7	10	6	4	6	4	0	0	6	10	2	0	4	10	7	10	10	10	7	4	0	10
4	5,0	5,0	5,0	4	0	10	6	5	1	7	1	5	1	9	10	2	0	1	10	7	10	10	10	10	10	10	10
5	0,0	5,0	5,0	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
6	2,5	10,0	5,0	10	5	6	10	10	6	5	10	10	2	10	10	7	2	2	10	10	10	10	10	10	10	10	10
7	2,5	5,0	5,0	10	5	5	10	4	1	10	5	10	0	10	10	7	1	5	10	10	10	10	10	10	10	10	10
8	2,5	4,0	5,0	10	4	10	6	5	10	5	10	2	0	7	10	10	0	5	10	10	10	10	10	7	6	10	4
9	0,0	0,0	0,0	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	0	10
10	2,5	5,0	0,0	10	2	10	10	0	1	10	4	10	1	7	10	10	0	1	10	10	10	10	10	10	6	10	10
11	2,5	5,0	5,0	7	10	8	10	7	10	7	7	10	4	10	7	10	1	7	6	10	10	10	10	5	10	10	10
12	0,0	10,0	10,0	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
13	2,5	4,0	5,0	7	8	7	7	10	10	10	10	10	7	10	10	10	6	10	6	10	10	10	10	6	10	4	10
14	2,5	5,0	5,0	10	6	10	10	5	10	7	8	10	1	10	7	10	1	8	4	10	10	10	10	10	10	10	10
15	5,0	0,0	10,0	10	2	7	10	6	1	6	1	5	1	8	4	5	4	5	4	7	4	10	10	5	4	7	2
17	2,5	4 XT	5,0	10	10	10	10	10	10	10	10	10	10	10	10	10	10	8	7	10	10	10	10	10	10	10	10

Table 2, results of experimental design series after 2 months exposure (blisters were scored against ISO 4628-2 and ranked 0-10 (worst to best) according to the conversion table of ANNEX II

3.3 ANOVA (Analysis Of Variance) analysis

In this mathematical approach, the DOE Statease software uses the results of the tests to compute a model that will predict behavior of the test panels with respect to blistering.

Models for both the water and oil phase were computed.

Response	1	Performance water				
ANOVA for Response Surface Reduced 2FI Model (Aliased)						
Analysis of variance table [Classical sum of squares - Type II]						
	Sum of		Mean	F	p-value	
Source	Squares	df	Square	Value	Prob > F	
Model	470,31	14	33,59	7,77	< 0.0001	significant
A-Acid number	224,01	1	224,01	51,84	< 0.0001	
C-H2S	14,22	1	14,22	3,29	0.0712	
D-coating	88,76	6	14,79	3,42	0.0031	
E-type epoxy	22,67	1	22,67	5,25	0.0231	
G-Solvent composition	29,61	1	29,61	6,85	0.0096	
AD	48,86	3	16,29	3,77	0.0117	
CE	16,06	1	16,06	3,72	0.0554	
Residual	816,73	189	4,32			
Lack of Fit	658,56	153	4,30	0,98	0.5526	not significant
Pure Error	158,17	36	4,39			
Cor Total	1287,04	203				

Table 3, results of the analysis of the DOE Statease software program giving the significant factors influencing blisters in the water phase

The program analyses the relevance of the data and has been set to omit insignificant factors. Significance of a factor is expressed by the P-value. The lower this factor the more significant the effect of that factor on the result. The factor is disregarded if the p-value exceeds 0.1

The model calculated by the program is significant (see last column of table 3, above). This means the model constructed by the program is able to predict the results.
A very significant factor is the Acid Number. Significant factors are coating brands and, to a lesser extent, the solvent composition used for the test. Significant interactions are found between the acid number and the coating and between the type of epoxy and level of H_2S.
The fact that “Lack of Fit” is shown as insignificant proofs that the model fits the results.

Response	2	performance oil				
ANOVA for Response Surface Reduced 2FI Model (Aliased)						
Analysis of variance table [Classical sum of squares - Type II]						
	Sum of		Mean	F	p-value	
Source	Squares	df	Square	Value	Prob > F	
Model	1581,33	20	79,07	17,33	< 0.0001	significant
A-Acid number	410,89	1	410,89	90,06	< 0.0001	
B-Solvent content	4,33	1	4,33	0,95	0.3312	
C-H2S	37,50	1	37,50	8,22	0.0046	
D-coating	119,27	6	19,88	4,36	0.0004	
F-Substrate	288,58	1	288,58	63,25	< 0.0001	
G-Solvent composition	53,00	1	53,00	11,62	0.0008	
AB	50,17	1	50,17	11,00	0.0011	
AF	148,03	1	148,03	32,44	< 0.0001	
BF	41,34	1	41,34	9,06	0.0030	
CF	31,17	1	31,17	6,83	0.0097	
DF	147,90	4	36,98	8,10	< 0.0001	
FG	39,28	1	39,28	8,61	0.0038	
Residual	834,92	183	4,56			
Lack of Fit	643,92	147	4,38	0,83	0.7862	not significant
Pure Error	191	36	5,31			
Cor Total	2416,25	203				

Table 4, results of the analysis of the DOE Statease software program giving the significant factors influencing blisters in the oil phase

For the oil phase, the model necessary to derive a good fit is more complex than the model created for the water phase results. Again the model is shown to be significant.
The most significant factor is again the Acid Number, and secondly the substrate and the interaction between Acid Number and substrate.
Also significant are coating and the interactions between the substrate and solvent content, and the H_2S level, coating, and solvent composition.
The solvent content is insignificant, but shown since it has a very significant interaction with the substrate.
The fact that “Lack of Fit” is shown as insignificant proofs that the model fits the results.

3.4 Conclusions from experimental design results

From the ANOVA computed results it can be concluded that

- Largest effect is the acid number. The influence of Acid Number is supported by the tests carried out by Xiamen Ship Coating testing Station in China and reported in DE 53/INF.4
- Significant effect:
  - Coating
  - Substrate (for the oil phase only)
- Minor effect:
  - Type of coating (modified versus pure epoxy)
  - Interaction between H_2S and type of coating
  - Interaction between acid number and coating
  - Interaction between substrate and acid number (for the oil phase only)
- Effect of H_2S and solvent content is statistically insignificant

3.5 Effect of substituting benzene with xylene in model immersion medium (test liquids 17 versus 8 and 13)

			XT		BT		BT	
			Solution 17		Solution 8		Solution 13	
Paint supplier	Coating typ	Substrate	W	O	W	O	W	O
1	p	s	10	10	10	4	7	8
1	p	b	10	10	10	6	7	7
1	m	s	10	10	5	10	10	10
1	m	b	10	10	5	10	10	10
2	p	s	10	10	2	0	10	7
2	p	b	10	10	7	10	10	10
2	m	s	10	10	10	0	10	6
2	m	b	8	7	5	10	10	6
3	p	b	10	10	10	10	10	10
3	m	b	10	10	10	10	10	10
4	p	b	10	10	7	6	6	10
4	m	b	10	10	10	10	4	10
5	p	s	10	10	-	-	-	-
5	p	b	10	10	-	-	-	-
5	m	s	10	0	-	-	-	-
5	m	b	10	10	-	-	-	-
6	p	s	10	10	-	-	-	-
6	p	b	10	10	-	-	-	-
6	m	s	10	10	-	-	-	-
6	m	b	10	10	-	-	-	-
7	p	s	10	10	-	-	-	-
7	p	b	10	1	-	-	-	-
7	m	s	8	8	-	-	-	-
7	m	b	10	4	-	-	-	-

Table 5, results of the experimental design series, test liquid 17 versus the standard liquids 8 and 13

For the evaluation of replacement of benzene by xylene, an additional test medium was tested. For composition of this liquid number 17 see table 1. In figure 2 the averaged results including the standard deviation are given.

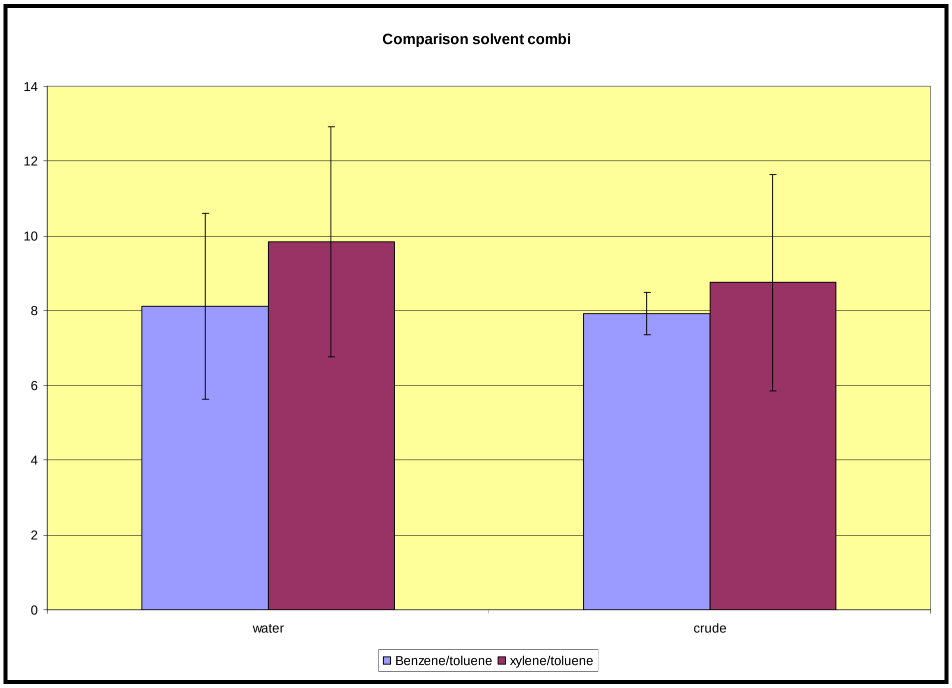

Figure 2, averaged results of the test liquid 17 compared to the standard liquids 8 and 13 to see effect of replacement of benzene by xylene (Left columns: Water phase – Right columns: oil phase)

Conclusion: Replacing benzene by xylene does not result in statistically significant lower aggressivity in this test. This conclusion is supported by the tests carried out by Xiamen Ship Coating testing Station in China and reported in DE 53/INF.4.

4 Discussion

After the comprehensive testing described in this report it is evident that the current test protocol will not allow coatings which today serve successfully in the cargo tanks of oil tankers to pass.

At the May 2009 JWG meeting a group (JWG 2) was set up to obtain feedback on the performance of coating systems in real life. The number of vessels that qualified for such a reference list proved to be low, given that historically coal-tar epoxy paints were used in cargo oil tanks, and as a result we have a relatively short list of vessels to date. However, no single poor performing vessel has been brought to the attention of the JWG as yet.

The coating systems used in the two test series detailed in this report are all used in cargo oil tanks and have proven track records. The fact that 7 out of the 14 tested coating systems after three months, and 9 out of the 14 after six months failed in the first immersion test at 60°C clearly demonstrates the test is too severe. For this reason, in order to correlate with practice, the test medium should be modified.

In this discussion it must not be forgotten that the immersions liquid used in the second test series is more aggressive than the crude oils used in the test leading to DE 51/19, namely:

1. The immersion liquid combines the three aggressive factors (acid number, aromatic concentration and hydrogen sulphide concentration) in one test liquid in contrast to the first test, where each factor was tested individually
2. The most influential factor, the acid number, is 2.5 mg KOH/g in comparison with the "greater than 1 mg KOH/g" used in the first test protocol
3. The acid used in the later test is the lowest molecular weight naphthenic acid, i.e.1-methylhexanecarboxylic acid. The aggressivity of this low molecular weight naphthenic acid is higher than the larger molecular size acids present in crude oils.
4. The mixture of aromatic compounds is composed of the most aggressive aromatics, namely benzene and toluene, and not benzene, toluene and xylene as in the first test protocol

The experimental design test provides an excellent tool for suggesting ways to modify the test liquid. The acid number of the immersion liquid is, as explained, the major factor determining the aggressiveness, in the oil phase as well as in the water phase. A reduction from an acid number of 2.5 mg KOH/g therefore appears to be the best tool to obtain test results more in line with performance of coatings in real life.

In addition, the experimental design test results also suggest that benzene can be replaced by xylene in the immersion liquid, and this is supported by work done in China (DE53/ INF.4).

IPPIC also accept the general opinion that the test temperature shall be 60°C to be in line also with future transport requirements. Further, we agree to use a gas composition corresponding to generally recognized inert gas (ISGOTT and SIGTTO) compositions with added hydrogen sulphide.

London, 18th of February 2010

Annex 1

Attendees for Joint Working Group meetings, May and October 2009:

Mr. Masanori Yoshida	: Japan Ship Technology Research Association (*Chairman CG on corrosion protection of COT*)

For IACS:

Mr. Edward Jansen	: American Bureau of Shipping
Mr. David Howarth	: Lloyd's Register
Mr. Richard Dawson	: Lloyd's Register

For ship owners, INTERTANKO:

Mr. Dean Tseretopoulos	: INTERTANKO
Dr. Timothy Gunner	: INTERTANKO
Mr. David Tongue	: International Chamber of Shipping:

Test Institutes:

Mrs. Lynda Barron	: Exova
Mr. Phil Dent	: Exova
Mr. Maurice Walrave	: COT
Mr. Trevor Parry	: STS

Ship yards (CESS)

Mr. Kiyotaka Takeda	: Universal Shipbuilding Cooperation

Other:

Mr. Rodney Towers	: Safinah

IPPIC:

Mr. Yasuto Hikiji	: CMP
Mr. Eiichi Yoshikawa	: CMP
Mr. Ole Borring Sørensen	: Hempel (*Chairman of PSPC COT JWG 1*)
Ms. Judith Fergus	: International Paints
Mr. Colin Watson	: International Paints (*Chairman of PSPC COT JWG 2*)
Mr. Jim Sell	: IPPIC
Mr. Tormod Svartdal	: Jotun
Mr. Tatsuhiko Yamazaki	: JPMA
Mr. Hirokazu Kaji	: Nippon
Mr. Yoshihiro Honda	: NKM
Mr. Kees van Vliet	: PPG (*Chairman of PSPC COT JWG 3*)
Mr. Evert van Rietschoten	: PPG

Annex II

Conversion table for blister rating from ISO 4628-2 to a 0-10 scale

ASTM D714				ISO 4628-2						Number
F	**M**	**MD**	**D**	**0**	**1**	**2**	**3**	**4**	**5**	
10	10	10	10	0	0	0	0	0	0	10
9					S1	S1				9
8						S2				8
6	9					S3	S1			7
4	8					S4	S2			6
	6	9					S3	S1		5
2	4	8	9			S5	S4	S2	S1	4
										3
	2	6	8				S5	S3	S2	2
		4	6					S4	S3	1
		2	4 / 2					S5	S4 /S5	0