PROGRESS REPORT VII

(September 1 - November 30, 1984)

De-icing and Prevention of Ice Formation off/on Offshore Oil-Drilling Platforms

Grantor: U.S. Army Corps of Engineers, CRREL
Hanover, New Hampshire 03755
Grantee: Clarkson University
Potsdam, New York 13676

Grant No.: DACA 89-33-0003

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Date Submitted:

PROGRESS REPORT VII

(SEPT. 84 - NOV. 1984)

DE-ICING AND PREVENTION OF ICE FORMATION OF/ON OFFSHORE OIL-DRILLING PLATFORMS

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The effect of a water jet mixed with air on the coatings has been further investigated (see progress Report VI, (5)-(9).

Film thickness 1.20mm, LR5630

TABLE 1

(1) Cumulative Effect of Erosion:

EROSION Time h			ADHESIVE SHEAR STRENGTH kg/cm^2
8	Time of Storage after Erosion	19 days	0.16
16	" " " " "	1 day	1.38
		2 days	0.59
		3 days	0.31
		20 days	0.17
16	" " " " "	~~1~~8 days	0.45
18	" " " " "	0 days*	2.58
		1 day	1.98
		2 days	0.54
		5 days	0.73

* This sample was not dried before adhering ice to it again.

It is apparent from the above results that the shear strength is lowered again after the coats are stored after erosion; actually the specified shear strength is attained again on storage while at once after erosion, the shear strength has increased beyond the specified shear strength.

Polycarbonate - Poly Siloxane - Co-Polymer XD-11

This polymer has a high T_G (100° C) and is somewhat tougher than LR 5630. Its examination was discountinued at an earlier stage (see program report VI, A-(2).)
The solvent ($CH_2\ Cl_2$) was changed to dioxane.
The compostions of the coatine mixtures were:
(a) XD-11 0.5g, Dioxane 2.5ml, Toluene 2.5ml
(b) XD-11 0.5g, Dioxane 5.0ml
A clear solution was obtained in either case but the first mixture became a gel during storage.

Both solutions were used for coating Al-plates. Thick coats of 0.1mm or more separated from the plates on drying. Hence, only thin coats were prepared. The coat of the mixture (a) was heated at 100°C for 1h prior to testing. The heating did not affect the adhesive strength to a noticeable extent.

The adhesive strength of the coat made from (b) is larger than of (a). The reason for this is probably the fact that only one solvent was used for (b);generally evaportation is less smooth for a single solvent than for a mixture of solvents. TABLE 2 gives results.

TABLE 2

SAMPLE		SHEAR ADHESIVE STRENGTH		
				AVERAGE
(a)	without silicone oil	0.69	1.15	0.92
(a)	with 10% Thomas silicone oil	0.76	1.67	1.20
(b)	without silicone oil	----	----	1.91

A sample of 1.15 kg/cm^2 adhesive strength was exposed to erosion for 4h without drying; ice was adhered again at -10 °C. The adhesive shear strength increased to 2.87 kg/cm^2. Thus XD-11 is not better than LR 5630 of similar thickness.

POLYCARBONATE (PC),(LEXAN, GRADE 100-111, GE)

(a) LR 5630 Plus PC:

(1)	PC	0.1g
	LR 5630	0.1g
	Dioxane	8.0g
	Toluene	2.0ml

A turbid mixture was obtained, PC and LR 5630 are not miscible. A thick coat separated from the Al-Plate on drying. A thinner coat adhered to Al. (Coater gap 0.35mm). The coat was heated at 100° C for 1h. The pencil hardness was < 6B and the adhesive strength 2.91 kg/cm^2, which is rather large.

(2)	PC	0.95g
	LR 5630	0.05g
	Dioxane	8.0ml
	Toluene	2.0ml

Again, a turbid mixture was obtained although the amount of LR 5630 was reduced. The coating properties of this mixture were the same as for case (1) (heated at 100°C for 1h, pencil hardness < 6B); shear adhesive strength 7.44kg/cm^2.

(b) FLUOROLUBE S-30 (Hooker Chemical Corporation):

(1)	PC	1.0g
	Dioxiane	8.0ml
	Toluene	2.0ml

Fluorolube up to ca. 6% by weight.

The mixture was turbid due to Fluorolube. Fluorolube was added in stages i.e. 1%, 2%, 4%, 6% Coats were dried at room temperature for 3 days before testing.

TABLE 3

FLUOROLUBE CONTENT Weight %	ADHESIVE STRENGTH kg/cm^2	THICKNESS OF COAT μm	REMARKS
0	0.02	45	Coat not uniform*
1	Too weak to measure	40	"
ca. 2	-----	20	"
ca. 4	-----	50	Coat separates
ca. 6	-----	ca. 40	from Al-plate

* During erosion (16h), half of the coat separated from A .

(2) PC 1.0g

Dioxane 10.0ml

Fluorolube up to ca. 4% by weight.

A clear solution was obtained without Fluorolube.

Fluorolube was added in stages as before. The coats were dried at room-temperature for 3 days before testing.

TABLE 4

FLUOROLUBE CONTENT Weight %	ADHESIVE STRENGTH kg/cm^2	THICKNESS μm	REMARKS
0	Too weak to measure	50	Clear uniform coat
1	0.03	45	Slightly turbid uniform coat
ca.2	----	75	Turbid, non-uniform
ca.2	----	45	Coat separating from Al

The low value of $0.03kg/cm^2$ was later found to be due to residual dioxane in the coat.

(c) Double coat (PVB Primer/PC-topcoat; PVB Polyvinyl-Butyral)

It was hoped that a primer would make the coat adhere better to the substrate. Both polymers are soluble in dioxane.

(1)	PC	2.0g
	Dioxane	18.0ml

A slightly turbid solution was obtained. This was coated on top of the PVB film (primer). The coat was left at room temperature for one day before testing. The shear strength was $1.47\ kg/cm^2$.

Coating was carried out as above, except that a coater of gap width 0.4mm was used. The coat was thin and smooth. It was dried at room temperature for one day.

Adhesive strength was 0.43 kg/cm^2. The PC topcoat was removed during testing from the primer at several spots after drying for 5h at room temperature. The adhesive strength increased to 3.07 kg/cm^2; the next day it was 4.50 kg/cm^2. The reason for this increase is obscure.

(d) EFFECT OF DIOXANE on PC-COAT.

(1) The PC-solution in dioxane was coated on an Al-plate with a coater of 0.4mm gap-width. The coat was dried at room temperature.

TABLE 5

DRYING TIME h	ADHESIVE STRENGTH kg/cm^2
ca.4	0.03
24	1.55
48	4.38

(2) Here a coater of 0.7mm gap-width was used as the thicker coat showed small wrinkles.

TABLE 6

No. of Coating	Appearance	DRYING TIME(h) AT ROOM TEMPERATURE		
		ca. 4	24	48
		ADHESIVE STRENGTH, kg/cm^2		
1	Smooth	0.29	1.48	3.66
2	Not uniform	0.28	1.91	3.65
3	" "	0.05	----	----

The adhesive strength increased considerably on exposure to erosion. Table 6 shows that residual dioxane in the coat decreased the adhesive strength appreciably.

(e) Poly(dimethylsiloxane) (Silicone oil from Polysciences)-Polycarbonate.

(1) PC/Silicone oil 35/36 by WT. This is the same ratio as in the co-polymer LR5630.

Dioxane 10.0ml

Silicone oil; MW10000; DP=140.

The oil did not dissolve in the PC-solution; PC and the oil separated in the coat on Al.

(2) Silicone oil (oil MW 100 000, DP 1351)

PC	0.35g
Dioxane	10.0ml
Silicone oil	0.65g

Silicone oil separated from the solution.

(3) The Silicone oil (MW 100 000) was reduced to

	0.25g
PC	0.75g
Dioxane	10.0

However the oil still separated. The oil was further reduced to 0.15 g.

PC	0.9 g
Dioxane	10.0ml

The solution became slightly turbid. An uneven coat was obtained by this solution of an adhesive strength 1.88 kg/cm^2. The coat was dried prior to testing at room temperature for 5h.

(h) LR-5630 exposed to erosion:

(1) LR 5630 2.0g
Toluene 8.0ml

Thomas oil, SF-1154 or Fluorolube 0.2g (i.e 10% W/W of the co-polymer.)

TABLE 7

OIL	SOLUTION APPEARANCE	THICKNESS OF COAT mm	EROSION TIME h	ADHESIVE STRENGTH kg/cm^2				
				Without Erosion	Ice Prepared After Days of Erosion			
					0[*2]	1	2	19
Thomas	Turbid	0.65	8	0.04	---	1.91	0.95	0.45
SF-1154	Clear	0.60	3.5	0.23	---	1.49	---	0.37[*3]
Fluorolube	Clear	0.18[*1]	21	0.28	3.59	---	---	---

*1 The solution was repelled by the Al-surface and it was difficult to obtain a thicker coat.

*2 Immediately after erosion without drying.

*3 18 days

It appears that none of the adhesive strength values was below the specified maximum strength (1.76 kg/cm^2) immediately after erosion.

(2) Silicone Gum (Polydimethyl Siloxane) Supplied by Polysciences)

Compositions of coating mixtures

TABLE 8

SAMPLE NO.	1	2	3	4
SAMPLE				
LR5630/Silicone Gum	100/0	90/10	75/25	50/50
LR-5630, g.	2.0	1.8	1.5	1.0
Silicone Gum, g	---	0.2	0.5	1.0
Toluene, ml	8.0	8.0	8.0	8.0
Thickness of Coat, mm	0.17	0.45	0.20	0.25

LR-5630 and silicone gum were separatly soluble in toluene, but LR 5630 and the gum were not miscible. The liquid mixtures were turbid, also the coats were turbid and the two polymers separated in the coat. Example No.2 was subjected to erosion for 3h. and immediately after exposure ice was adhered to the coat. The adhesive strength was 2.22 kg/cm^2. After storing of the sample for one and two days, the adhesive strengths were 4.24 kg/cm^2 and 3.34 kg/cm^2, respectively.

The surface of the coating was apparently damaged on exposure to erosion.

(3) Crosslinking of LR 5630 with Benzoylperoxide. The composition and characteristics were as follows:

TABLE 9

	1	2
BZO_2 (w/w % in LR5630)	5.0	2.5
LR5630,g	2.0	2.0
B_zO_2,g	0.1	0.05
Toluene, ml	8.0	8.0
Thickness of Coat, mm	0.17	0.38
Adhesive Strength, kg/cm^2	0.34	0.13
Adhesive strength immediately After Erosion	4.36	----
Stored for 3 days After Erosion	4.53	----

The solutions were clear; the coats, dried at room temperatue, showed many needle-like crystals of B_zO_2. The coats were heated at 100° C for 1h for the purpose of crosslinking. However after heating, the coat was still soluble in toluene at room temperature indicating that crosslinking had not taken place.

(4) Compostions containing high MW Poly (dimethylsiloxane).

Composition and characteristics are given in TABLE 10

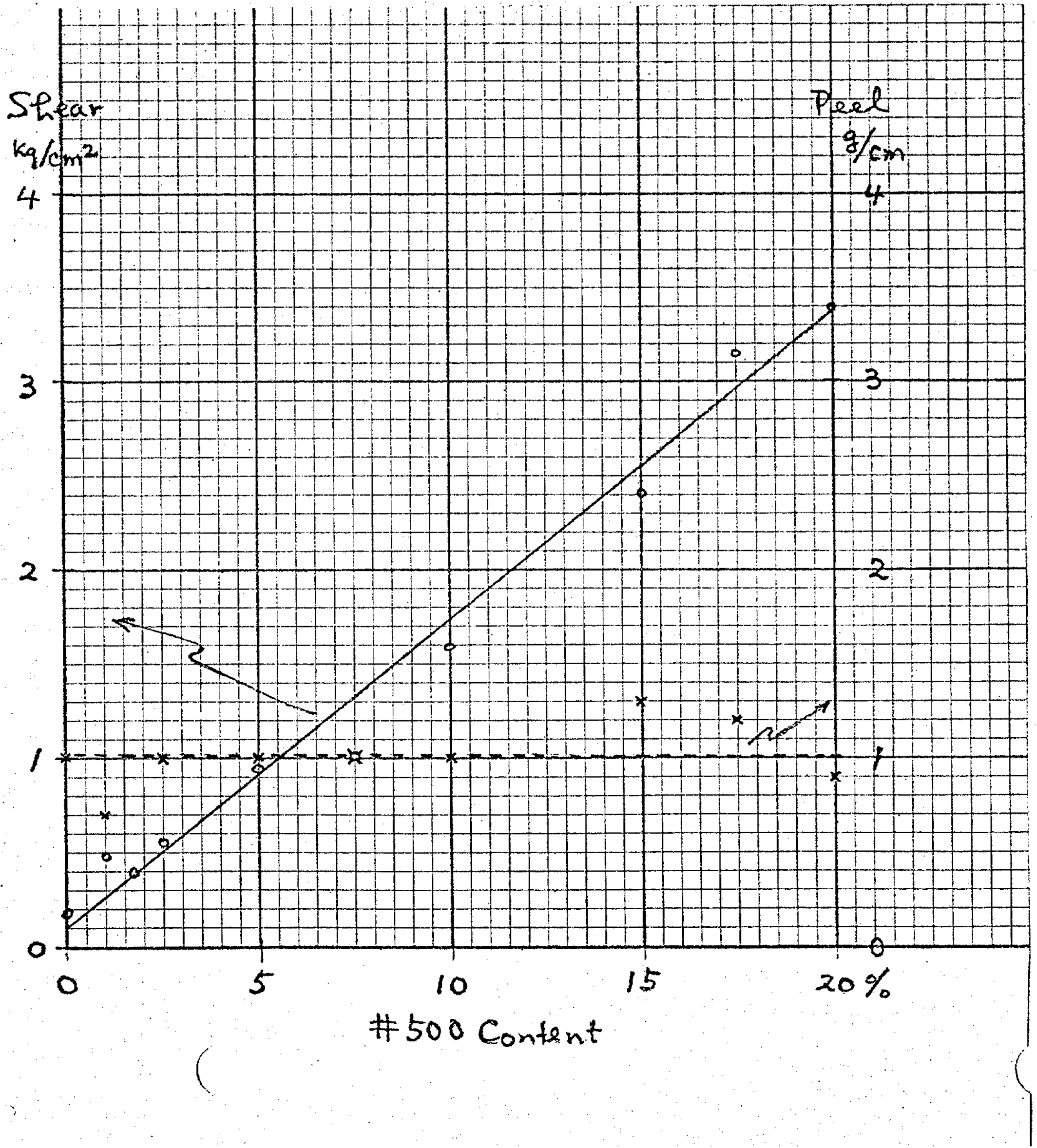
TABLE 10

Polycarbone Repeat Unit/ Poly Siloxane Repeat Unit	30/70	[1*] 35/65	40/60
LR5630, g	2.0	---	---
LR-3320,g	---	0.61	0.80
Poly (dimethysiloxane 1.MW 100 000g	0.3	0.39	0.35
Toluene, ml.	10.0	5.0	5.0
Dioxane, ml	---	5.0	5.0
Thickness of Coat, mm	0.275	-[*2]	-[*2]
Adhesive Strength, kg/cm^2	0.05	0.42	1.27

---

*1 This is the same ratio as in LR5630

*2 Coats were not uniform; copolymer and silicone separated in the coat.



Shear
kg/cm²
Peel
g/cm
4
3
2
1
0
4
3
2
1
0
0
5
10
15
20%
#500 Content

(5) Cross-linked silicone gum

(a) Silicone gum	2.0g
Toluene	8.0ml
B_zO_2	0.1g

A clear, viscous solution resulted. It was coated on an Al-plate and heated at 150°C for 0.5h. The coat was not uniform and was slightly colored. It was very fragile and its adhesive strength could not be measured.

(b) Silicone gum	2.0g
Toluene	8.0ml
Me $Si(OEt)_3$	0.2g

(for cross-linking)

Again a clear, viscous solution was obtained. The coat on Al was heated at 100°C for 1h. After crosslinking of the gum, the coat had a grease-like consistency; its adhesive strength was 0.06 kg/cm^2 (sliding).

(c) Tullanox # 500 and LR 5630

LR 5630 2.0g, various amounts of Tullanox #500 and toluene 10ml were mixed in a ball-mill for 16h and coated on Al. All coats were heated at 110°C for 1h.

Adhesive strength (kg/cm^2) and peel strength (g/cm) are plotted versus % Tullanox # 500 in the accompanying figure.

It is interesting to note that while the adhesive strength increases linearly with the % Tullanox content, the peel strength remains constant for the whole range of Tullanox percentages. Apparently, the surface becomes rougher with increasing Tullanox-powder content but the adhesion is not affected with respect to peeling.

One sample (15 % w/w of Tullanox #500) was subjected to erosion for 4.5h; for adhesive and peel strengths are given in TABLE 11 below.

TABLE 11

SAMPLE 3, TULLANOX #500, 15% w/w

		SHEAR STRENGTH (kg/cm^2)	PEEL g/m
Before Erosion		0.40	---
A few hours after Erosion		4.34	---
Stored for 1 day	After Erosion	3.15	---
Stored 18 days	After Erosion	1.55	2.9

Both adhesive and peel strength increase considerable on exposure to erosion.

(7) Effect of Erosion on Peel Strength.

(2) LR-5630	2.0g
Polydimehylsiloxane MW 100000)	0.3g
Toluene	10.0ml

A 225 µm thick coat on Al was prepared, its adhesive strength was 0.05 kg/cm^2. The coat was exposed to erosion for 18.5h and after erosion, peel tests were carried out.

	PEEL STRENGTH g/cm
Immediately after erosion	3.4
Stored for 1 day after erosion	0.7

The recovery appears to be remarkable.

(2) A LR-5630 coat(1.1mm thick) was exposed to erosion for 4.5h and its peel strength was measured:

	PEEL STRENGTH g/cm
Immediately after erosion	3.6
Stored 1 day	2.8
Stored 2 days	1.9

(8) Miscellaneous Compositions

(a) TAR -Epoxy-Enamel Subtrate

This surface was treated with dimethyldiethoxy silane ($Me_2Si(OEt)_2$ and left for 2h. It was anticipatated that the silane would be hydrolyzed in presence of moisture and would turn into silicone oil. The shear adhesive strength of such a coat was > 4.5 kg/cm^2.

(b) Polyainylidene fluoride (PVDT) was dissolved in warm cyclohexanone and the solution was coated on a warm Al-plate. Two coats were prepared,one was milky and the other one was practically transparent; these were tested.

Milky Coat	8.29 kg/cm^2
Transparent coat	5.64kg/cm^2

Coats Separated from the substrate after testing.

(c) Poly (vinyl butyral) (PVB)

(1) Butvar B-90 was dissolved in toluene and EtoH was added giving a clear solution:

Butvar B-90	2.6g
Toluene	16.0ml
EtoH	4.0ml

A coat ca.70 μm on Al wrinkled on heating to 100°C for 1h. The shear strength amounted to 5.51 kg/cm^2.

To such a coat Me_2 $Si(OET)_2$ was added at room temperature and left about 0.5h. This compound was expected to react with -OH- groups. (18-20%) as PVA in PVB. The adhesive strength was 6.25 kg/cm ^{2}.

(2) $ME_2Si(OEt)_2$ (CA.20 to PVB) was added to the PVB-solution as prepared above. The Al-coat was heated at 100 °C for 1h prior to testing. Milky patterns appeared in the coat (0.15 mm thick): its adhesive strength was 9.32kg/cm^2.

(3) The following compostion was examined

Butvar B-90	0.8g
Poly (dimthylsiloxane), MW 100 000	0.2g
Toluene	8.0ml
Etoh	2.0ml

The solution was slightly turbid, the coat on Al was very turbid. Shear adhesive strength was 4.39 kg/cm^2. This strength was not reduced by adding silicone oil.

(4) A PVB-solution was prepared as above; it was coated on the specially prepared TAR-Epoxy-Substrate. After a first coat had dried, a second one was applied. However the PVB solution attacked the substrate and the latter bulged. The PVB could be easily peeled off.

(d) Polystyrene and Poly- α -methyl styrene did not show promising results.

(e) Erosion-Resistant Coat.

(1) Preliminary experiments

(a) LR-5630	1.0g
Toluene	9.0ml

Coats were prepared on Al. Two of the coats, Fluorolube s-30 or GE- Silicone oil SF-1154 were applied for one day prior to testing. Fluorolube proved to repel LR-5630 and it was difficult to obtain a uniform coat. The coats were exposed to erosion for 1.5h and immediately afterwards ice was adhered to them. Results are given below.

TABLE 12

SAMPLE	THICKNESS OF COAT mm	ADHESIVE STRENGTH kg/cm^2
LR-5630 control	0.10	3.18
LR-5630 with Fluorolube	0.11	0.85
LR-5630 with SF-1154	0.09	0.37

This is the first time that an adhesive strength value was obtained lower than $1.00kg/cm^2$ immediately after exposure to erosion.

(b) Preliminary Experiment-2

Previously prepared coats were treated with SF-1154. They were stored at room temperature prior to exposure to erosion. After a 1.5h long erosion, samples were eroded again (16h LR-5630, and 5h LR3320).

Results are given below.

TABLE 13

SAMPLE		THICKNESS OF COAT mm	ADHESIVE STRENGTH, kg/cm^2 No Erosion	After 1st Erosion 1.5h	After 2nd Erosi 16h
LR-5630	SR-1154	0.26	0.47	0.04	1.09
LR-5630		0.13	2.50	0.02	2.37

LR-5630 is well within the specified range (First Experiment)

(c) LR-5630/SF-1154 Compositions.

Seven different compositions were prepared:

LR-5630	1.0g
Toluene	4.0ml
SF-1154	various amounts, see TABLE 14.

TABLE 14

SF- 1154,g	0.0	0.1	0.2	0.4	0.6	0.8	1.0
%w/w	0	10	20	40	60	80	100
Coat thickness, *[1] mm	0.26	0.29	0.32	0.37	0.42	0.47	0.58
Adhesive Strength, kg/cm^2 before erosion	0.38	0.22	0.12	0.06	0.07	0.17	---
Immediately after erosion, kg/cm^2	2.87	3.71	1.81	0.20	0.61	1.16	0.71
16 h after erosion*[2]	DATA NOT YET READY				0.68	2.57*[3]	1.61

---

*1 Calculated values

*2 Cumulative erosion i.e. 19h

*3 24h instead of 16h

These last results will be discussed in the next report. Experiments with G.E. silicone varnish are now in progress. Overall, the results show that LR-5630 plus SF-1154 is the most promising system provided coats are relatively thick.

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* This sample was not dried before adhering ice to it again.

It is apparent from the above results that the shear strength is lowered again after the coats are stored after erosion; actually the specified shear strength is attained again on storage while at once after erosion, the shear strength has increased beyond the specified shear strength.

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A clear solution was obtained in either case but the first mixture became a gel during storage.

Both solutions were used for coating Al-plates. Thick coats of 0.1mm or more separated from the plates on drying. Hence, only thin coats were prepared. The coat of the mixture (a) was heated at 100°C for 1h prior to testing. The heating did not affect the adhesive strength to a noticeable extent.

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A sample of 1.15 kg/cm^2 adhesive strength was exposed to erosion for 4h without drying; ice was adhered again at -10 °C. The adhesive shear strength increased to 2.87 kg/cm^2. Thus XD-11 is not better than LR 5630 of similar thickness.

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(1)

PC	0.1g
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(2)

PC	0.95g
LR 5630	0.05g
Dioxane	8.0ml
Toluene	2.0ml

Again, a turbid mixture was obtained although the amount of LR 5630 was reduced. The coating properties of this mixture were the same as for case (1) (heated at 100°C for 1h, pencil hardness < 6B); shear adhesive strength 7.44kg/cm^2.

(b) FLUOROLUBE S-30 (Hooker Chemical Corporation):

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PC	1.0g
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Fluorolube up to ca. 6% by weight.

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* During erosion (16h), half of the coat separated from A .

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Coating was carried out as above, except that a coater of gap width 0.4mm was used. The coat was thin and smooth. It was dried at room temperature for one day.

Adhesive strength was 0.43 kg/cm^2. The PC topcoat was removed during testing from the primer at several spots after drying for 5h at room temperature. The adhesive strength increased to 3.07 kg/cm^2; the next day it was 4.50 kg/cm^2. The reason for this increase is obscure.

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No. of Coating	Appearance	DRYING TIME(h) AT ROOM TEMPERATURE		
		ca. 4	24	48
		ADHESIVE	STRENGTH,	kg/cm^2
1	Smooth	0.29	1.48	3.66
2	Not uniform	0.28	1.91	3.65
3	" "	0.05	----	----

The adhesive strength increased considerably on exposure to erosion. Table 6 shows that residual dioxane in the coat decreased the adhesive strength appreciably.

(e) Poly(dimethylsiloxane) (Silicone oil from Polysciences)-Polycarbonate.

(1) PC/Silicone oil 35/36 by WT. This is the same ratio as in the co-polymer LR5630.

Dioxane 10.0ml

Silicone oil; MW10000; DP=140.

The oil did not dissolve in the PC-solution; PC and the oil separated in the coat on Al.

(2) Silicone oil (oil MW 100 000, DP 1351)

PC	0.35g
Dioxane	10.0ml
Silicone oil	0.65g

Silicone oil separated from the solution.

(3) The Silicone oil (MW 100 000) was reduced to

	0.25g
PC	0.75g
Dioxane	10.0

However the oil still separated. The oil was further reduced to 0.15 g.

PC	0.9 g
Dioxane	10.0ml

The solution became slightly turbid. An uneven coat was obtained by this solution of an adhesive strength 1.88 kg/cm^2. The coat was dried prior to testing at room temperature for 5h.

(h) LR-5630 exposed to erosion:

(1) LR 5630 2.0g

Toluene 8.0ml

Thomas oil, SF-1154 or Fluorolube 0.2g (i.e 10% W/W of the co-polymer.)

TABLE 7

OIL	SOLUTION APPEARANCE	THICKNESS OF COAT mm	EROSION TIME h	ADHESIVE STRENGTH kg/cm^2				
				Without Erosion	Ice Prepared After Days of Erosion			
					0[*2]	1	2	19
Thomas	Turbid	0.65	8	0.04	---	1.91	0.95	0.45
SF-1154	Clear	0.60	3.5	0.23	---	1.49	---	0.37[*3]
Fluorolube	Clear	0.18[*1]	21	0.28	3.59	---	---	---

*1 The solution was repelled by the Al-surface and it was difficult to obtain a thicker coat.

*2 Immediately after erosion without drying.

*3 18 days

It appears that none of the adhesive strength values was below the specified maximum strength (1.76 kg/cm^2) immediately after erosion.

(2) Silicone Gum (Polydimethyl Siloxane) Supplied by Polysciences)

Compositions of coating mixtures

TABLE 8

SAMPLE NO.	1	2	3	4
SAMPLE				
LR5630/Silicone Gum	100/0	90/10	75/25	50/50
LR-5630, g.	2.0	1.8	1.5	1.0
Silicone Gum, g	---	0.2	0.5	1.0
Toluene, ml	8.0	8.0	8.0	8.0
Thickness of Coat, mm	0.17	0.45	0.20	0.25

LR-5630 and silicone gum were separatly soluble in toluene, but LR 5630 and the gum were not miscible. The liquid mixtures were turbid, also the coats were turbid and the two polymers separated in the coat. Example No.2 was subjected to erosion for 3h. and immediately after exposure ice was adhered to the coat. The adhesive strength was 2.22 kg/cm^2. After storing of the sample for one and two days, the adhesive strengths were 4.24 kg/cm^2 and 3.34 kg/cm^2, respectively.

The surface of the coating was apparently damaged on exposure to erosion.

(3) Crosslinking of LR 5630 with Benzoylperoxide. The composition and characteristics were as follows:

TABLE 9

	1	2
BZO_2 (w/w % in LR5630)	5.0	2.5
LR5630, g	2.0	2.0
B_zO_2, g	0.1	0.05
Toluene, ml	8.0	8.0
Thickness of Coat, mm	0.17	0.38
Adhesive Strength, kg/cm^2	0.34	0.13
Adhesive strength immediately		
After Erosion	4.36	----
Stored for 3 days		----
After Erosion	4.53	

The solutions were clear; the coats, dried at room temperatue, showed many needle-like crystals of B_zO_2. The coats were heated at 100° C for 1h for the purpose of crosslinking. However after heating, the coat was still soluble in toluene at room temperature indicating that crosslinking had not taken place.

(4) Compostions containing high MW Poly (dimethylsiloxane).

Composition and characteristics are given in TABLE 10

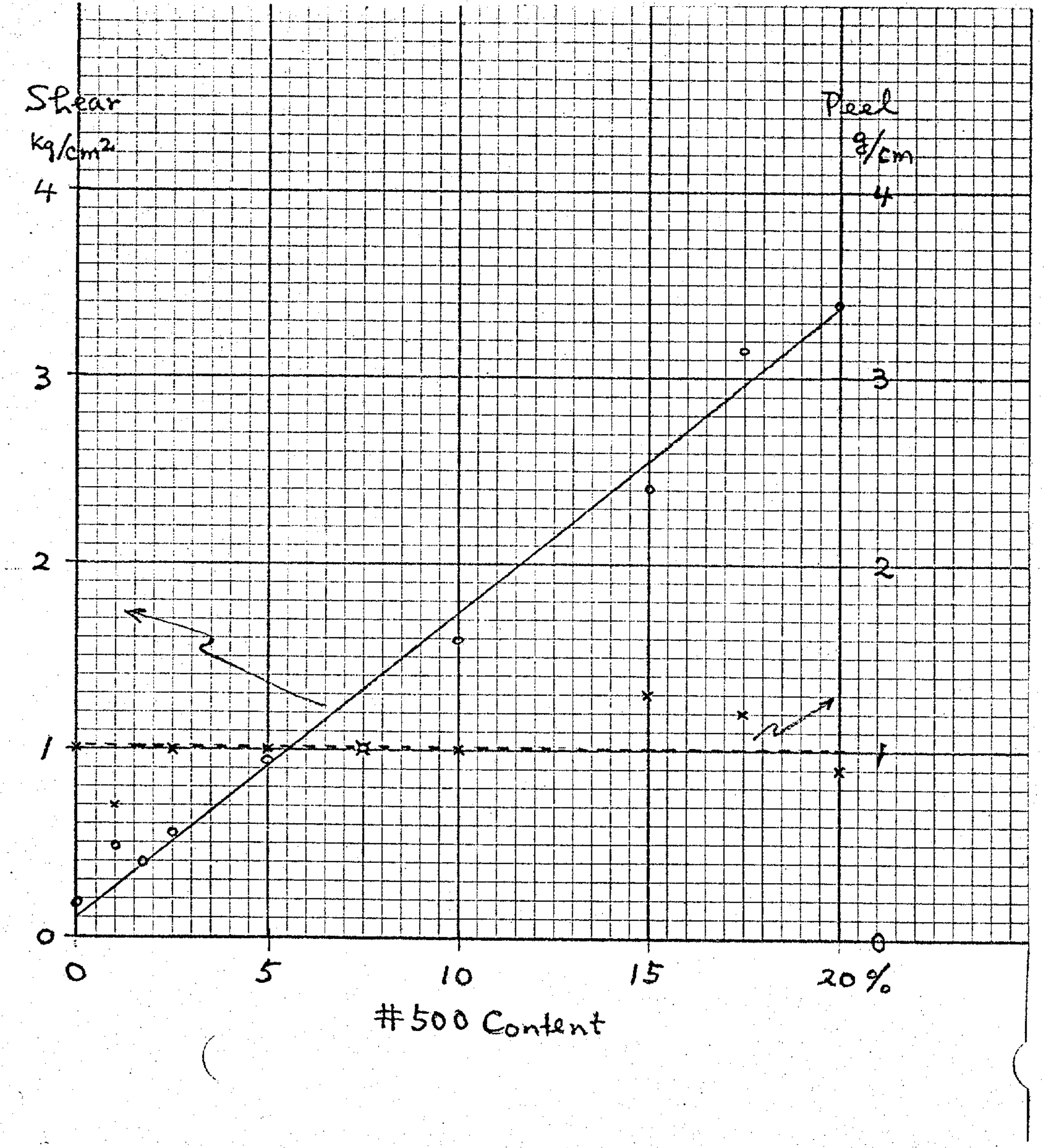
TABLE 10

Polycarbone Repeat Unit/ Poly Siloxane Repeat Unit	30/70	1* 35/65	40/60
LR5630, g	2.0	---	---
LR-3320,g	---	0.61	0.80
Poly (dimethysiloxane 1.MW 100 000g	0.3	0.39	0.35
Toluene, ml.	10.0	5.0	5.0
Dioxane, ml	---	5.0	5.0
Thickness of Coat, mm	0.275	_*2	_*2
Adhesive Strength, kg/cm^2	0.05	0.42	1.27

---

*1 This is the same ratio as in LR5630

*2 Coats were not uniform; copolymer and silicone separated in the coat.



Shear
kg/cm²
Peel
g/cm
4
3
2
1
0
4
3
2
1
0
0
5
10
15
20%
#500 Content

(5) Cross-linked silicone gum

(a) Silicone gum	2.0g
Toluene	8.0ml
B_zO_2	0.1g

A clear, viscous solution resulted. It was coated on an Al-plate and heated at 150°C for 0.5h. The coat was not uniform and was slightly colored. It was very fragile and its adhesive strength could not be measured.

(b) Silicone gum	2.0g
Toluene	8.0ml
Me Si(OEt)$_3$	0.2g

(for cross-linking)

Again a clear, viscous solution was obtained. The coat on Al was heated at 100°C for 1h. After crosslinking of the gum, the coat had a grease-like consistency; its adhesive strength was 0.06 kg/cm^2 (sliding).

(c) Tullanox # 500 and LR 5630

LR 5630 2.0g, various amounts of Tullanox #500 and toluene 10ml were mixed in a ball-mill for 16h and coated on Al. All coats were heated at 110°C for 1h.

Adhesive strength (kg/cm^2) and peel strength (g/cm) are plotted versus % Tullanox # 500 in the accompanying figure.

It is interesting to note that while the adhesive strength increases linearly with the % Tullanox content, the peel strength remains constant for the whole range of Tullanox percentages. Apparently, the surface becomes rougher with increasing Tullanox-powder content but the adhesion is not affected with respect to peeling.

One sample (15 % w/w of Tullanox #500) was subjected to erosion for 4.5h; for adhesive and peel strengths are given in TABLE 11 below.

TABLE 11

SAMPLE 3, TULLANOX #500, 15% w/w

		SHEAR STRENGTH (kg/cm^2)	PEEL g/m
Before Erosion		0.40	---
A few hours after Erosion		4.34	---
Stored for 1 day	After Erosion	3.15	---
Stored 18 days		1.55	2.9

Both adhesive and peel strength increase considerable on exposure to erosion.

(7) Effect of Erosion on Peel Strength.

(2) LR-5630	2.0g
Polydimehylsiloxane MW 100000)	0.3g
Toluene	10.0ml

A 225 µm thick coat on Al was prepared, its adhesive strength was 0.05 kg/cm^2. The coat was exposed to erosion for 18.5h and after erosion, peel tests were carried out.

	PEEL STRENGTH g/cm
Immediately after erosion	3.4
Stored for 1 day after erosion	0.7

The recovery appears to be remarkable.

(2) A LR-5630 coat(1.1mm thick) was exposed to erosion for 4.5h and its peel strength was measured:

	PEEL STRENGTH g/cm
Immediately after erosion	3.6
Stored 1 day	2.8
Stored 2 days	1.9

(8) Miscellaneous Compositions

(a) TAR -Epoxy-Enamel Subtrate

This surface was treated with dimethyldiethoxy silane ($Me_2Si(OEt)_2$ and left for 2h. It was anticipatated that the silane would be hydrolyzed in presence of moisture and would turn into silicone oil. The shear adhesive strength of such a coat was > 4.5 kg/cm^2.

(b) Polyainylidene fluoride (PVDT) was dissolved in warm cyclohexanone and the solution was coated on a warm Al-plate. Two coats were prepared,one was milky and the other one was practically transparent; these were tested.

Milky Coat	8.29 kg/cm^2
Transparent coat	5.64kg/cm^2

Coats Separated from the substrate after testing.

(c) Poly (vinyl butyral) (PVB)

(1) Butvar B-90 was dissolved in toluene and EtoH was added giving a clear solution:

Butvar B-90	2.68
Toluene	16.0ml
EtoH	4.0ml

A coat ca.70 µm on Al wrinkled on heating to 100°C for 1h. The shear strength amounted to 5.51 kg/cm^2.

To such a coat Me_2 $Si(OET)_2$ was added at room temperature and left about 0.5h. This compound was expected to react with -OH- groups. (18-20%) as PVA in PVB. The adhesive strength was 6.25 kg/cm ^{2}.

(2) $ME_2Si(OEt)_2$ (CA.20 to PVB) was added to the PVB-solution as prepared above. The Al-coat was heated at 100 ℃ for 1h prior to testing. Milky patterns appeared in the coat (0.15 mm thick): its adhesive strength was 9.32kg/cm^2.

(3) The following compostion was examined

Butvar B-90	0.8g
Poly (dimthylsiloxane), MW 100 000	0.2g
Toluene	8.0ml
Etoh	2.0ml

The solution was slightly turbid, the coat on Al was very turbid. Shear adhesive strength was 4.39 kg/cm^2. This strength was not reduced by adding silicone oil.

(4) A PVB-solution was prepared as above; it was coated on the specially prepared TAR-Epoxy-Substrate. After a first coat had dried, a second one was applied. However the PVB solution attacked the substrate and the latter bulged. The PVB could be easily peeled off.

(d) Polystyrene and Poly- α -methyl styrene did not show promising results.

(e) Erosion-Resistant Coat.

(1) Preliminary experiments

(a) LR-5630	1.0g
Toluene	9.0ml

Coats were prepared on Al. Two of the coats, Fluorolube s-30 or GE- Silicone oil SF-1154 were applied for one day prior to testing. Fluorolube proved to repel LR-5630 and it was difficult to obtain a uniform coat. The coats were exposed to erosion for 1.5h and immediately afterwards ice was adhered to them. Results are given below.

TABLE 12

SAMPLE	THICKNESS OF COAT mm	ADHESIVE STRENGTH kg/cm^2
LR-5630 control	0.10	3.18
LR-5630 with Fluorolube	0.11	0.85
LR-5630 with SF-1154	0.09	0.37

This is the first time that an adhesive strength value was obtained lower than 1.00kg/cm^2 immediately after exposure to erosion.

(b) Preliminary Experiment-2

Previously prepared coats were treated with SF-1154. They were stored at room temperature prior to exposure to erosion. After a 1.5h long erosion, samples were eroded again (16h LR-5630, and 5h LR3320).

Results are given below.

TABLE 13

SAMPLE	THICKNESS OF COAT mm	ADHESIVE STRENGTH, kg/cm^2 No Erosion	After 1st Erosion 1.5h	After 2nd Erosi 16h
LR-5630 } SR-1154	0.26	0.47	0.04	1.09
LR-5630	0.13	2.50	0.02	2.37

LR-5630 is well within the specified range (First Experiment)

(c) LR-5630/SF-1154 Compositions.

Seven different compositions were prepared:

LR-5630	1.0g
Toluene	4.0ml
SF-1154	various amounts, see TABLE 14.

TABLE 14

SF- 1154,g	0.0	0.1	0.2	0.4	0.6	0.8	1.0
%w/w	0	10	20	40	60	80	100
Coat thickness, *^{1} mm	0.26	0.29	0.32	0.37	0.42	0.47	0.58
Adhesive Strength, kg/cm^2 before erosion	0.38	0.22	0.12	0.06	0.07	0.17	---
Immediately after erosion, kg/cm^2	2.87	3.71	1.81	0.20	0.61	1.16	0.71
16 h after erosion*^{2}	DATA NOT YET READY				0.68	2.57*^{3}	1.61

---

*1 Calculated values

*2 Cumulative erosion i.e. 19h

*3 24h instead of 16h

These last results will be discussed in the next report. Experiments with G.E. silicone varnish are now in progress. Overall, the results show that LR-5630 plus SF-1154 is the most promising system provided coats are relatively thick.