65-F

Final Report

(March 1983 - June 1985)

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

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Contents

I. Introduction

II. Preliminary Experiments
  1. Tensile Apparatus
  2. Various Preliminary Results Using Polydimethylsiloxane-Polycarbonate Block-Co-Polymers
  3. Hardness of Coatings
  4. Summary
  References

III. Tensile Modulus of Film for Coating

IV. Abhesion Tests of Coats of LR-5630 Coating Formulations

V. Erosion of LR-5630 Coats

VI. Tensile Moduli and Adhesive Strengths of Polydimethylsiloxane-Polycarbonate Block-Co-Polymer Coatings

  1. LR-5630/Silicone Oil (Thomas)
  2. LR-3320/Silicone Oil (Thomas)
  3. Experiments on Milling Tullanox #500 into LR-5630 with or without Silicone Oil
  4. Some Miscellaneous Polymer Coats
  5. The Effect of Pentafluoro-octyl alcohol
  6. LR-5630 and LR-3320 with Silicone Oils
  7. Heating of Coats
  8. Coat: Hi-Mil Sher-Tar Epoxy Enamel, Sherwin Williams
  9. Tensile Modulus as Function of LR-5630/#500 Composition and Temperature
  10. Shear Adhesive Strength As Function of Tensile Modulus
  11. Shear Adhesive Strength As Function of Film Thickness
  12. Summary

VII. Peel Adhesive Strength of Copolymer Film from an Ice Surface
  1. Peel Adhesive Strength Tester
  2. Test Results of Peel Adhesive Strength

VIII. Effect of Erosion (Air-Water Jet) on Adhesive Strength
  1. Gale Tunnel for Weathering Test
  2. Preliminary Experiments
  3. Poly(dimethylsiloxane)-Polycarbonate Block-Co-Polymers, XD-11 and 131-848
  4. G.E. Silicone Varnish (Sample #4124)
  5. Dow Corning Compound 5.
  6. LR-5630 Co-polymer Coats
  7. LR-3320 Co-polymer Coats
  8. Summary

IX. Coats on Sherwin Williams Hi-Mil-Sher-Tar Epoxy Enamel Coat

X. Polycarbonate (PC) Coatings
  1. PC/LR-5630
  2. PC/Fluorolube S-30
  3. Double Coat (PVB Primer/PC-Top-coat)
     (PVB: Poly(vinyl butyral))
  4. Effect of Dioxane on PC-Coat
  5. PC/Poly(dimethylsiloxane)

XI. Co-polymer Coatings
  1. LR-5630 Coat exposed to Erosion
  2. LR-5630/Tullanox #500
  3. Effect of Erosion on Peel Adhesive Strength

XII. Miscellaneous Coatings
  1. Tar-Epoxy-Enamel Substrate
  2. Poly(vinylidene flouride)
  3. Poly(vinyl butyral)
  4. Polystyrene and Poly(α-methyl styrene)
  5. Erosion-Resistant Coats

XIII. Polyethylene Foam Mat

IX. Dow Corning Varnish #997
  1. Preliminary Experiments
  2. Curing Conditions
  3. #997 Varnish Modified with Dimethyldiethoxysilane
  4. Addition of Silicone Oil

X. SR80M Silicone Electrical Resin Mady by G.E.
  1. Curing Experiments
  2. Coating Experiments
  3. Modification of SR80M
  4. Addition of Silicone Oil SF-1154

XI. Silicon PS 255 (Fluka Chemical Corp.)

XII. Vinyl-acrylate Copolymer Lacquer

XIII. Dow Corning 3145 RTV Clear Adhesive-Sealant
  1. 3145 RTV Silicone Paste
  2. Adhesive Shear Strength
  3. Tensile Strength of RTV Silicone Coats

XIV. Final Conclusions

Appendix: Preparative Procedure for Most Promising Coatings
Including Polyethylene Foam Sheet

FINAL REPORT

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by

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I. Introduction

The objective of this research is the development of efficient de-icing methods for prevention of ice formation of/on oil drilling platforms located off-shore in cold ocean regions.

Coatings are investigated first.

The requirements for such a coating are:

(1) About 90% or more reduction of adhesive strength of the ice/coating interface.

(2) Sufficient adhesive strength of the coat to the substrate.

(3) Resistance to cracking or peeling of the coating due to impacts by sea spray and waves.

(4) Resistance of coating to other environmental deterioration, particularly to near u.v. light radiation of the sun.

(5) Easy application of coating to substrate.

The block-co-polymer LR5630 (polysiloxane and polycarbonate) was investigated first because of its superior properties for de-icing of lockwalls.[1]) This co-polymer contained 65% w/w polysiloxane, T_g was $-66^{\circ}C$.

II. Preliminary Experiments

Point (3) above, i.e. mechanical-rheological properties and hardness of coating of LR5630 was investigated first.

A tensile (strength) apparatus was designed and made in our workshop (see Fig. 1). Hardness measurements were preliminarily carried out by the pencil hardness method. Coating compositions were varied by trying to crosslink the polydemethylsiloxane component or by using double layers (i.e., undercoats). The experimental part of this work is described below.

1. Tensile Apparatus

Fig. 1 shows a schematic drawing of the tensile apparatus: (A) sample between chucks; always 1 cm, (B) micrometer screw for making contact between the elastic piece of spring (D) and the lever of the Statham strain gauge (C).

The sample is held between the pulley and spring by nylon fish line. The strain rate is 2.9 mm/s, but will be made changeable in the future. The dimensions on the samples are: length, ℓ_o, between chucks 1.0 cm, width 0.5 cm (these dimensions remain constant); thickness is measured for each sample (ca. 50-100 μ.); testing temperature $20-21^{\circ}C$.

Fig. 2 gives a magnified view of the sample held by the chucks; it is self-explanatory.

For such a sample (i.e. LR5630) Young's (tensile) modulus can be calculated from the initial slope of the stress-strain curve. The result is 9 kg/cm^2 (8.8×10^6 $dyne/cm^2$, 9×10^5 Pa/cm^2).

Leverne-Williams et al.2) measured rheological properties of the same block-co-polymer at a strain rate of 0.3 mm/s. From his small graph the tensile modulus can be derived as about 11 kg/cm^2.

It was ascertained that Young´s modulus obtained from the slope of the linear parts of our strain vs. stress curves are quite similar to the one obtained by Leverne-Williams2) for the same block-polymer. Numerical results will be discussed in more detail later.

This indicates that the tensile apparatus functions satisfactorily for our purpose. A preliminary experimental result is given below.

Young´s (i.e. tensile) Modulus of LR5630

	Present Work	Leverne-Williams2)
Young´s Modulus	9.1 x kg/cm^2	11 kg/cm^2
Strain rate	2.9 mm/s	0.3 mm/s (2 cm/mm)
Dimension of Sample:		
Width	5 mm	-
Span Between Chucks i.e. Length	10 mm	-
Thickness	ca. 50 μ - 100 μ	-
Temperature	20°C - 21°C	23°C

Some preliminary results are give below:

2. Various Preliminary Results Using Polydimethylsiloxane-Polycarbonate Block-Co-Polymers

(1) LR5630: Film thickness 0.18 mm; film width 0.5 cm, distance between chucks 1.1 cm. The break occurred at one of the chucks:

Tensile strength 23 kg/cm^2 (ca. 22°C); elongation at break was not measured.

(2) LR5630: Film thickness 0.050 mm, width 0.6 cm, chucks 0.7 cm.
Tensile Strength 38 kg/cm^2, elongation at break 974%, 22°C; strain rate 2.9 mm/s; (sensitivity of Sanborn recorder: 3.6 ± 0.1 mm/g.)
A thickness of ca. 0.050 mm was found to be preferable over thicker films.

3. Hardness of Coating

We know from previous work that LR5630 was the best abhesive polymer for de-icing lockwalls. We also know that the abhesive force does not vary for such a coating when kept under water for various time periods.

A stock solution of LR5630 was prepared having a composition as follows:

LR5630	4.0 g
Silicone Oil (Thomas No. 6407)	0.4 g
Toluene	20.0 ml

A coat was made on a surface - oxidized (rusty) iron plate (3" x 3"). The dried film had a thickness of 0.15 to 0.2 mm.

A jet of saline water (3.5% w/v NeCl) was directed onto this coat. The jet nozzle had a diameter of 5.4 mm. The jet was kept on for 2.5 h. The volume exit rate was 800 ml/s and the linear rate 3.9 m/s. The film resisted this treatment without damage.

However under actual conditions, the impact of waves and spray are about 10 times stronger; ice particles and possibly other particles are contained in sea water sprays.

Hence experiments were carried out dropping a sphere (18.6_g) inside a glass tube on a one mm thick film coated on a rough iron plate. The velocity at impact was 313 cm/s and the kinetic energy 9.1×10^6 erg. It was apparent that around the indentation of the film especially at rough spots of the substrate surface, the coating was damaged.

Hence, the next step of the work consisted in trying to make this coating harder without altering appreciably the ice/coating adhesive strength.

First, crosslinking of the polysiloxane-blocks in co-polymer was attempted; benzoyl-peroxide (BzO_2) was used as the crosslinking agent. 2.5% w/w BzO_2 was added to the above stock solution. A coat was spread on an Al-plate. This was heated to 125°C for 0.5 h, 1.0 h and 2.0 h, respectively. Adhesion to the Al-plate improved with time of heating. However, the film remained soluble in toluene and the hardness of the film remained the same. Thus, crosslinking was not achieved in this case.

Next, siloxane, high gum (Polysciences, Inc.) was dissolved in the stock solution, 5% w/w of BzO_2 was added. The coating was heated similarly as before. Still, crosslinking did not occur. Here, the stickiness of the coating decreased on heating.

The block-polymer XD-11 (25% w/w polysiloxane; T_g 100°C) which is harder than LR5630 was tested. Its stock-solution composition was as follows:

XD-11	1.5 g
Toluene	5.0 ml
CH_2Cl_2	10.0 ml

Coats were prepared on glass-plates with increasing amounts of silicone oil (Thomas) of 0.15 ml up to 0.75 ml. As adding 0.9 ml silicone oil, polymer and oil separated in solution.

The hardness of the XD-11 films was also tested by the pencil hardness method. Even the softest pencil (6B) penetrated the film (thickness ca. 10). Adhesion of the film to glass decreased with increasing silicone oil content.

Also, polysiloxane gum was tested. Up to 40% of the gum was added to the XD-11 films. But again, all films were penetrated by the pencil (6B).

The next experiments dealt with double coats of Butvar B-90 and LR5630. It had been found during previous work (lockwalls) that LR5630 is improved in its mechanical properties by a Butvar primer (probably also mutual diffusion takes place to a certain extent). Previously, it proved to be the best double coat system.

The stock solution for Butvar B-90 was as follows:

Butvar B-90	1.5 g
Toluene	10.0 ml
Ethanol	8.0 ml

Coats were made on glass plates and dried at room temperature for one day. Even the hardest pencil (H-6) did not damage this coat.

4. Summary

Preliminary experiments have been carried out.

1. (1) A tensile apparatus was designed and built which proved to be satisfactory.
2. (2) Experiments showed that the polysiloxane-polycarbonate block-co-polymer proved to be too soft to withstand impact of waves and sea spray as expected under actual conditions.
3. (3) Crosslinking of the siloxane component in the block-co-polymer by benzoylperoxide was not achieved.
4. (4) The hardness of films of the block-co-polymer, XD-11, even when modified by additions, was also not sufficiently resistant.
5. (5) Double coats of Butvar B-90 (Primer) and LR5630 appeared to be sufficiently hard.

References

(1) H.H.G. Jellinek, H. Kachi, S. Kittaka, N. Lee and R. Yokota, Ice Releasing Block-Co-Polymer Coatings, Coll. Polym. Sci. 256, 544-551 (1978).

(2) W. Maung, K.M. Chua, T. H. NG and H. Leverne-Williams, Dynamic Mechanical and Thermomechanical Properties of Silicone-polycarbonate Block-Co-Polymers, Pol. Eng. Sci., 23, 439-445 (1983).

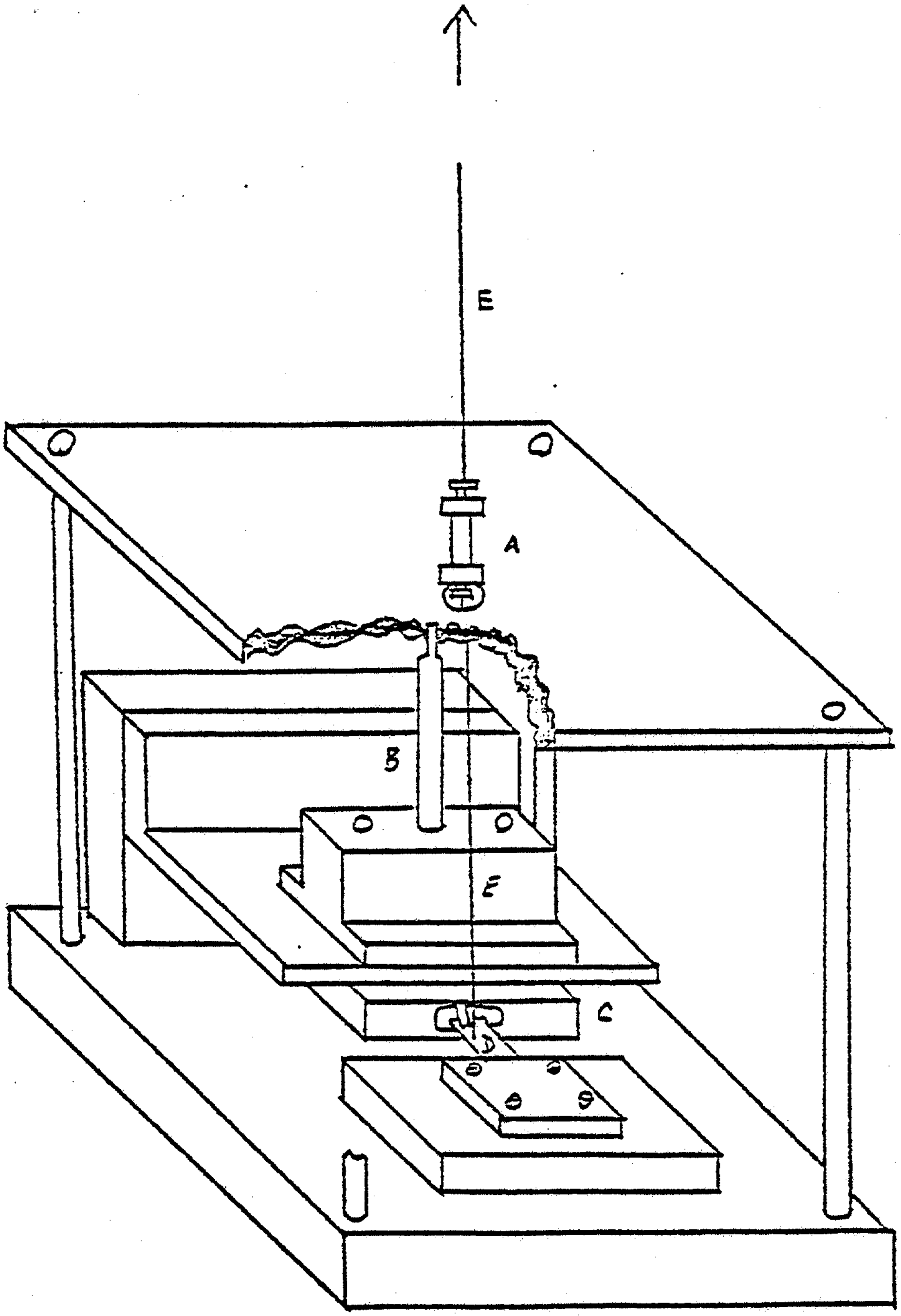


FIGURE 1: Tensile Tester

A: Sample Holder

B: Micrometer screw for moving the transd

C: Transducer (Statham Transducers, Inc. Model G10B-0.3-350)

D: Stainless steel spring

E: Nylon thread (475 μ diameter)

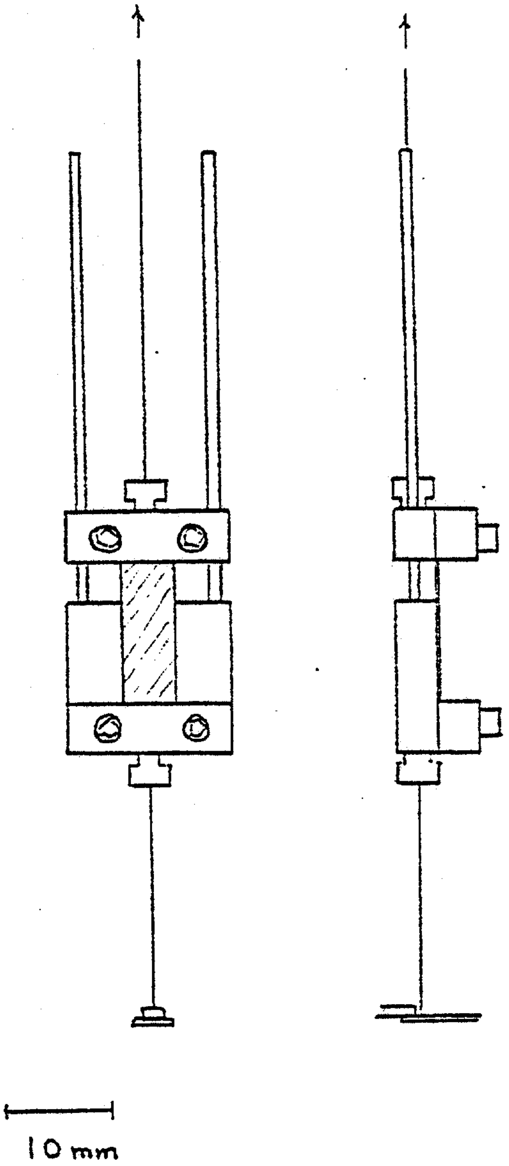


FIG. 2

III. Tensile Modulus of Film for Coating

The work on strength of films with a variety of added compounds has been carried on with the tensile strength apparatus described in Paragraph II. In addition, some shear abhesion and erosion tests by impact of water jet were performed.

Tensile Strength Experiments.

Young's modulus of sample LR5630.

Parameters for these tests were given in Paragraph II.

2 g of the polysiloxane-polycarbonate co-polymer LR5630 were dissolved in a mixture of 4.0 ml toluene plus 4.0 ml methylene dichloride (CH_2Cl_2). Certain amounts of silicone oil were added to such solutions (H. Thomas 6428-R15). The oil is not completely miscible and the solution became increasingly more milky as additional amounts of silicone oil were added. Films were cast from such mixtures and the film surfaces were progressively more oily as with increasing silicone oil content, noticeably so beyond a mixing ratio of LR5630: silicone oil = 100/60 w/v. A 1:1 mixture of LR5630 to silicone oil separated out.

Films were cast on glass-slides and spread with a knife-like coater. The films were dried not longer than two days at room temperature. A film sample for tensile tests could be easily obtained by peeling the film off the slide. The range of film thickness was about 50 to 100 μm. The temperature was controlled to ± 1°C. Each tensile value in Table 1 represents the average of about 10 tests.

TABLE 1

Young's (Tensile) Modulus of LR5630 Films Plus Various Amounts of Silicone Oil

(See also Fig. 3)

Temp. °C	(Young's) Tensile Modulus, $E(\overline{kg/cm^2})$					
	LR5630/Silicone Oil					
	100/0	100/10	100/20	100/40	100/60	100/80
20	9.8 ± 0.5	8.3 ± 0.7	6.1 ± 1.0	5.7 ± 0.7	5.5 ± 0.6	4.3 ± 0.3
10	13.5 ± 1.3	11.8 ± 1.8	10.5 ± 1.3	7.9 ± 1.7	7.3 ± 0.7	6.7 ± 1.4
0	19.6 ± 3.6	15.9 ± 0.9	12.1 ± 1.1	11.5 ± 1.5	9.1 ± 1.3	7.8 ± 1.6
-10	24.1 ± 3.4	19.4 ± 3.8	18.2 ± 4.8	12.3 ± 2.8	10.4 ± 3.1	8.9 ± 3.9
-20	30.6 ± 4.0	24.1 ± 9.3	21.5 ± 2.9	16.5 ± 4.3	12.1 ± 3.3	10.4 ± 1.2

The results can be formally respresented by an Arrhenius type energy of activation plotting $\log_{10}$ (tensile modulus) vs. the reciprocal absolute temperature (E ~ Young's Modulus)

$$\log_{10} E = \frac{E_{Arrh}}{2.303RT} \quad \log A$$

E_{Arrh} is the apparent Arrhenius energy of activation, 'A' the pre-exponential factor and R the ideal gas constant.

All values for 20°C showed systematic lower deviations from the respective straight line; they were not included in the evaluation of the energy of activation. The reason for this is not understood at present (See Fig. 4). It is possible that at +20°C, the co-polymer starts to enter an elastomeric range.

TABLE 2

(Formal) Apparent Energies of Activation for Young's Modulus

(See Figs. 4 and 5)

LR5630/Silicone Oil (w/v)	E_{Arrh}(kcal/mol)
100/0	4.2
100/10	3.7
100/20	3.4
100/40	2.8
100/60	2.7
100/80	2.3

These energies of activation also indicate increased mobility with increasing oil content.

IV. Abhesion Tests of Coats of LR-5630 Coating Formulations

The apparatus and procedure were the same as used in previous work [See H.H.G. Jellinek, H. Kachi, S. Kittaka, M. Lee and R. Yokota, Colloid and Polym. Sci., 256, 544-551, (1978)].

TABLE 3

Adhesive Strength of LR5630

Plus Silicone Oil

LR5630/Silicone Oil (w/v)	Adhesive Strength kg/cm^2	No. of Tests
(1) 100/20 1g LR5630 : 10.0 ml Toluene: 0.2 ml oil	0.045 ± 0.003	5
(2) 100/0 3.5g LR5630 : 15 ml Toluene: -	0.61 ± 0.14	5
(3) 3.5g LR5630 : 15.0 ml Toluene plus Tullanox #500 An Al-plate was coated with LR5630 film and dried; it was immersed in #500 Tullanox powder for one minute and brushed off. Film thickness 60-70 µm.	0.97 ± 0.71	5

Tullanox (formerly Silanox) is a silica powder made hydrophobic by a surface layer of silanes. The hydrophobic CH_3-groups "stick" out from the surface of the particles. "Tullanox" has a so-called "super-hydrophobic" repellency of water. Tullanox #500 has a particle size of about 70 $\mathring{A} = 7 \times 10^{-7}$ cm, hence it has a very large specific surface area. The contact angle of water is extraordinarily large ($\theta = 138^{\circ}$). This is due to its hydrophobicity and surface roughness. A monolayer of Tullanox #500 consists of about 2×10^{12} particles/cm^2. Such a surface is relatively rough and therefore holds a drop of water slightly above the coated surface. An effect is produced which is similar to water-shedding surfaces found in nature (insects, foliage). A sheen or so-called "gaseous plastron" effect is observed on immersion in water.

The roughness explains the increased adhesive strength of films with Tullanox measured by shear. The hydrophobicity is certainly very high as a drop of water shows a contact angle above 90°C. Thus it appears that adhesive strength measurements will have to be modified to some kind of peeling procedure.

A number of additional abhesion tests were performed with Tullanox #500 added.

TABLE 4

Adhesive Strength of LR5630
Plus Tullanox #500

	Adhesive Strength	No. of Tests
(4) LR5630 LR5630 1.0g; 2.5 ml Toluene; 2.5 CH_2Cl_2	0.30 ± 0.18	5
(5) LR5630; brush coating of #500; otherwise, same composition as (4).	2.41 ± 0.37	5
(6) LR5630; #500 applied by knife-like coater; otherwise, same composition as (4). 0.5g Tullanox suspension in 10.0 ml Toluene.	0.92 ± 0.23	5
(7) LR5630; #500 milled into mixture. ball-milled solution; LR5630 1.0g, toluene 10.0 ml, #500 0.6g. (milled for 11 h)	0.58	1

Contact angles of water with (5) and (6) were > 90° and also larger than for #(4) and #(7).

V. Erosion of LR5630 Films

A coat of LR5630, ca 0.15 mm thick containing 10% by volume of silicone oil was cast on a rusty iron plate (7.5 cm x 7.5 cm). A jet stream of water was directed on to the coat having a linear velocity of ca. 14 m/s. The diameter of the nozzle was 0.3 cm and the volume rate 100 ml/s. The film was only slightly damaged.

According to information received from CRREL, the wind velocity hitting an oil drilling system will be in the range of 40-70 mi/h (24 m/s). We estimate that our water jet has a larger impact than such a wind.

FIG. 3

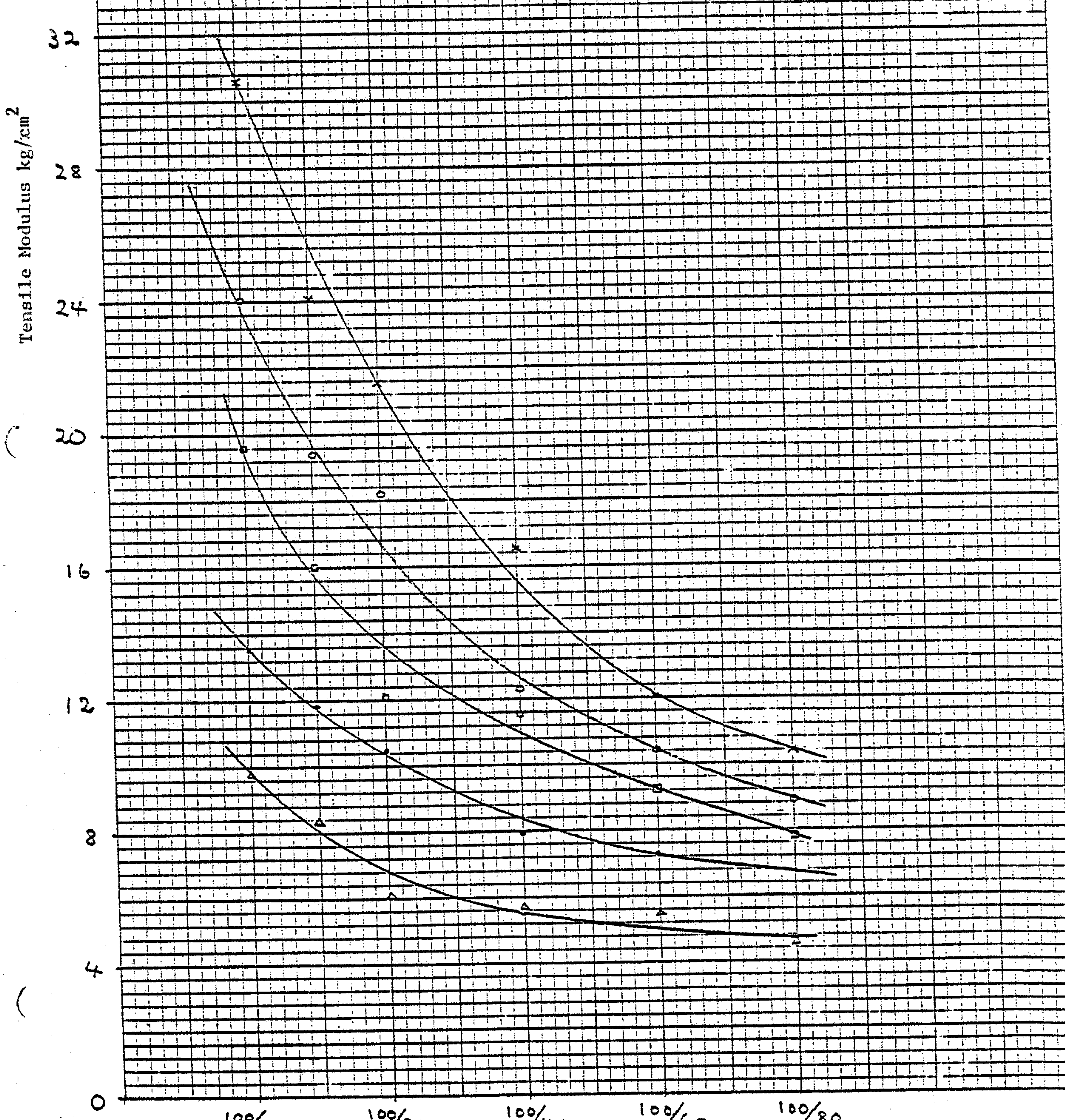

Tensile Modulus kg/cm2
32
28
24
20
16
12
8
4
0
100/0
100/20
100/40
100/60
100/80
10 Squares to the Inch

FIG. 4

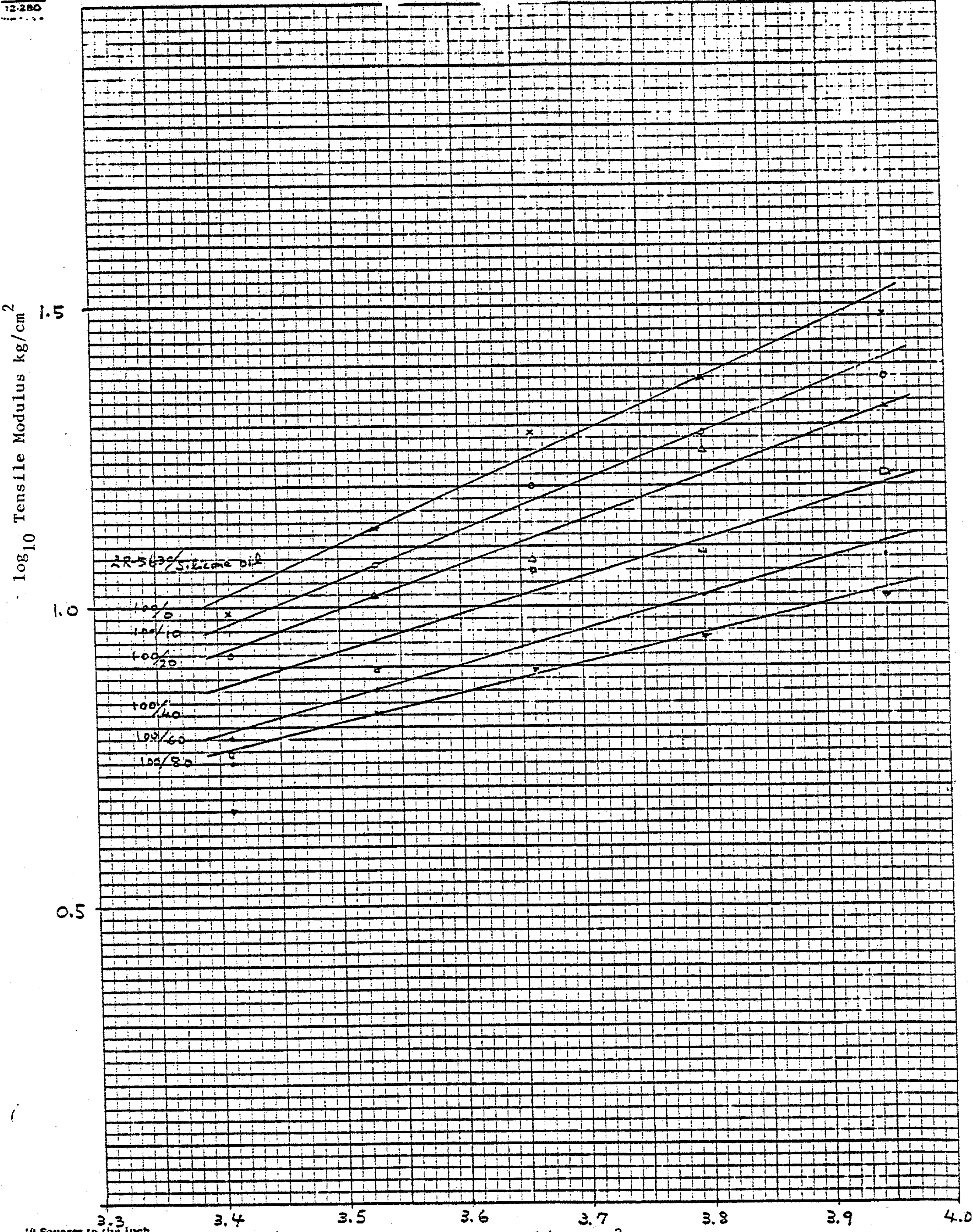
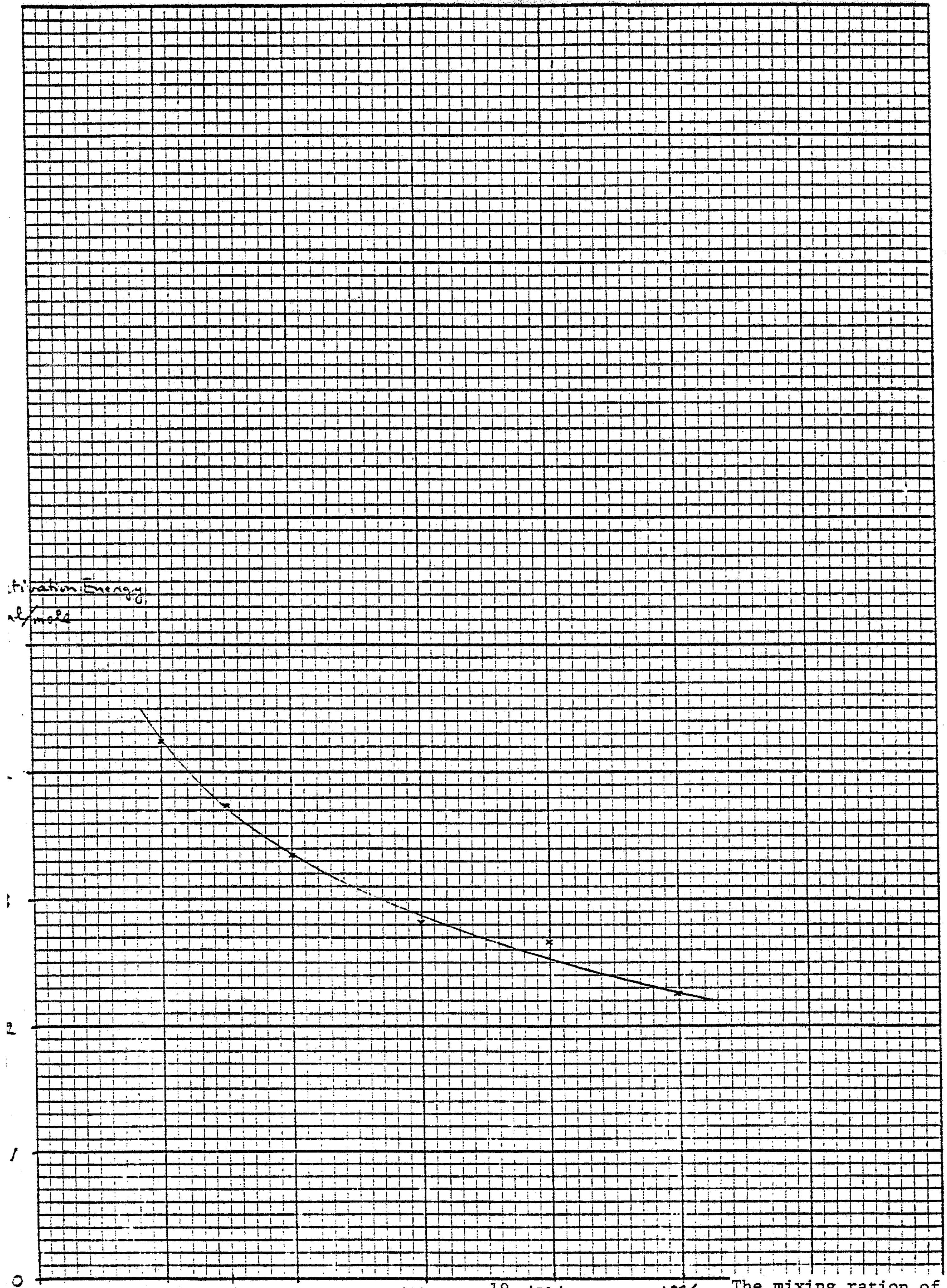

$\log_{10}$ Tensile Modulus kg/cm^2
1.5
1.0
0.5
2R-5639/Silicone oil
100/0
100/10
100/20
100/40
100/60
100/80
3.3
3.4
3.5
3.6
3.7
3.8
3.9
4.0

FIG. 5



VI. Tensile Moduli and Adhesive Strengths of Poly(dimethylsiloxane) - Polycarbonate block-co-polymer Coatings

The tensile and adhesive strength measurements have been continued with a variety of mextures of the poly(dimethylsiloxane) - polycarbonate block-co-polymers with and without added silicone oils of different composition. The technique is the same as described in the previous Paragraphs I – III. Thomas and G.E. (SF-1154) Silicone oils and some other mixtures were investigated.

1. LR-5630/Silicone Oil (Thomas)

(a) Tests with Thomas Silicone oil 20% w/w (A_2) without oil (A_1), without heating of the coat (B_2) and with heating at 125°C for 1 h in air (B_1), with Tullanox #500 were carried out. A coated Al-plate was submerged in #500; the excess of #500 was blown off (C_1); the coat without Tullanox #500 was also tested (C_2). Also surface-properties were considered: D_1 - rough (coating was applied to the Al-plate using a polymer solution containing many tiny air bubbles): D_2 - smooth (coating was applied in the same way as above but most bubbles were removed). The results of adhesive strength tests (shear), which always were carried out at -10 ± 1°C are given below as mean-values of four tests in each case (± standard deviation).

TABLE 5

Adhesive Strength/kg/cm^2(-10°C)

A_1	0.78 ± 0.41	B_1	1.13 ± 0.41	C_1	1.20 ± 0.41	D_1	0.74 ± 0.69
A_2	0.71 ± 0.41	B_2	0.35 ± 0.41	C_2	0.28 ± 0.41	D_2	0.78 ± 0.69

The F-statistical test applied to this data shows that the differences between B_1 and B_2 and C_1 and C_2 are significant. The magnitude of the effect on the parameters of the coats is in the order:

$$C > B > A > D$$

Too much heating of these coats increases the adhesive strength. But if the temperature is not so high, favorable results are obtained (see later below).

(b) Relative Adhesive Strength of the Coats with Respect to the Substrate (Al).

This adhesion was examined in a very simple way by rubbing the coats with the fingers. Relative results were obtained as follows:

(1) Heating without silicone oil does not increase adhesion of the coat to the substrate.

(2) A slight increase of adhesion was observed when adding silicone oil and heating.

(3) Application of Tullanox #500 on the surface of the coat increases adhesion regardless of the addition of silicone oil.

(4) Mixing Tullanox #500 into the coat and heating makes the coat to adhere well; in this case it can only be peeled off with difficulty.

(5) The results are similar to (4) without heating of the coats (i.e., Tullanox #500 mixed in).

2. LR-5630/Silicone Oil (Thomas)

The tensile modulus of LR-3320 is about 13 times larger than that of LR-5630. the latter is the best abhesive of this series of block-co-polymers; it is expected that a coat of LR-5630 is mechanically much stronger than that of LR-5630 coats with or without silicone oil. These expectations are confirmed by the experimental results given below. At least 4 tests each were performed in every case.

TABLE 6

LR-3320/Silicone Oil (Thomas) by wt.	Tensile Modulus kg/cm^2		Adhesive Strength kg/cm^2 (-10°C)	Thickness of Coat µm
	-10°C	+20°C		
100/0	275 ± 70	135 ± 12	3.42 ± 0.61	50 ± 2
100/10	254 ± 12	138 ± 12	2.71 ± 0.64	56 ± 2
100/20	263 ± 25	143 ± 16	1.94 ± 0.06	60 ± 3
100/40	190 ± 22	97 ± 10	2.07 ± 0.28	66 ± 3
100/50[x]	201 ± 26	107 ± 10	3.62 ± 0.67	68 ± 1
100/60[xx]	155 ± 19	100 ± 10	2.64 ± 0.64	83 ± 9

[x] A Small amount of silicone oil separates from the polymer coat.

[xx] Silicone separates; a smooth coat could only be obtained by making it thicker.

The decrease in tensile modulus with the addition of silicone oil is moderate, i.e., the co-polymer is not very much softened by the oil. The adhesive strength is large (ca. 20 x larger than found previously in the published paper). The reason for this is obscure at present. The adhesive strength varies irregularly with the oil content (see Fig. 6).

3. Experiments on milling Tullanox #500 into LR-5630 with or without silicone oil.

The milling took 3-10 h to make uniform solution. Al-plates were coated with solution. The results are given below.

TABLE 7

LR-5630/#500/Silicone 0.1 by wt.	Tensile Modulus kg/cm^2		Adhesive Strength kg/cm^2	Thickness of Coat
	-10°C	20° - 22°C	(-10°C)	μm
100/0/0	22 ± 2	9.8 ± 0.5	0.30 ± 0.18	88 ± 8
100/60/0	69 ± 22	32 ± 13	0.58*	--
100/25/0	--	16.1 ± 1.6	--	111 ± 11
100/25/0	37 ± 4	18 ± 3	4.53 ± 3.0	61 ± 3
100/30/0	--	16.8 ± 2.0	--	186 ± 14
100/10/0	27 ± 3	20 ± 3	--	199 ± 61
100/25/10	29 ± 3	13 ± 1	3.78 ± 0.21	70 ± 3
100/0/10	19.4 ± 3.8	8.3 ± 0.7	0.16 ± 0.05	92 ± 8

* One sample only.

Films increase in tensile modulus and adhesive strength with the amount of #500. One reason why the adhesive strength (shear) increases with #500 is the increasing roughness of coated surface due to the small Tullanox particles adhering to the surface. Addition of silicone oil reduces both quantities.

4. Some Miscellaneous Polymer Coats

Coats of mixtures of Lexan (G.E., Grade 100-11 polycarbonate) or XD-11 (a block-co-polymers of polycarbonate and polydimethylsiloxane with a higher T_g value than either that of LR-5630 or LR-3320) with or without silicone oils) were tested in order to ascertain whether their tensile moduli are high. However their adhesive strength values were not low enough to carry the experiments through.

TABLE 8

Composition by wt.	Tensile Modulus kg/cm^2		Adhesive Strength kg/cm^2 (-10°C)	Thickness of Coat μm
	-10°C	20°C		
Lexan/LR-5630/Silicone Oil(Thomas) = 100/50/10	789 ± 100	564 ± 90	3.05 ± 0.45	50
Ditto = 100/10/10	688 ± 91	291 ± 42	3.00 ± 0.80	45
XD-11/LR-5630 = 50/50	--	--	>4.92*	--
XD-11/Silicone Oil (SF-1154) - 100/50	--	--	2.37 ± 0.31	--

* One sample only.

5. The Effect Pentadecafluoro-octyl Alcohol (PFOA)

Coats of Lexan (polycarbonate) containing 1 w/w% of PFOA and Formvar 15/95 E Grade (Monsanto) also containing 1 w/w% of PFOA are suppose to have fairly good abhesive properties. The results, given below, actually show that the abhesive properties of coats are quite poor.

TABLE 9

Composition by wt.		Adhesive Strength kg/cm^2 (-10°C)
Formvar 15/95E/PFOA	100/5	4.16 ± 0.38
Formvar 15/95E/PFOA	100/10	4.24 ± 0.21

Coat of Lexan/PFOA=100/20 did not stick to Al-substrates.

6. LR-5630 and LR-3320 with Silicone Oils

Thomas silicone oil consists probably mainly of methyl-silicone oil, while SF-1154 (G.E., for high temperature baths) contains aromatic groups, i.e. phenyl-silicone. These two oils are not miscible, even not at 120°C. Their solubilities in the block-co-polymers are also different. Thomas oil is scarcely miscible with either LR-5630 or LR-3320. SF-1154 is miscible with these block-co-polymers. The effect of these oils on the abhesive strength of LR-5630 and LR-3320 were examined. The results are given below.

(a) LR-5630/LR-3320/Thomas Silicone Oil

TABLE 10

LR-5630/LR-3320/Oil by wt.	Adhesive Strength kg/cm^2 (-10°C)	Tensile Modulus kg/cm^2	
		-10°C	+20°C
100/0/10	0.16 ± 0.05	19 ± 4	8 ± 1*
75/25/10	0.09 ± 0.04	32 ± 2	17 ± 2
50/50/10	0.56 ± 0.48	110 ± 11	43 ± 5
27/75/10	4.15 ± 0.12	197 ± 30	93 ± 12
0/100/10	2.71 ± 0.64	254 ± 12	138 ± 12**

*See Table 1.

**See Table 6.

It should be noted that both, adhesive strength and tensile modulus, increasing appreciable for a LR-3320 content of 25% w/w and higher (see Fig. 7).

(b) LR-5630/LR-3320/SF-1154 Silicone Oil

TABLE 11

LR-5630/LR-3320/Oil by wt.	Adhesive Strength kg/cm^2 (-10°C)	Tensile Modulus, kg/cm^2	
		-10°C	20°C
100/0/20	0.10 ± 0.02	15 ± 2	7 ± 1
75/25/20	0.03 ± 0.01	25 ± 3	9 ± 1
50/50/20	0.71 ± 0.24	39 ± 4	15 ± 1
25/75/20	1.61 ± 0.24	90 ± 7	33 ± 2
0/100/20	0.67 ± 0.12	199 ± 30	80 ± 13

See also Fig. 8 for the above results.

Adhesive strength increases with tensile modulus up to a ratio LR5630/LR3320 = 25/75. But for 0 parts LR5630, the adhesive strength drops considerably (see also Fig. 4). The tensile modulus, however, increases steadily throughout without any sign of the decrease in adhesive strength.

The next results show that either oil has a comparable effect on the adhesive strength of LR-5630.

TABLE 12

LR-5630/Silicone Oil by wt.	Tensile Modulus kg/cm^2		Adhesive Strength, kg/cm^2 (-10°C)
	-10°C	20°C	
100/20 (Thomas)	18 ± 5	6 ± 1	0.04 ± 0.003
100/20 (SF-1154)	15 ± 2	7 ± 1	0.10 ± 0.02

Thomas silicone oil is only partially miscible with LR-5630, but SF-1154 is completely miscible. Nevertheless, the tensile moduli are nearly the same for both cases. However, the effect of the oils increases if appreciable amounts of LR-3320 are added to the above mixture:

TABLE 13

LR-5630/LR-3320/Oil by wt.	Tensile Modulus kg/cm^2		Adhesive Strength, kg/cm^2 (-10°C)
	-10°C	20°C	
0/100/20 (Thomas)	263 ± 25	143 ± 16	1.74 ± 0.06
0/100/20 (SF-1154)	119 ± 30	86 ± 13	0.67 ± 0.12
25/75/20 (Thomas)	198 ± 30	53 ± 5	3.43 ± 0.45
25/75/20 (SF-1154)	90 ± 7	33 ± 2	1.61 ± 0.24

The tensile moduli are rather large, but the adhesive strengths have only moderately increased.

(c) LR-3320/SF-1154

TABLE 14

LR-3320/SF-1154 by wt.	Adhesive Strength kg/cm^2 (-10°C)	Tensile Modulus kg/cm^2	
		-10°C	+20°C
100/0	3.42 ± 0.61	275 ± 70	135 ± 1.2
100/10	1.21 ± 0.14	177 ± 21	94 ± 9
100/20	0.67 ± 0.12	199 ± 30	86 ± 13
100/50	0.58 ± 0.41	78 ± 9	19 ± 3
100/100	0.31 ± 0.17	36 ± 3	14 ± 1

Increase of SF-1154 oil does not change the adhesive strength of LR-3320 appreciably. However there is a large decrease in adhesive strength passing from LR-3320 without oil to 20 w/w% of added oil (See Fig. 9).

Thomas oil decreases the adhesive strength of LR-3320 less than SF-1154:

TABLE 15

R-3320/Silicone Oil by wt.	Adhesive Strength kg/cm^2 (-10°C)		Tensile Modulus, kg/cm^2			
			-10°C		20°C	
100/20	Thomas	SF-1154	Thomas	SF-1154	Thomas	SF-1154
100/20	1.74 ± 0.06	0.67 ± 0.12	263 ± 25	119 ± 30	143 ± 16	86 ± 13
100 50	3.62 ± 0.67	0.58 ± 0.41	201 ± 26	78 ± 9	107 ± 10	19 ± 3

SF-1154 decreases the tensile modulus of LR-5630 in a similar way as it does in the case of LR-3320:

TABLE 16

LR-5630/Oil by wt.	Adhesive Strength kg/cm^2 (-10°C)	Tensile Modulus, kg/cm^2 -10°C	+20°C
100/0	0.61 ± 0.14	24 ± 3	10 ± 1
100/20 (Thomas)	0.045 ± 0.003	18 ± 5	6 ± 1
100/20 (SF-1154)	0.10 ± 0.002	15 ± 2	7 ± 1

(d) LR-5630/LR-3320/SF-1154/Thomas Oil

TABLE 17

LR-5630/LR-3320/SF-1154/Thomas by wt.	Adhesive Strength kg (-10°C)	Tensile Modulus kg/cm^2	
		-10°C	+20°C
100/0/50/10	0.04 ± 0.01	10 ± 2	4 ± 1
0/100/50/11	0.48 ± 0.14	66 ± 9	20 ± 2
100/0/20/14	0.08 ± 0.02	13 ± 2	6 ± 1
100/0/10/10	0.17 ± 0.24	15 ± 2	8 ± 1

The use of both oils did not enhance the effect on abhesion.

7. Heating of Coats Before Testing

There are indications that the properties of the coats become more favorable by moderate heating; this is tested.

TABLE 18

	LR-5630/LR-3320/ SF-1154/Thomas by wt.	Adhesive Strength kg/cm^2 (-10°C)		Tensile Modulus, kg/cm^2			
				-10°C		20°C	
		Not Heated	Heated*	Not Heated	Heated	Not Heated	Heated
A	50/50/20/0	0.17 ± 0.24	0.12 ± 0.24	39 ± 4	37 ± 3	15 ± 1	17 ± 2
	100/0/10/10	0.17 ± 0.24	0.64 ± 0.24	15 ± 2	14 ± 2	8 ± 1	7 ± 1
	25/75/20/0	1.61 ± 0.24	0.75 ± 0.24	90 ± 7	77 ± 7	33 ± 2	36 ± 3
B	0/100/20/0	0.67 ± 0.12	0.67 ± 0.12	199 ± 30	186 ± 24	86 ± 13	67 ± 8
	25/75/0/10	4.15 ± 0.12	4.05 ± 0.12	257 ± 36	178 ± 29	115 ± 9	93 ± 12

*Heated at 105°C for 1 hour.

The heating effect appears to be a complicated one. No systematic change of the tensile modulus is apparent.

Expts. A: The heating seems to decrease adhesive strength.

Expts. B: Practically no effect is apparent in these cases. Heating at higher temperatures than 105°C for 1 h increases the adhesive

TABLE 19

LR-5630/LR-3320/SF-1154 = 50/50/20 by wt.			
Heating in air	Adhesive Strength kg/cm^2 (-10°C)	Tensile Modulus, kg/cm^2	
		-10°C	20°C
No heating	0.17 ± 0.11	39 ± 4	15 ± 1
105°C, 1 hr.	0.12 ± 0.11	48 ± 4	20 ± 4
120 130°C, 1 hr.	0.26 ± 0.11	64 ± 10	25 ± 4
140°C, 1 hr.	0.55 ± 0.11	64 ± 8	20 ± 2

Fig. 10 illustrates the above results.

Tensile moduli increased by heating at increasingly higher temperature.

Another coat: LR-3320/SF-1154 = 100/10 was heated at 90°C for various lengths of time.

TABLE 20

Adhesive Strength in kg/cm^2 (-10°C) LR-3320/SF-1154 = 100/10 Coat Heated at 90 C° as Function of Time

	4 samples	one sample each			
Heating time, h	0	1	2.1	4.5	7.5
Adhesive Strength, kg/cm^2	1.21 ± 0.14	0.82	1.11	1.15	1.24

Heating at 90-105°C for 1 h appears to be beneficial as far as adhesive strength is concerned (compare Tables 18A, 19 and 20).

8. Coat: Hi-Mil Sher-Tar Epoxy Enamel, Sherwin Williams (supplied by L.D. Minsk, CRREL).

TABLE 21

Expt.	Description	Adhesive Strength kg/cm^2 -10°C
(a)	Epoxy Enamel	3.73 ± 2.30
(b)	" " + 10% SF-1154	2.27 ± 2.30
(c)	" " + #500^x	7.46 ± 2.30

^{x}An epoxy enamel-coated Al-Plate was submerged in Tullanox #500; excess powder was blown off.

As pointed out before, the coats containing Tullanox #500 have a rough surface.

The contact angle of water on a surface containing #500 is >90°. Hence, the coat should have good abhesive properties. However, shear tests give high abhesive strength values. It appears to us that shear adhesive strength values give misleading values for abhesion due to surface roughness. A peeling type of adhesive test is being elaborated now which will be discussed later.

FIG. 6

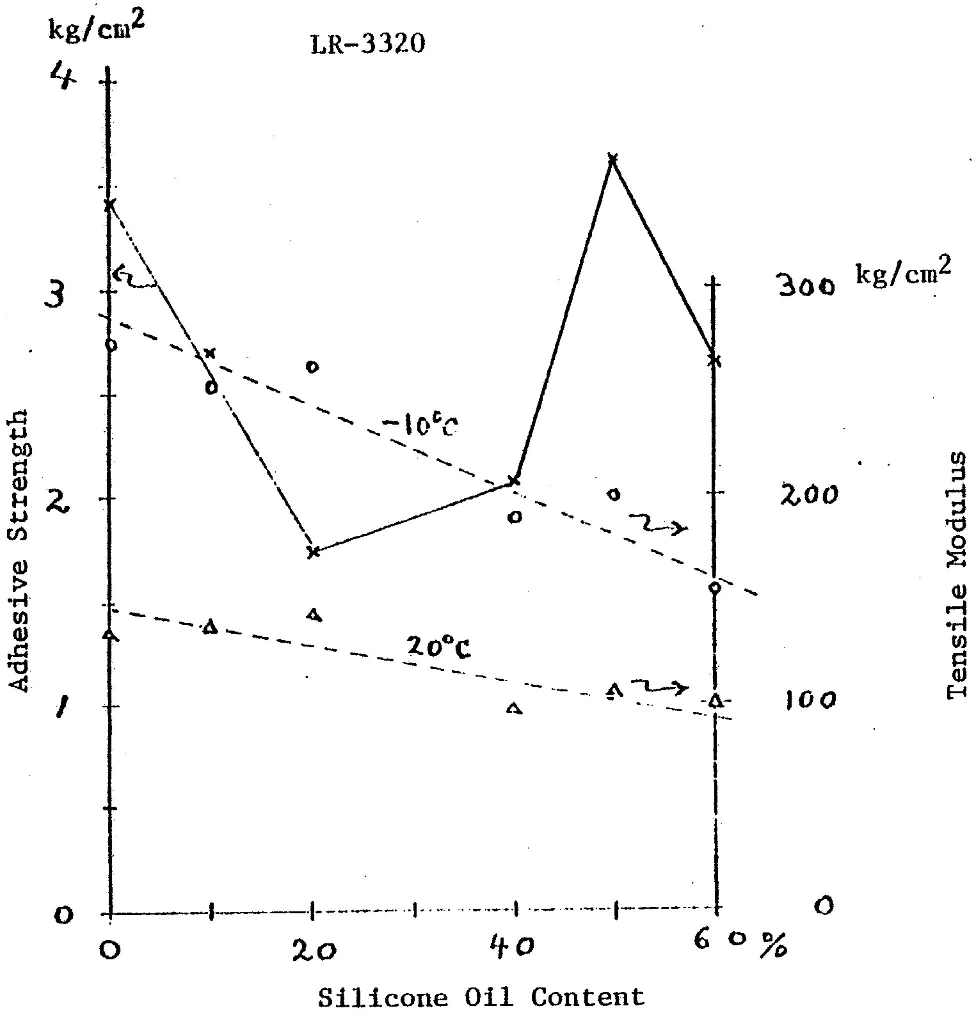

LR-3320
Adhesive Strength
kg/cm²
4
3
2
1
0
-10°C
20°C
0
20
40
60 %
Silicone Oil Content
Tensile Modulus
300 kg/cm²
200
100
0

FIG. 7

Silicone oil (Thomas) 10% added

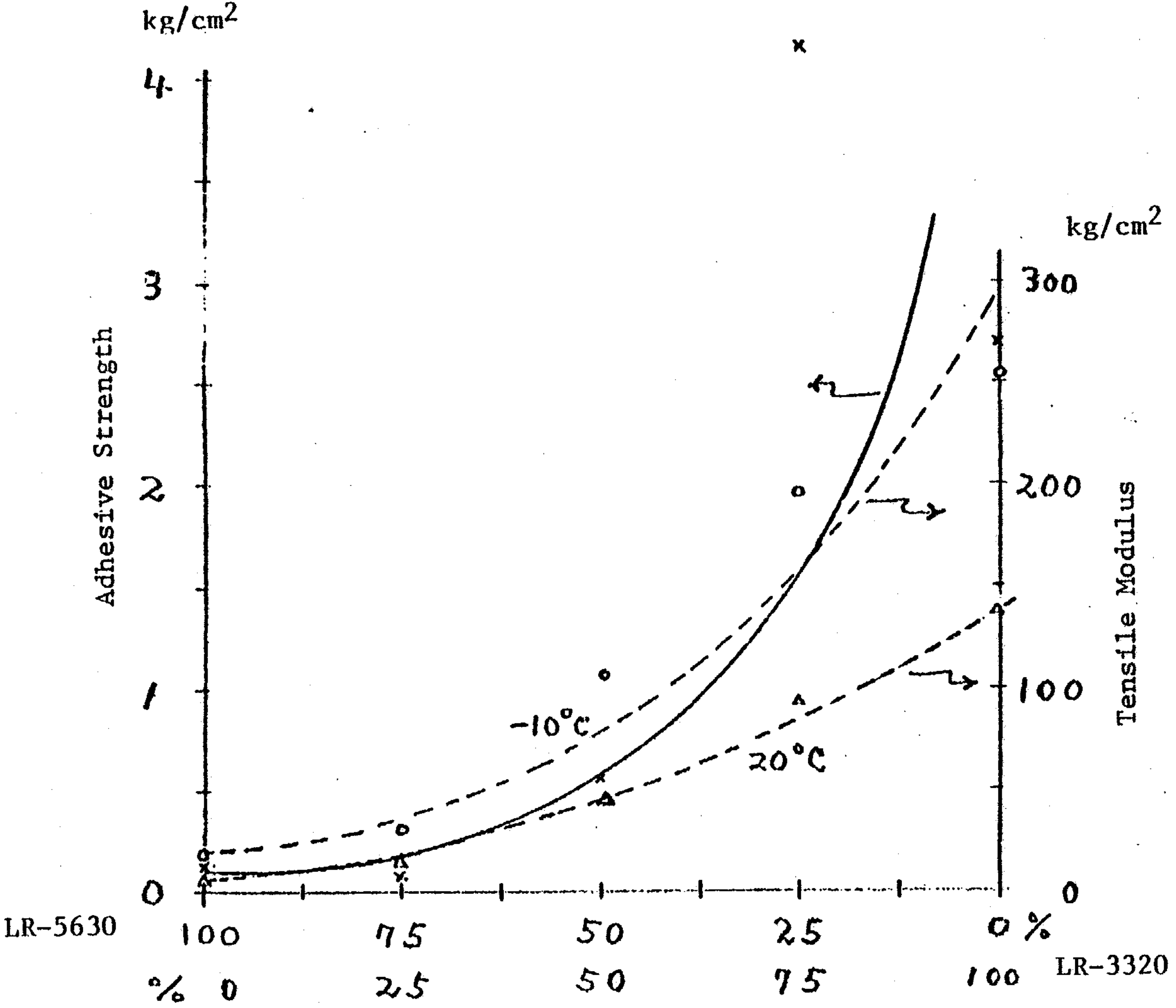


Fig. 8

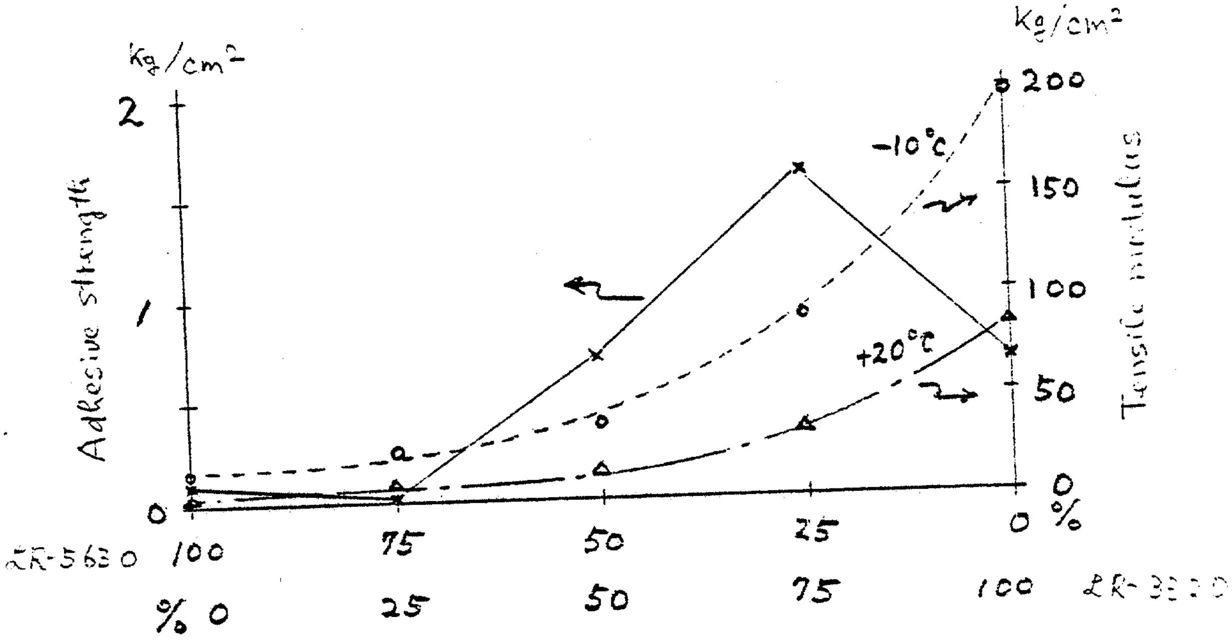

Kg/cm²
2
1
0
Adhesive strength
Kg/cm²
200
150
100
50
0
Tensile modulus
-10°C
+20°C
ℓR-5630
100
75
50
25
0 %
% 0
25
50
75
100
ℓR-3

FIG. 9

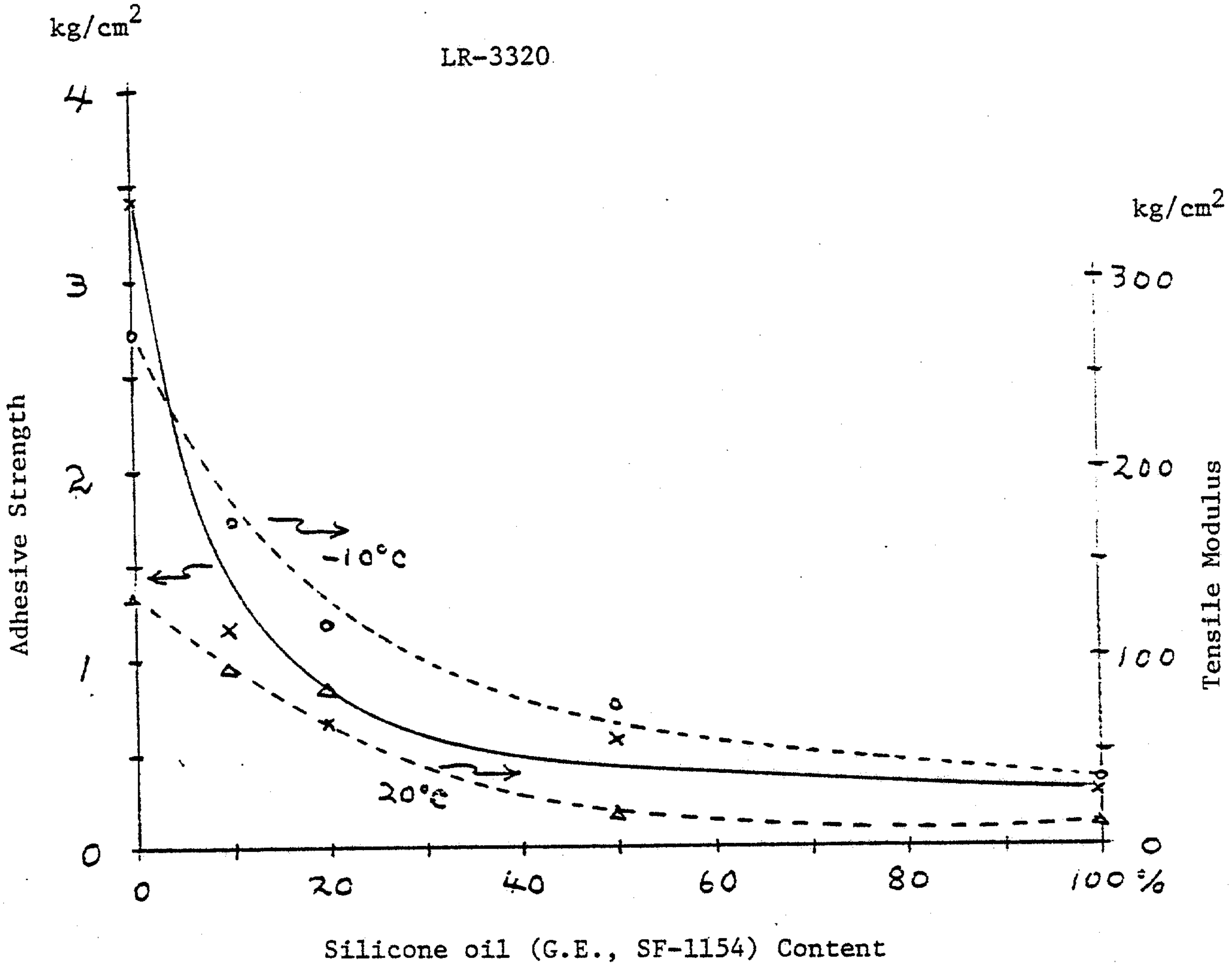
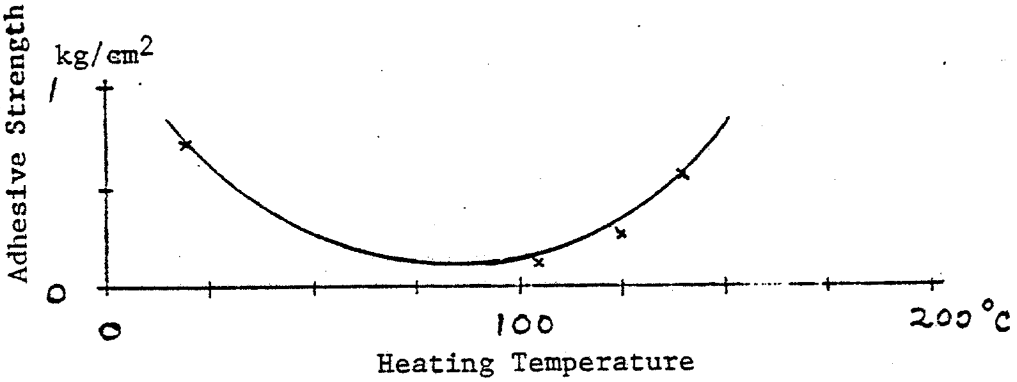

kg/cm^2
LR-3320
4
3
2
1
0
Adhesive Strength
-10°C
20°C
kg/cm^2
300
200
100
0
Tensile Modulus
0
20
40
60
80
100 %
Silicone oil (G.E., SF-1154) Content

FIG. 10



9. Tensile Modulus as Function of LR-5630/#500 Composition (No Silicone Oil) and Temperature.

Next, tensile modulus vs. Tullanox #500 content without silicone oil were measured as a function of temperature. (The values of 100/60 were taken from Table 7, at 20-22°C and -10°C.)

TABLE 22

Tensile Modulus as Function of LR5630/#500 Composition (No Silicone Oil) and Temperature

Composition	LR5630/#500 →	100/0	100/25	100/33	100/50	100/60
Ball-milling duration for Obtaining Homogeneous Product, h	Temperature °C	-	3	4	5	11
Tensile Modulus kg/cm^2	20	10 ± 1	32 ± 3	27 ± 9	-	32 ± 13
	10	14 ± 1	34 ± 3	28 ± 11	38 ± 10	54 ± 20
	0	20 ± 4	61 ± 22	49 ± 20	70 ± 13	61 ± 18
	-10	24 ± 3	55 ± 11	57 ± 25	57 ± 11	69 ± 22
	-20	31 ± 4	-	85 ± 30	-	89 ± 16

The tensile modulus increases with increasing Tullanox #500 content of LR-5630, e.g. the tensile modulus of the 100/25 film with #500 is about 3 times larger than that of the film without Tullanox #500. Tensile modulus and E_{Arrh}, the Arrhenius energy of activation, are plotted vs. #500 content in Figs. 11 and 13, respectively. Fig. 12 shows plots of $\log_{10}$ (tensile modulus in kg/cm^2) vs. $10^3/T$. The tensile moduli for LR-5630 plus #500 as a function of film composition (Fig. 11) give higher values than those without Tullanox. Fig. 13 shows that E_{Arrh} passes through a maximum for LR-5630 plus

33% Tullanox #500 (see also Fig. 12). The reason for this is not clear but may be due to defects in the films caused by increasing amounts of the Tullanox powder.

10. Shear Adhesive Strength As Function of Tensile Modulus.

Fig. 14 was obtained by plotting shear adhesive strength data for all samples except those containing Tullanox #500 vs. tensile modulus. Increasing tensile modulus values yield increasing adhesive strength values (linear relation).

11. Shear Adhesive Strength As Function of Film Thickness.

TABLE 23

Adhesive Strength as Function of Film Thickness

Film (A): LR5630/LR3320/SF-1154 (Silicone Oil) = 75/25/20						
Film Thickness (μm)	12	42	62 *	80	98	Av.
Adhesive Strength, kg/cm^2	0.02	0.07	0.03 ± 0.01	0.06	0.21	0.092 ± 0.06
Film (B): LR5630/LR3320/Thomas Silicone Oil = 75/25/10						
Film Thickness (μm)	51	58	67	82 *	100	Av.
Adhesive Strength, kg/cm^2	0.09	0.07	0.12	0.09 ± 0.04	0.07	0.09 ± 0.06

*Report in Tables 11 and 10, respectively.

The effect of film thickness is not large for the above thickness range. The surface of Film A was oily.

12. Summary

A great number of block-co-polymer films of a large variety of compositions have been systematically investigated as to their adhesive strength with respect to ice and their tensile moduli. It is anticipated that the resistance of films to environmental effects (storms, waves) will increase with increasing tensile modulus. Thus, it has been attempted to increase the tensile moduli of the films while increasing their adhesive strength moderately in order to stay within the maximum adhesive strength stipulated for this project, i.e. 25 p.s.i. or 1.76 kg/cm^2. The data of the most promising films so far are collected in Table 24.

TABLE 24

Most Promising Films Tested Yet

Composition	Adhesive Strength kg/cm^2 (-10°C)	Tensile Modulus, kg/cm^2	
		-10°C	+20°C
LR5630/LR3320/ Silicone Oil (Thomas) 50/50/10	0.56 ± 0.48	110 ± 11	43 ± 5
LR3320/Silicone Oil (SF-1154) 100/20	0.67 ± 0.12	199 ± 30	86 ± 13
LR3320/Silicone Oil(Thomas) 100/20	1.74 ± 0.06	263 ± 25	143 ± 10
LR3320/Silicone Oil (SF-1154) 100/10	1.21 ± 0.14	172 ± 21	94 ± 9
LR3320/SF-1154 Heated, 105°C, 1h 100/20	0.67 ± 0.12	186 ± 24	67 ± 8

The best film on the basis of adhesive strength and tensile modulus appears to be:

LR3320/SF-1154 = 100/20

It is, of course, arbitrary to take films which have tensile moduli above 100 kg/cm^3; however, we are designing an erosion test apparatus which will give linear water velocities of up to about 70 m.p.h. This will give a more realistic test for erosion resistance.

In addition, films of still higher tensile modulus and adhesive strength (the latter within the permitted limits) will be prepared. These will consist most likely of chemically crosslinked rubber instead of the block-co-polymers.

Fig. 11

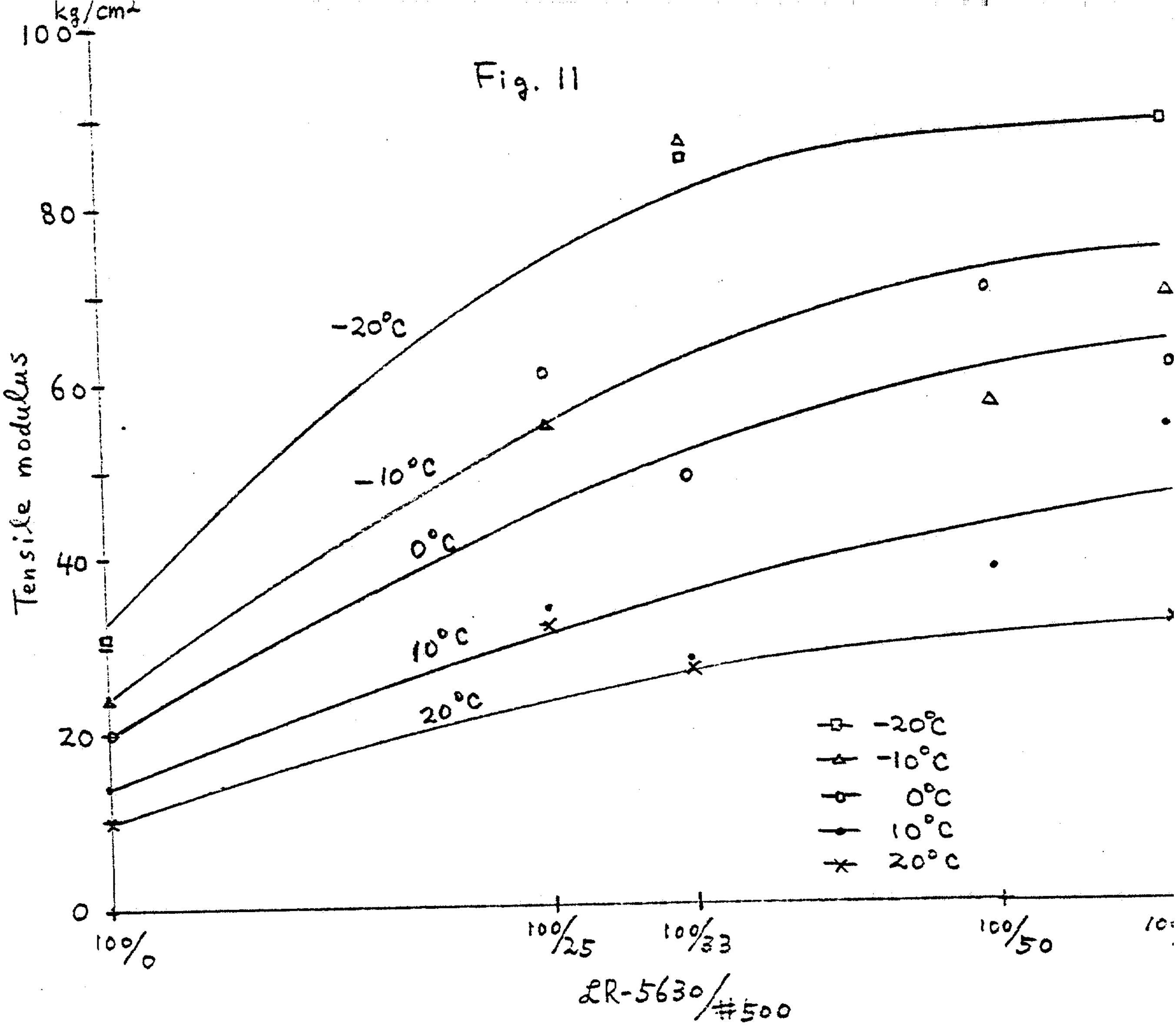

kg/cm²
100
80
60
40
20
0
Tensile modulus
-20°C
-10°C
0°C
10°C
20°C
-20°C
-10°C
0°C
10°C
20°C
100/0
100/25
100/33
100/50
ℒR-5630/#500

Fig.12

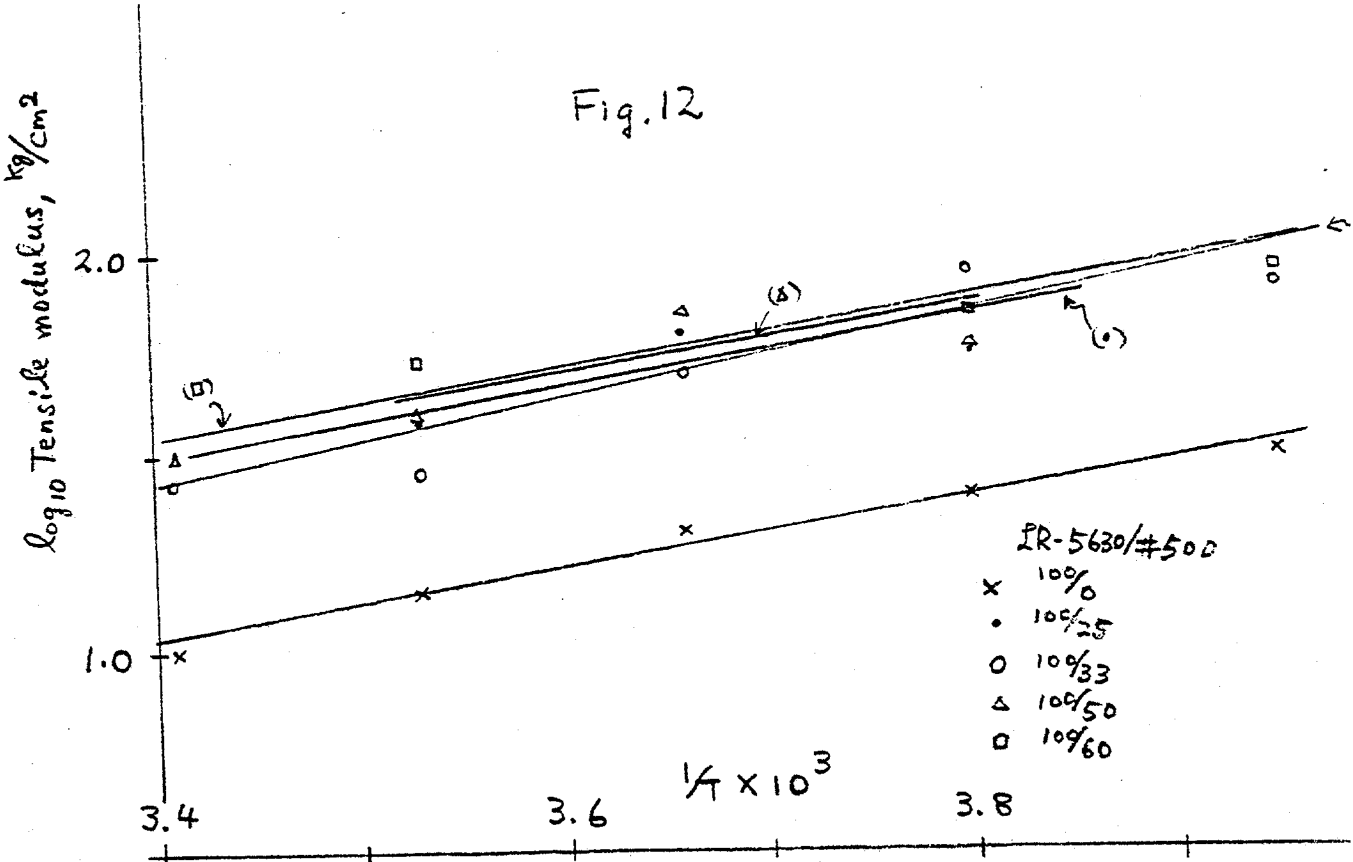

log₁₀ Tensile modulus, kg/cm²
2.0
1.0
(□)
(Δ)
(•)
ℒR-5630/#500
× 100/0
• 100/25
○ 100/33
Δ 100/50
□ 100/60
1/T × 10³
3.4
3.6
3.8

Fig. 13

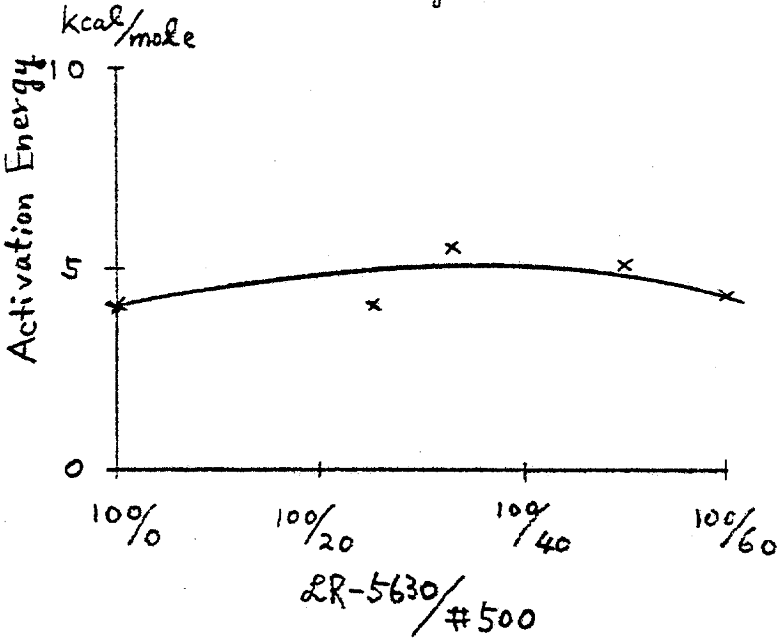
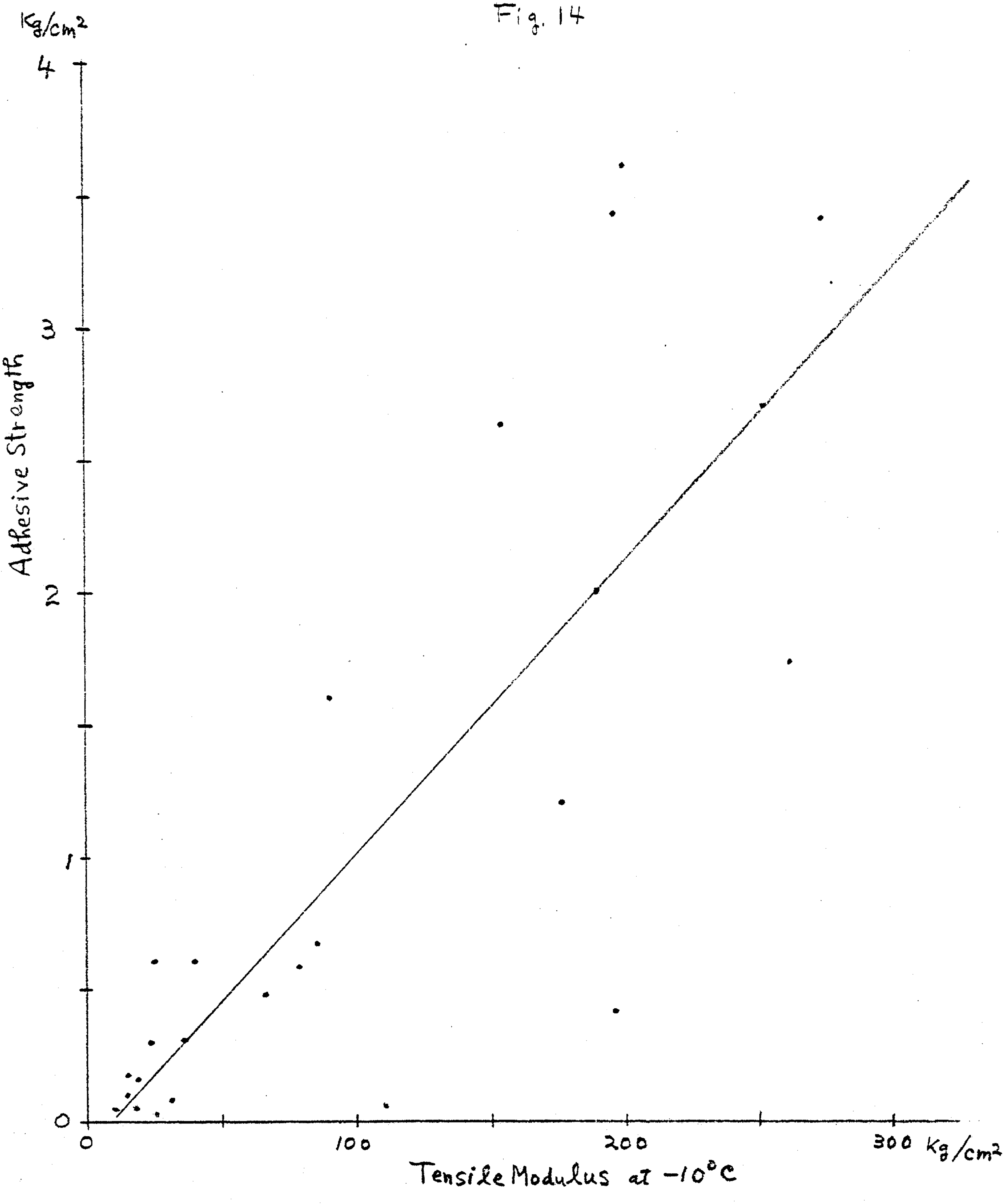

kcal/mole
Activation Energy
10
5
0
100/0
100/20
100/40
100/60
LR-5630/#500

Fig. 14



Kg/cm²
4
3
2
1
0
Adhesive Strength
0
100
200
300 Kg/cm²
Tensile Modulus at -10°C

VII. Peel Adhesive Strength of Co-polymer Film from an Ice Surface

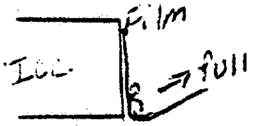
(1) Peel Adhesive Strength Tester

An Apparatus for measuring very small forces of peeling strength has been designed and built. The apparatus is shown in Fig. 15.

(2) Test Results of Peel Adhesive Strength

(a) Film Thickness

The peel adhesive strength of co-polymer film from an ice surface is very low with comparing to peel adhesive strength in case of ordinary adhesive. Therefore, the radius (R) of film to the ice surface as measuring peeling strength shall change depending on the bending modulus of individual film and the peeling strength of film shall be affected accordingly. This has been examined by changing the film thickness of a sample for the peel adhesive strength test.



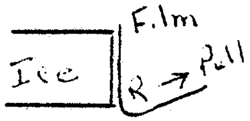


TABLE 25

LR-3320 film

Film Thickness, μm	Peel Adhesive Strength, g/cm	Remarks
30 ± 11	15.8 ± 9.0	7 samples
45 ± 4	20.0 ± 5.3	12 samples
54	24.4	Average of 2 samples

LR-3320 film coated with Tullanox #500 powder

Film Thickness, μ	Peeling Strength, g/cm	Remarks
38 ± 5	4.3 ± 1.1	3 samples
43	3.5 ± 0.6	28 samples
48 ± 2	3.8 ± 0.6	4 samples
68	5.2	Average of 2 samples

The film thickness, i.e., the bending modulus of film seems to be not affected to the peel adhesive strength measurement.

The peel adhesive strength of film coated with Tullanox #500 was about one fifth of that of film without #500. This is in contrary to shear adhesive strength of film to an ice surface.

The coating of Tullanox on film was done by applying powder of Tullanox on the film and then brushing away excess powder from the film surface. Tullanox coated film had a milky surface, i.e., a small amount of Tullanox powder was coated on the film surface.

(b) Kind of co-polymer

TABLE 26

	Film Thickness, μ	Peel Adhesive Strength, g/cm	Remarks
LR-5630	70 ± 16	26.8 ± 5.5	5 samples
LR-5630 with #500	65 ± 4	4.9 ± 0.5	4 samples

No peel adhesive strength difference between LR-5630 and LR-3320 was found by comparing data in Table 26 to data in Table 25.

(c) Silicone oil (General Electric SF-1154)

TABLE 27

Composition of Film	Film Thickness, μm	Peeling Strength, g/cm	Remarks
LR-3320/SF-1154 = 100/10	57 ± 3	56.9 ± 14.1	3 samples
LR-3320/SF-1154 = 100/10 (with #500)	63	7.1	Average of 2 sample

Film of LR-3320/SF-1154(100/10) showed higher peel adhesive strength from an ice surface with comparing to film without silicone oil listed in Table 25.

It, however, is still premature to conclude it.

(d) Co-polymer mixture with silicone oil (Thomas)

TABLE 28

LR-5630/LR-3320/Silicone Oil	Film Thickness, μm	Peel Adhesive Strength, g/cm	Remarks
75/25/10	95 ± 37	28.5 ± 8.3	6 samples
75/25/10 with #500	102 ± 44	2.3 ± 1.4	3 samples
25/75/20	66 ± 1	26.4 ± 9.3	3 samples
25/75/20 with #500	90 ± 20	4.0 ± 0.4	3 samples

The mixing ratio of co-polymer and the addition of silicone oil (Thomas) did not affect to the peel adhesive strength of film from an ice surface.

(e) Procedure for Preparing a sample for measurement of peel adhesive strength.

Cast co-polymer film is laid on an aluminum plate (3" x 3" x 3/16"). Then an aluminum cylinder with 40 mm inside diameter is placed on the film. Boiled and then cooled water is poured into the cylinder for making ice on the surface of film.

VIII. Effect of Erosion (Air-Water Jet) on Adhesive Strength

1. A Gale Tunnel for Weathering Test.

A gale tunnel apparatus as shown in Fig. 16 was designed and built for measuring durability of polymer coat against gale.

The air supplied to the tunnel from a blower is 47.2ℓ/sec. according to the specification of the blower. The air supplied to the tunnel from an aspirator is 0.27ℓ/sec. measured by a flowmeter. Water supplied to the tunnel from the aspirator (tap water) is 0.2ℓ/sec. measured by using a beaker and a stopwatch. Therefore, the velocity of gale (air and water) in the tunnel (a glass tubing with 3.7 cm inner diameter) is 99 m.p.h.

The gap between the end of the gale tunnel and a sample surface was set as making the shortest distance and sucking the maximum amount of air by the aspirator, i.e., free from back pressure produced by hitting the sample surface with gale. It is 1.8 cm.

Co-polymer coat on an aluminum plate was tested by applying gale. The coating composition was LR-5630/LR-3320/Silicone Oil (Thomas) = 75/25/10. The thickness of the coat was 0.22 mm.

Some spots of the coat lost adhesion to the aluminum surface after gale was applied for ca. 3 hrs.

Fig. 16

Gale Tunnel

1. Blower (Air fed: 47.2ℓ/sec.).
2. Aspirator (Water fed: 0.2ℓ/sec. and Air sucked in: 0.27ℓ/sec.).
3. Wire screen for dispersing water.
4. Gale tunnel (Diameter (ID) 3.7 cm and 30 cm long.
5. Aluminum plate coated with co-polymer (Sample for test).
6. Movable platform.

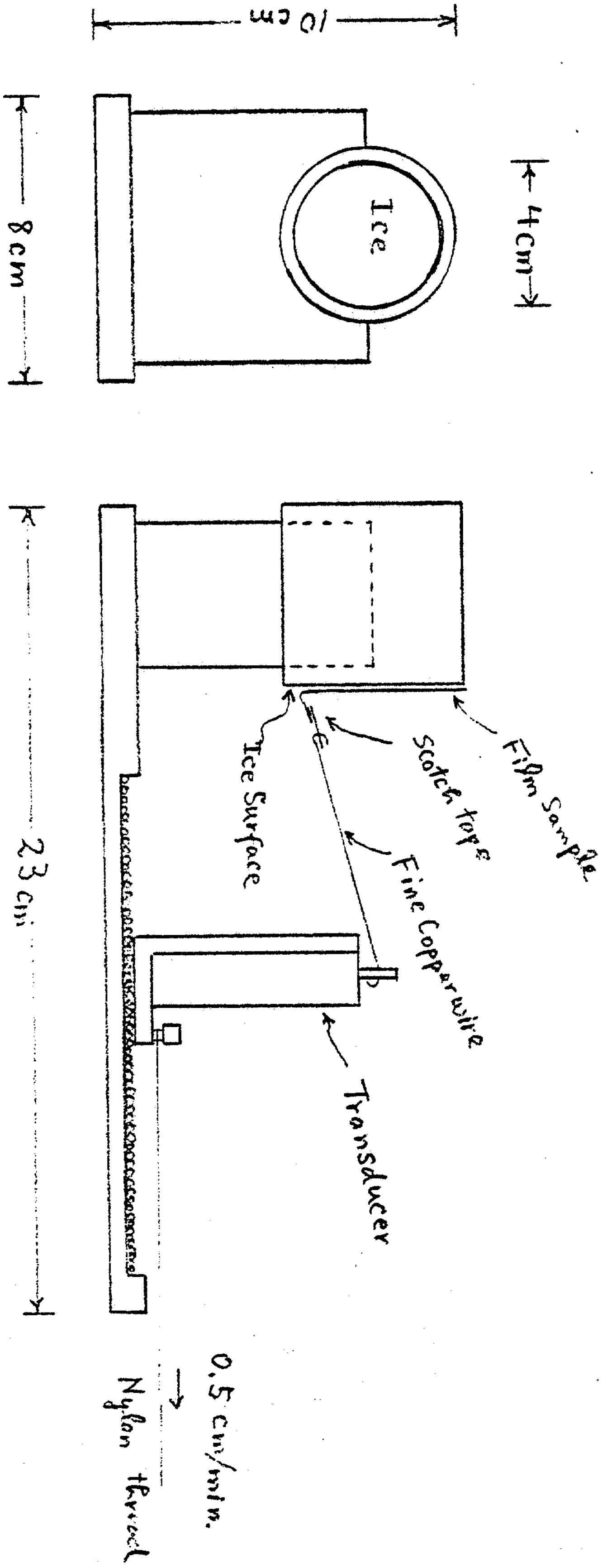
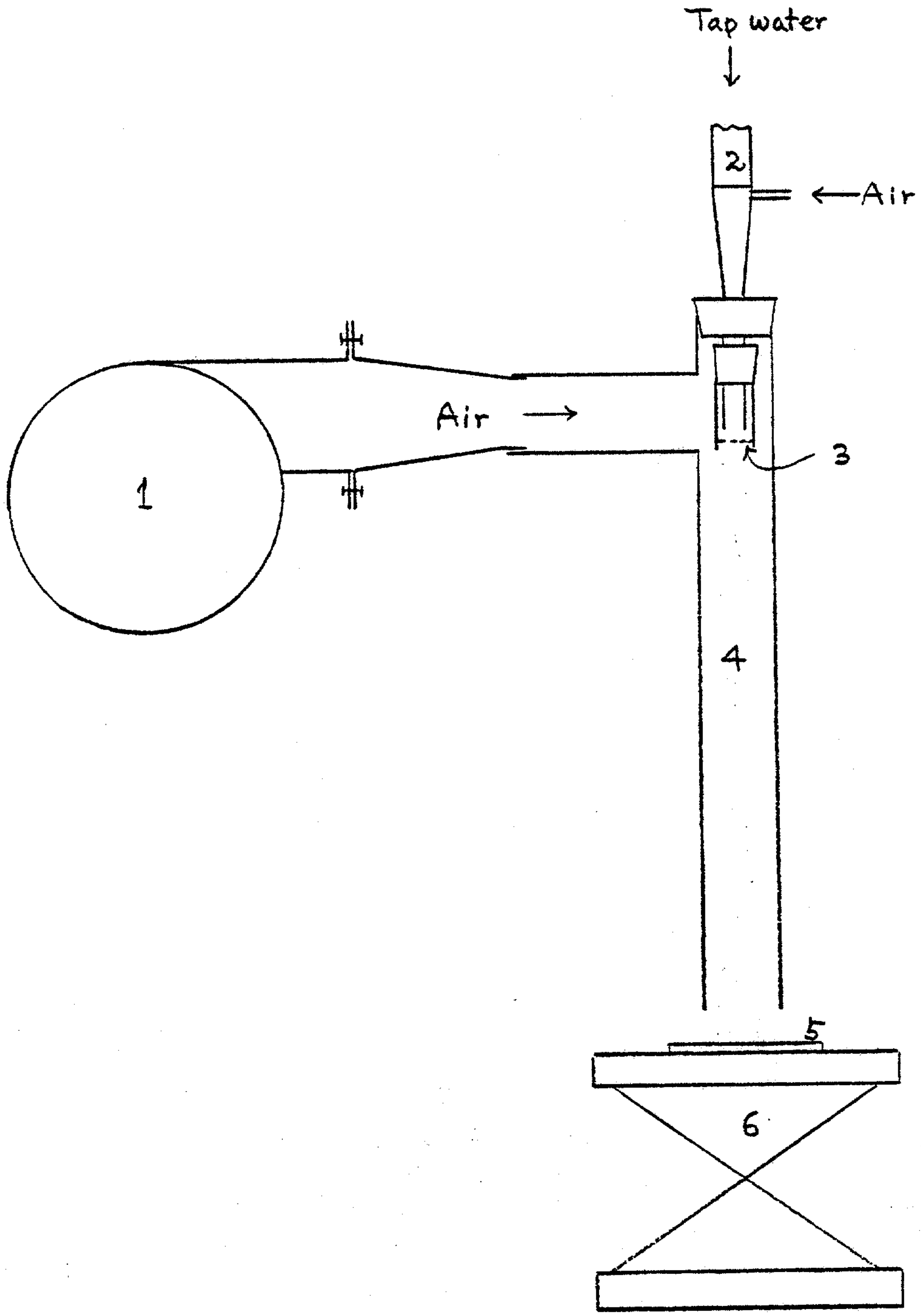

10 cm
8 cm
Ice
4cm
Film Sample
Scotch tape
Ice Surface
Fine Copper wire
Transducer
23 cm
0.5 cm/min.
Nylon thread

Fig. 15

Fig.16



2. Preliminary Experiments

A co-polymer solution was prepared having a composition as follows:

LR-5630	1.5g
LR-3320	0.5g

Dissolved in:

CH_2Cl_2	3.0 ml
Toluene	7.0 ml added afterwards

Thomas silicone Oil 0.2 ml (or g) added afterwards

Composition of coating is then LR-5630/LR-3320/Silicone Oil-75/25/10.

This solution was coated on Al-plates by using rollers of various gaps-thicknesses. These coats had a milky appearance. Coated plates were exposed to "erosion"; their shear adhesive strength was then measured (See Table 29). Two abhesive peaks appeared. The first one is due to abhesion (not complete abhesion but only at some patches) between coat/Al and the second to abhesion at coat/ice.

TABLE 29

Plate	Coat Thickness mm	Erosion Time h	Shear Adhesive Strength, kg/cm^2	
			1st Peak	2nd Peak
A	0.20	19.5	0.56	-
B	0.13	0	too weak to measure	
C	0.12	7.0	-	1.78
D	0.22	ca. 3.0	0.74	1.73

The data show that erosion took place; the coats were damaged and they were loosened from the Al-surface; the ice/coat adhesive strength increased as a consequence.

3. Polycarbonate-Polysiloxane Co-polymers, XD-11 and 131-848 (see our paper,

Colloid and Polymer Sci. 256, 544-551 (1978)) were tested.

These co-polymers have harder coats than that of LR-5630. They also have higher T_g values than LR-5630.

Solution for Co-Polymers

XD-11 or 131-848	0.4g	dissolved first
CH_2Cl_2	2.0 ml	
Toluene	2.0 ml	added afterward (131-848 solution is slightly milky)

Al-plates were coated. The XD-11 coat showed small white areas whereas 131-848 was completely white (pencil hardness of either was 4B).

TABLE 30

Coat	Shear Adhesive Strength, kg/cm^2	
	Without Erosion	With Erosion (3 h)
XD-11	2.14 (16 μ)	2.62 (16 μ)
131-848	2.31 (12 μ)	2.74 (12 μ)

In addition to some erosion, the adhesive strength values are too high.

Poly(dimenthylsiloxane)-Polycarbonate - Co-Polymer XD-11 has a high T_g (100°C) and is somewhat tougher than LR-5630.

The solvent (CH_2 Cl_2) was changed to dioxane.

The compositions of the coatine mixtures were:

(a) XD-11 0.5g, Dioxane 2.5 ml, Toluene 2.5 ml

(b) XD-11 0.5g, Dioxane 5.0 ml

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 0.1 mm 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 1 h prior to testing. The heating did not affect the adhesive strength to a noticable 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 evaporation is less smooth for a single solvent than for a mixture of solvents. TABLE 31 gives results.

TABLE 31

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 4 h 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.

4. G.E. Silicone Varnish (Sample 4124)

This varnish is crosslinked on heating yielding a hard coat. Four Al-plates were coated with this varnish and heated at 100°C for 1 h. Two of the plates were heated subsequently at 150°C. Two samples were exposed to erosion.

Two other Al-plates were coated with a mixture of Thomas Silicone Oil and Varnish (Oil:Varnish = 2:8). They were heated at 100°C for 1 h and one of these plates was exposed to erosion. Results are give below.

TABLE 32

Plate No.	Sample (Heating Condition) (Erosion Exposure 3 h)	Thickness of Coat μ	Pencil Hardness	Shear Adhesive Strength kg/cm^2
1	varnish (100°C, 1 h)	31	3 H	2.50
2	varnish (100°C, 1 h) erosion	35	3 H	1.81
3	varnish (100°C, 1 h → 150°C, 1 h)	30	-	2.23
4	varnish (100°C, 1 h → 150°C, 1 h) erosion	26	3 H	2.12
5	varnish/oil (~100°C)	24	-	1.33
6	varnish/oil (~100°C) erosion	28	4 B	1.77

Samples No. 1,2,3,5 were heated at 150°C for one additional hour.

Results are presented below (the Nos. are designated by primes).

TABLE 33

Plate No.	Shear Adhesive Strength, kg/cm^2
1′	2.10 (2.50)
2′	2.28 (1.81)
3′	2.36 (2.23)
5′	1.59 (1.33)

Values in parentheses are the adhesive strength values before further heating (see above).

Samples 1′,2′,3′,4′,5′, and 6′ were further coated with Thomas Silicone Oil and designated with double primes.

TABLE 34

Plate No.	Shear Adhesive Strength, kg/cm^2	Erosion
1"	0.19	None
2"	2.30	After Erosion
3"	0.20	None
4"	1.93	After Erosion
5"	0.35	None
6"	0.20	None

The silicone oil on top of the coat reduces the adhesive strength but was washed off by erosion (jet). The oil is a good softening agent mixed into the varnish (pencil hardness 6B). Results are given below:

TABLE 35

Sample No.	Composition	Preparation	Shear Adhesive Strength kg/cm^2
7	Silicone varnish/SF1154 =100/10	100°C, 1 h, plus 160°C, 1.5 h	3.76
8	Silicone varnish/SF1154 =100/10	100°C, 1 h, plus erosion 3 h	5.40
9	Silicone varnish/SF1154 =100/20	100°C, 1 h, plus 160°C, 1.5 h	2.98
10	Silicone varnish/SF1154 =100/20	100°C, 1h, plus erosion 3 h	2.01

The relatively large addition of SF-1154 silicone oil reduced the shear adhesive strength to ice. However, 10% oil increased the strength after erosion while 20% reduced it only somewhat. Apparently, the oil is washed off. In other experiments, Thomas Oil was mixed with the varnish before coating. Many air bubbles remained in the coat, which was heated at 100° for 1 h before testing. Results were as follows:

TABLE 36

Sample	Shear Adhesive Strength, kg/cm^2
Fresh Coat	0.07
After 3 h Erosion	·1.59

Silicone oil was apparently leached out during erosion.

5. Dow Corning Compound 5

This compound is a water-repellent silicone grease. An Al-plate was coated with this compound and exposed to erosion for 30 minutes. However, the compound was washed off.

6. LR-5630 Co-Polymer Coats

(a) A solution of the following composition was prepared:

LR-5630	2.0 g
Dioxane	4.0 ml
Toluene	4.0 ml

The coat was applied in several stages. The total thickness amounted to 1.20 mm. For the first coating LR-5630 was dissolved in the composition as given above. The next two coatings were carried out with a composition as follows:

LR-5630	2.0 g
Toluene	8 ml

(Apparently, dioxane is not needed at all.)

The results are given below.

TABLE 37

Cumulative Exposure Time for Erosion	Shear Adhesive Strength
	kg/cm^2
0	0.16
1	0.14
2	0.26
4	0.58
8	1.75

The sample exposed for 8 h to erosion was stored at room temperature (ca. 22°C) to see whether adhesive strength would decrease due to diffusion of the siloxane components to the surface (self-mending). The results were as follows:

TABLE 38

Storing Time of Sample After 8 h of Erosion Days	Shear Adhesive Strength kg/cm^2
12	0.76
16	0.32
19	0.16

It should be noted that the abhesive strength after 8 h exposure is still within the range required by the specifications (i.e., 25 psi or 1.76 kg/cm^2). However, the mending time is too long. In addition, we want to improve the abhesive strength. Also much longer erosion times were investigated.

TABLE 39

Cumulative Effect of Erosion

Erosion Time h	Time of Storage after Erosion Day	Adhesive Shear Strength kg/cm^2
8	19	0.16
16	1	1.38
	2	0.59
	3	0.31
	20	0.17
16	1	0.45
18	0*	2.58
	1	1.98
	2	0.54
	5	0.73

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

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

The coat thickness effect was also investigated. The solution was made as follows:

LR-5630	3.0 g
Toluene	6.0 ml
Dioxane	6.0 ml

The coats on Al-plates were heated at 100°C for 1 h.

The results were as follows:

TABLE 40

Erosion Exposure Time h	Coat Thickness μm	Shear Adhesive Strength kg/cm^2
0	60	0.10
1	59	0.84
2	61	0.98
4	39	1.61
8	38	4.48

The thicker the coat the more resistant it is to erosion. This must have something to do with the elastic properties of the coat having sufficient resilience. It should be noted that the sample exposed for 8 hours recovered completely with respect to its adhesive strength within 19 h at room temperature.

A solution of LR-5630 (2 g in 8.0 ml toluene) was coated on an Al-plate, heated at 100°C for 1 h. Next, it was coated with ethoxy-dimethyl silicone $(C_2H_5O)_2Si(CH_3)_2$ and stored at room temperature for 16 h. This silicone is expected to be hydrolyzed by water adsorbed from the atmosphere producing a thin silicone oil film. Its thickness was about 0.25 mm and its shear adhesive strength 0.2 kg/cm^3, however after 1 h erosion the adhesive strength increased to 4.34 kg/cm^2.

The effect of coat-thickness of LR-5630 is given below.

TABLE 41

Sample No.	Formulation					Heated at 100°C 1 h*	Thickness µm	Shear Adhesive Strength kg/cm^2
	LR5630 g	CH_2Cl_2 ml	Toluene ml	Dioxane ml	Methylisobutyl ketone ml			
1	2.0	4.0	4.0	-	-	+	0.3	0.26
2	2.0	-	4.0	4.0	-	-	0.25	0.04
3	2.0	-	8.0	-	-	-	1.2	0.16
4	2.0	-	7.2	-	8.0	-	0.2	0.34
5	2.0	-	6.0	6.0	-	+	0.06	0.10
6	2.0	-	8.0	-	-	+	0.25	0.12
7	2.0	-	8.0	-	-	+	0.3	0.17
7	2.0	-	8.0	-	-	+	0.6	0.12
7	2.0	-	8.0	-	-	+	0.85	0.12

* + Heating

− No Heating

No definite relation was found between thickness and strength.

(b) LR-5630/LR-3320 Coats

A solution was made up as follows,

$$\left.\begin{array}{ll}\text{LR-5630} & 12.0\text{ g}\\ & \\ \text{LR-3320} & 4.0\text{ g}\end{array}\right\}\ 75/25$$

Toluene	88.0 ml	79/31
Dioxane	40.0 ml	

It was coated on Al and heated at 100°C for 1 h; its thickness was 0.1 mm. Results were obtained as follows:

TABLE 42

Cumulative Erosion Time, h	Shear Adhesive Strength, kg/cm^2
0	0.21
1	0.12
2	4.34

The solution of a mixture of LR-5630/LR-3320 = 75/25 was also coated on Al in different thicknesses. They were again heated at 100°C for 1 h:

TABLE 43

Thickness (mm)	Shear Adhesive Strength, kg/cm^2
0.05	0.54
0.1	0.21
0.6	0.64

The number of samples is too small for proper evaluation, but indications are that there is no relation for thickness in this range of thickness.

7. LR-3320 Coats

Solutions of this co-polymer were prepared as follows:

LR-3320	1.0 g
Toluene	4.0 ml
Dioxane	4.0 ml

The coat on Al was heated at 100°C for 1 h. The results were as follows: exposed to erosion for several hours 1.14 kg/cm^2, prior to erosion 0.20 kg/cm^2. LR-3320 is harder than LR-5630, but the resistance to erosion was not improved.

The effect of thickness was also investigated. The results were as follows (all coats heated at 100°C for 1 h; no erosion).

TABLE 44

Sample No.	Formulation			Thickness mm	Shear Adhesive Strength kg/cm^2
	LR3320 g	Dioxane ml	Toluene ml		
1	1.0	2.0	6.0	-	-
2	1.0	3.0	5.0	0.1	2.95
3	1.0	4.0	4.0	0.1	0.20
4	1.0	7.0	1.0	0.15	0.49
4	1.0	7.0	1.0	0.35	0.43
4	1.0	7.0	1.0	0.40	0.19

There does not appear to be a relation between strength and coat-thinkness in the above range of thickness.

Dioxane is a good solvent for the co-polymers while toluene is much less so. The b.p. and evaporation rates for toluene and 1.4 dioxane are 111°C and 101°C and 4.5 and 5.0 respectively (taking the ethylether evaporation rate as 1). The soluability of toluene in water is 0.047 g/100 g H_2O, that of dioxane is ∞ at room temperature.

Sample No. 1 contained many tiny gel particles formed during evaporation of solvents. No. 2 had a good appearance.

8. Summary

The most promising experiments so far are those with thick (at least 1 mm) LR-5630 coats (see A. 5(a)). These appear to have the desired elastic properties (resilience) for withstanding prolonged erosion. The shear adhesive strength values are still in the range required by the specifications (i.e., 25 p.s.i. or 1.76 kg/cm^2) after 8 h exposure to erosion. However, we expect to be able to improve on these values considerably by making the coat still more erosion-resistant and by accelerating its recovery. Such experiments are described later. Also the G.E. Silicone Varnish shows some promising features.

IX. Coats on Sherwin Williams Hi-Mil-Sher-Tar Epoxy Enamel Coat

Preliminary Experiments

The tar was coated on Al-plates using a roller-coater of 6 mm gap-width. This coat was dried for nine days at room temperature and its thickness (calculated from its weight) was about 0.39 mm. It was difficult to obtain a smooth tar-surface.

This tar was coated with co-polymer solutions as shown below:

TABLE 45

Sample. No.	Formulation							Thickness µm	Shear Adhesive Strength kg/cm^2	
	LR5630 g	LR3320 g	Silicone Oil Thomas g	Silicone Oil SF-1154 g	Solvents p-xylene ml	Solvents toluene ml	Solvents dioxane ml		1st Peak	2nd Peak
1	2.0	-	0.2	-	20.0	-	-	4	0.61	1.6
2	2.0	-	0.2	-	20.0	-	-	4	0.79	1.1
3	1.5	0.5	-	0.5	15.0	-	5.0	7	0.37	1.1
4	1.5	0.5	-	0.5	15.0	-	5.0	9	0.56	1.6
5	1.5	0.5	0.2	-	-	10.0	-	61	0.43	1.2

All adhesive strength measurements showed two abhesion peaks. The first (always smaller) one is due to abhesion between the tar/co-polymer and the second to the coat/ice interface. The co-polymer coat adheres less well to the tar surface than the ice to the polymer, but the ice/polyer values were appreciably larger than expected. This appears to be due to contamination of the polymer coat by the tar as the latter is soluble to a certain extent in the solvents. Thus, a satisfactory primer has to be applied to the tar surface before a coat of the polymer can be applied. A primer consisting of Butvar B-90 (polyvinylbutyral, Monsanto) was tested (solution: toluene/ethanol 6:4 by volume). This 5% polymer solution was sprayed on the tar surface. This coat was cured (crosslinked) at room temperature for 48 h. However, the shear adhesive strength measurements still showed two peaks, as the results below indicate and the 2nd peak is of similar magnitude as before. The epoxy-tar surface requires suitable primer:

TABLE 46

Sample No.	Preparation	Shear Adhesive Strength kg/cm^2	
		1st Peak	2nd Peak
1	1st Butvar coat, 3 μ 2nd Butvar coat, ~3 μ 3rd coat LR5630 + 10% Thomas silicone oil, ca. 12 μ	0.45 0.45	1.51 1.51
2	1st Butvar coat, 3 μ 2nd Butvar coat + 15% Thomas silicone oil, ca. 3 μ 3rd coat LR5630 + 10% Thomas silicone oil, ca. 12 μ	1.09	1.67
3	1st Butvar coat, 10 μ 2nd Butvar coat + 30% Thomas silicone oil, ca. 5 μ 3rd Butvar coat + 30% Thomas silicone oil, 16 μ	0.65	3.37

X. Polycarbonate Coatings

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

1. PC/LR-5630

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

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 0.35 mm). The coat was heated at 100°C for 1 h. The pencil hardness was < 6B and the adhesive strength 2.91 kg/cm^2, which is rather large.

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

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 1 h, pencil hardness < 6B); shear adhesive strength 7.44g/cm^2.

2. PC/FLUOROLUBE S-30 (Hooker Chemical Corporation):

(a)	PC	1.0 g
	Dioxane	8.0 ml
	Toluene	2.0 ml

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 47

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.

(b)	PC	1.0 g
	Dioxane	10.0 ml

Fluorolube up to ca. 4% by weight.

A clear solution was obtained without Flourolube.

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

TABLE 48

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 0.03 kg/cm^2 was later found to be due to residual dioxane in the coat.

3. 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.

PC	2.0 g
Dioxane	18.0 ml

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 0.4 mm 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 5 h 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.

4. EFFECT OF DIOXANE on PC-COAT

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

TABLE 49

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

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

TABLE 50

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 50 shows that residual dioxane in the coat decreased the adhesive strength appreciably.

5. PC/Poly(dimethylsiloxane) (Silicone oil from Polysciences)

(a) Silicone oil (MW 10,000; DP=140) PC/Silicone oil 35/65 by WT. This is the same ratio as in the co-polymer LR-5630.

PC	0.35 g
Dioxane	10.0 ml
Silicone oil	0.65 g

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

(b) Silicone oil (MW 100,000, DP=1351)

PC	0.35 g
Dioxane	10.0 ml
Silicone oil	0.65 g

Silicone oil separated from the solution.

(c) The Silicone oil (MW 100,000) was reduced

PC	0.75 g
Dioxane	10.0 ml
Silicone oil	0.25 g

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

PC	0.9 g
Dioxane	10.0 ml
Silicone oil	0.15 g

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 5 h.

XI. Co-polymer Coatings

1. LR-5630 coat exposed to erosion.
2. Coating composition:

(a)	LR-5630	2.0 g
	Toluene	8.0 ml

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

TABLE 51

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*
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.

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

Compositions of coating mixtures

TABLE 52

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 separately 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 3 h 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.

(c) Crosslinking of LR-5630 with Benzoylperoxide.

The composition and characteristics were as follows:

TABLE 53

	1	2
B_zO_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 temperature, showed many needle-like crystals of B_zO_2. The coats were heated at 100°C for 1 h 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.

(d) Composition containing high MW Poly(dimethylsiloxane).

Composition and characteristics are given in TABLE 54.

TABLE 54

Polycarbonate Repeat Unit/Poly Siloxane Repeat Unit	30/70	35/65[1*]	40/60
LR-5630, g	2.0	---	---
LR-3320, g	---	0.61	0.80
Poly(dimenthylsiloxane), MW 100,000, g	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	0.50	0.42	1.27

*1 This is the same ratio as in LR-5630.

*2 Coats were not uniform; co-polymer and silicone separated in the coat.

(e) Cross-linked silicone gum

Silicone gum	2.0 g
Toluene	8.0 ml
B_zO_2	0.1 g

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

Silicone gum	2.0 g
Toluene	8.0 ml
Me $Si(OEt)_3$ (for cross-linking)	0.2 g

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

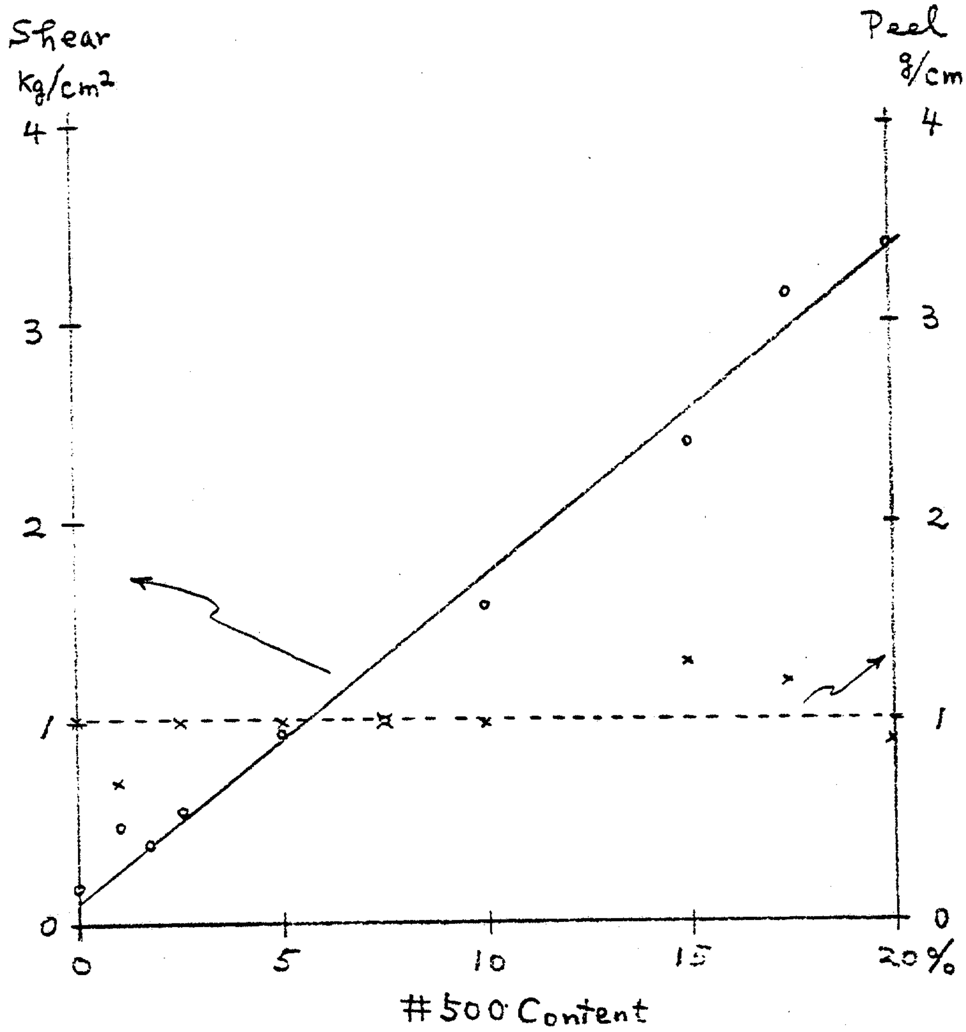
2. LR-5630/Tullanox #500

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

Shear adhesive strength (kg/cm^2) and peel adhesive strength (g/cm) are plotted versus % Tullanox #500 in Fig. 17.

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.

Fig. 17



One sample (15 % w/w of Tullanox #500 was subjected to erosion for 4.5 h; for shear adhesive and peel adhesive strengths are given in TABLE 55 below.

TABLE 55

	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 shear adhesive and peel adhesive strengths increase considerable on exposure to erosion.

3. Effect of Erosion on Peel Adhesive Strength.

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

A 225 μm thick coat on an Al-plate was prepared, its shear adhesive strength was 0.05 kg/cm^2. The coat was exposed to erosion for 18.5 h and after erosion, peel adhesive strength 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.

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

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

XII. Miscellaneous Coatings

1. TAR-Epoxy-Enamel Substrate

This surface was treated with dimethyldiethoxy silane ($Me_2Si(OEt)_2$ and left for 2 h. It was anticipated 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.

2. Polyvinylidene 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	5.64 kg/cm^2

Coats separated from the substrate after testing.

3. Poly(vinyl butyral) (PVB)

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

Butvar B-90	2.68
Toluene	16.0 ml
EtOH	4.0 ml

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

To such a coat $Me_2Si(OEt)_2$ was added at room temperature and left about 0.5 h. This compound was expected to react with -OH-groups (18-20%) was PVA in PVB. The shear adhesive strength was 6.25 kg/cm^2.

(b) $ME_2Si(OEt)_2$ (ca. 20% to PVB) was added to the PVB-solution as prepared above. The Al-coat was heated at 100°C for 1 h prior to testing. Milky patterns appeared in the coat (0.15 mm thick): its adhesive strength was 9.23 kg/cm^2.

(c) The following composition was examined:

Butvar B-90	0.8 g
Poly(dimethylsiloxane), MW100,000	0.2 g
Toluene	8.0 ml
EtOH	2.0 ml

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

(d) A PVB-solution was prepared as above; it was coated on the 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.

4. Polystyrene and Poly-α-methyl styrene did not show promising results.

5. Erosion-Resistant Coat.

(a) Preliminary Experiment - 1

LR-5630	1.0 g
Toluene	9.0 ml

Coats were prepared on an Al-plate. 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 1.5 h and immediately afterwards ice was adhered to them. Results are given below.

TABLE 56

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 1.00 kg/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 1.5 h long erosion, samples were eroded again (16 h LR-5630, and 5 h LR-3320). Results are given below:

TABLE 57

SAMPLE		THICKNESS OF COAT mm	ADHESIVE STRENGTH, kg/cm^2		
			No Erosion	After 1st Erosion 1.5h	After 2nd Eros 16h
LR-5630	SR-1154	0.26	0.47	0.04	1.09
LR-3320		0.13	2.50	0.02	2.37 (5h)

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

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

Seven different compositions were prepared:

LR-5630	1.0 g
Toluene	4.0 ml
SF-1154	Various amounts, see TABLE 58.

TABLE 58

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	4.33	4.55	1.37	1.50	0.68	2.57*3	1.61
Stored for 72 days after erosion	---	2.39	1.35	0.13	0.33	0.58	---

*1 Calculated values

*2 Cumulative erosion i.e. 19 h

*3 24 h instead of 16 h.

Overall, the results show that LR-5630 plus SF-1154 is the most promising system provided coats are relatively thick.

XIII. Polyethylene Foam Mat

A polyethylene foam mat (NALGENE "Clear Sheets," Nalgene 6281 series, closed cell, crosslinked (6 mm thick) was cut into a 3" square piece. This was stuck to an Al-plate (3" square) with double stick scotch tape. This sample was then suitable for shear adhesive strength tests except that the sample was too thick for such tests, but an approximate, preliminary value could be obtained. The shear adhesive strength amounted to, 0.53, 0.48 and 0.34 kg/cm^2, Av. 0.45 kg/cm^2. The mat was sliced to about half its original thickness and samples were measured (thickness 3±0.3 mm).

Sample Treatment	Shear Adhesive Strength, kg/cm^2
Without water (gale) erosion	0.45
3 h Erosion	0.34
Additional 6h Erosion (total 19h)	0.28

Erosion did not effect the shear strength although the surface of the foam was wet with water. The latter fact always increased the adhesive strength of other materials.

Polyethylene foam was coated with LR-5630 (1g)/SF-1154(0.5 g) in 12 ml toluene solution and in silicone masonary sealer (silicone resin 5% in petroleum thinner 95%, sold by True Value Store). The coat was applied with a 0.2 mm gap roll coater. The LR-5630/SF-1154 coat could be quite easily peeled off the foam i.e. the adhesive strength between the coat and the polyethylene foam is quite low.

Silicone Masonary Sealer-Coated PE-Foam

	Shear Adhesive Strength kg/cm^2
Without Erosion	0.25
After 3 h Erosion	0.44

After 3 h of erosion the surface of the sample was water repellent.

Sliced PE-Foam (3" square, 3 mm thick) was adhered to an Al-plate with cyanoacrylate adhesive under compression:

	Shear Adhesive Strength kg/cm^2
Without Erosion	0.61
Coated with SF-1154 and Eroded for 16h	0.21
After additional 16h of erosion (total 48h and dried for 1 day	0.67

All the above adhesive strength values are within the requested adhesive strength limit (i.e. 25 psi or 1.76 kg/cm^2), which is very encouraging.

Polyethylene foam tape (A 3 mm thick sheet is available commercially) coated with silicone masonary sealer or SF-1154 having pressure sensitive adhesive at its back appears to be a remarkable efficient system.

IX. Dow Corning Varnish #997

The recommended curing time and temperature are 3 h and 200 C.

1. Preliminary Experiments

An Al-plate was coated with #997 by flow-coating and heated on a hot plate. The ice/coat adhesive strength was measured (as always -10 C).

TABLE 59

Sample No.	Sample Conditions	Shear Adhesive Strength kg/cm^2
1	180°C 3h	3.85
2	Plus 240°C, 3h	4.24
2	Plus 240°C, 3h	2.25*
3	223°C, 1h	2.44
3	223°C, 1h	1.03*
4	220°C, 2h	1.40
5	225°C, 2h	4.24
5	225°C, 2h	1.03*

*Also coated with silicone oil (MW 340).

2. Curing Conditions

As the shear adhesive strength data appreciably fluctuate, the curing conditions for #997 were examined in more detail.

#997 was coated on an Al-plate with a coater (gap 0.4 mm) and heated to 200 ± 1.0°C for varying periods of time. The adhesive strength was then measured:

TABLE 60

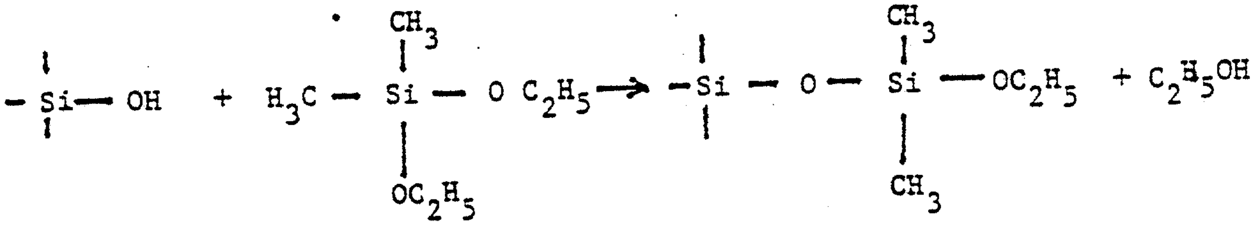
Heating time, h	1.5	3.0	4.0	4.5	5.0	6.0	7.5
Shear adhesive strength kg/cm^2	>4.74	>4.74	1.80	1.45	2.14	2.09	2.26

The adhesive strength as a function of curing time shows peculiar features, it decreases very rapidly at 4 h, reaches a minimum at ca. 4.5 h and then increases somewhat beyond this time.

A sample cured 4.5 h (i.e. which shows the minimum adhesive strength as a function of curing time) was subjected to erosion for 16 h. The adhesive strength amounted to 1.43 kg/cm^2 which lies under the requested value of 1.76 kg/cm^2.

3. #997 Varnish Modified with Dimethyl-diethoxy silane.

The assumed reaction is as follows:



$$-\overset{|}{\underset{|}{Si}}-OH + H_3C-\overset{CH_3}{\underset{OC_2H_5}{Si}}-O\,C_2H_5 \rightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-OC_2H_5 + C_2H_5OH$$

The silane $Me_2Si(OEt)_2$ functions as a chain extender was heated for 2 h and was then coated with a coater (gap 0.4 mm) on an Al-plate. The coat was heated at 200°C for 1.5 h. After shear adhesive strength testing it was further heated (i.e. total heating time 4.5 h).

TABLE 61

Sample	Adhesive Strength kg/cm^2	
#997/$Me_2Si(OEt)_2$ By Wt.	Cured at 200°C, 1.5h	Cured at 200°C, 4.5h
10/8	1.69	0.91
10/6	2.49	0.85
10/5	1.45	1.06
10/4	2.59	1.11
10/0	> 4.74	1.45

All values for the 4.5 h-cured sample lie below the specified value (1.76 kg/cm^2).

The above adhesive mixture was further heated for 5 h and coated on an Al-plate. The mixture contained some gel-particles and in the coat and many cracks after heating it at 200 C for 1.5 h. The results are given below and are represented in Fig. 18.

Reacting #997 with $Me_2Si(OEt)_2$ did not improve the abhesion properties of the coat appreciably.

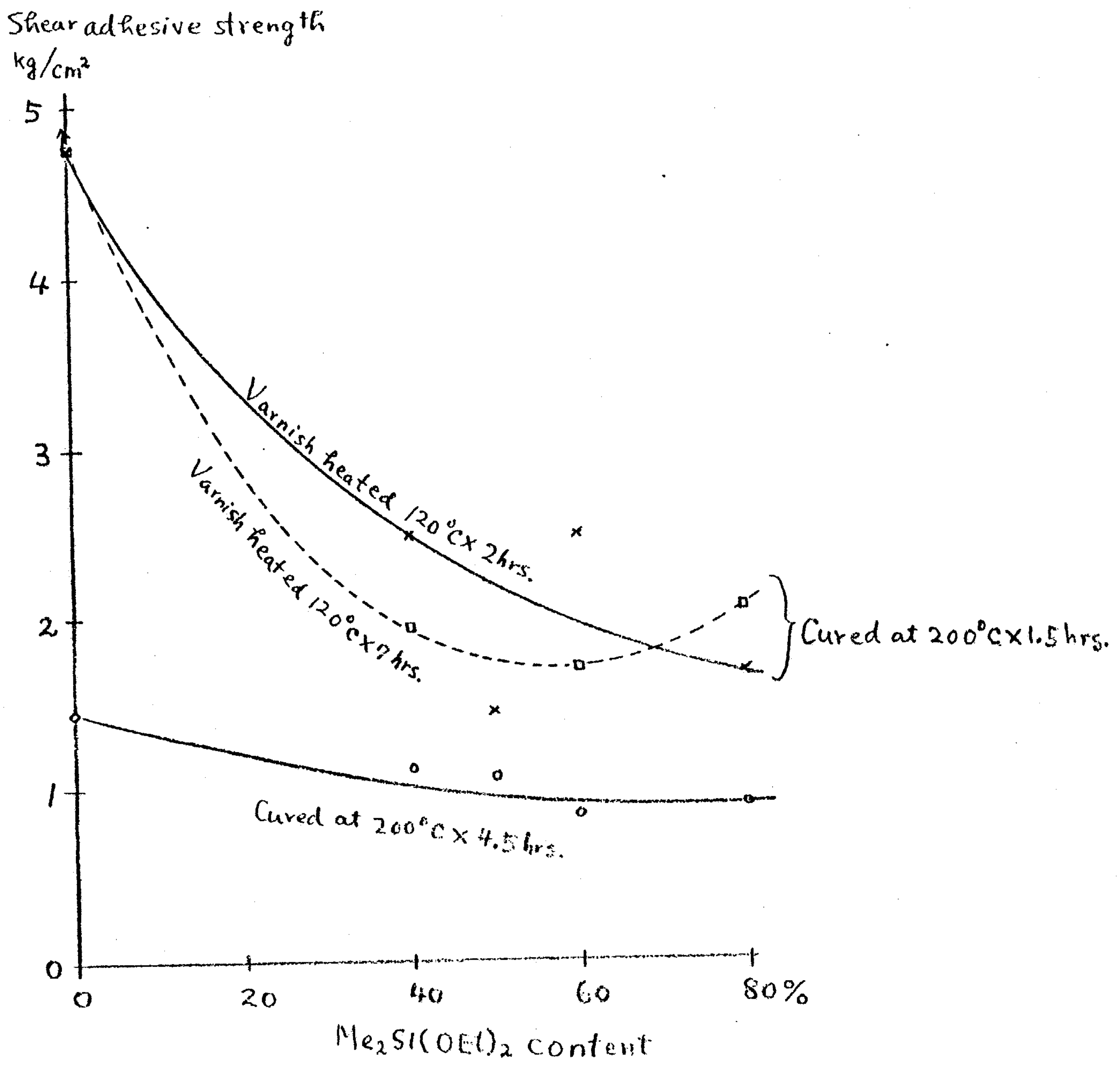
4. Addition of Silicone Oil

Silicone oils poly(dimethlysiloxane)(MW 1x10^5) and G.E. SF-1154 were mixed with #997 varnish. The mixture was coated on an Al-plate and tested:

TABLE 62

Sample	Composition #997/Silicone Oil By Wt.	Remarks (Appearance)	Adhesive Strength kg/cm^2
Polydimethyl Siloxane	10/0.5	silicone oil particles separated	0.86
Polydimethyl Siloxane	10/1	silicone oil particles separated	0.68
SF-1154	10/1	uniform coat	0.31
SF-1154	10/2.5	film is very weak	----
SF-1154	10/5	film is very weak	----

Fig. 18


Shear adhesive strength
kg/cm²
5
4
3
2
1
0
0
20
40
60
80%
$Me_2Si(OEt)_2$ content
Varnish heated 120°C× 2hrs.
Varnish heated 120°C×7hrs.
Cured at 200°C×1.5hrs.
Cured at 200°C × 4.5hrs.

The #997 mix with silicone oil SF-1154 was subjected to erosion for 15 h and stored at room temperature.

Time stored, days	0	10	11	12	14
Shear Adhesive Strength, kg/cm^2	1.06	1.94	1.76	0.77	1.31

The addition of SF-1154 (10 wt% to #997) only reduces the initial adhesive strength.

Generally the adhesive strength of #997 cured at 200°C for 4.5 h was slightly below the specified value and did not change much with erosion.

X. SR 80M Silicone Electrical Resin Made by G.E.

SR 80M consists of 34% silicone resin solution and changes to a tack-free film by drying at room temperature for 30 to 60 minutes.

The coating properties of SR-80M were poor compare with #997. It was difficult to obtain a smooth coat.

1. Curing Experiments

A SR 80M film was coated on a glass-slide using an eye dropper. The coat was cured under a variety of conditions listed below and was immersed in toluene for a curing test for 2 h.

TABLE 63

Curing conditions	Toluene Curing Test
Room temperature , 30 min.	Dissolves
" " , 24 h	Only a trace does not disolve
100°C , 1 h	Small amounts of film left
100°C , 2 h	Somewhat larger amount left but still small
100°C , 16 h	Large amount of film left

Results indicate that proper curing at room temperature will take a long time probably 100 days or more, even as the varnish is a so-called room temperature curing varnish.

2. Coating Experiments

SR 80M varnish was coated on two Al-plates which were heated to 100°C for 1 h and 16 h, respectively, the coats cracked when cooling to -10°C. Their adhesive strength was 1.31 kg/cm^2

3. Modification of SR 80M

SR 80M (1g) and $Me_2Si(OEt)_2$ (0.1 g) were mixed and heated to ca. 60°C for 3 h. However, no viscosity increase was observed.

4. Addition of Silicone Oil SF-1154

SF-1154 (15% by weight) was added to SR 80M as a plasticizer. A clear solution was obtained. It was dried at room temperature for 2.5 h and then heated at 100°C for 16 h. A turbid coat was obtained. The coat cracked on cooling to -10°C. Overall, SR 80M did not prove suitable for coating at low temperatures.

XI. Silicon PS 255 (Fluka Chemical Corp.).

PS 255 is a co-polymer of dimethylsiloxane and 1% to 3% methylvinylsilane. It is cured by the addition polymerization with vinyl groups.

1.2 g of PS 255 were dissolved in 7.2 ml of toluene for obtaining a coating solution. This solution has a suitable viscosity for coating.

A coat was prepared on a glass-slide and heated at 100°C for two hours; however the coat dissolved completely in toluene during 1 h at room temperature.

Next, a coat was heated at 150°C for 3.5 h. A sticky, clear coat resulted. This coat only dissolved completely in toluene after 19 h immersion. Thus PS 255 did not crosslink under these conditions.

A solution of 1g of PS 255 plus 0.004 g of dicumyl peroxide in 7 ml of toluene was coated on a glass-slide and heated at 150°C for 18 h. The sticky coat was heated again, this time to 200°C for 1 h. But crosslinking did not take place. It would take too long at this stage of the work to search for the proper crosslinking conditions.

XII. Vinyl-acrylate Co-polymer Lacquer

It consists of 18% by wt. of polymer in a 82% solution in a petroleum distillate. It is produced by Gilsonite Laboratories under the trade name "Drylok". The coat is supposed to be curable at room temperature, experimental data are shown in Fig. 19. Shear adhesive strength increases with progressive curing; the coat increased in hardness.

A coat on an Al-plate (adhesive strength 0.98 kg/cm^2 was exposed to erosion for 3 h, its adhesive strength increased to 4.5 kg/cm^2.

Adhesion between the co-polymer LR-5630 and vinyl-acrylate co-polymer was found not to be suitable. Vinyl-acrylate is not satisfactory for our purpose.

XIII. Dow Corning 3145 RTV Clear Adhesive-Sealant

1. 3145 RTV Silicone Paste

It was cured at room temperature within 2 h to a tack-free silicone rubber, while it was cured to a rubbery solid within 1/2 h (1/8" thick coat). Results for RTV silicone paste are given below.

Fig. 19

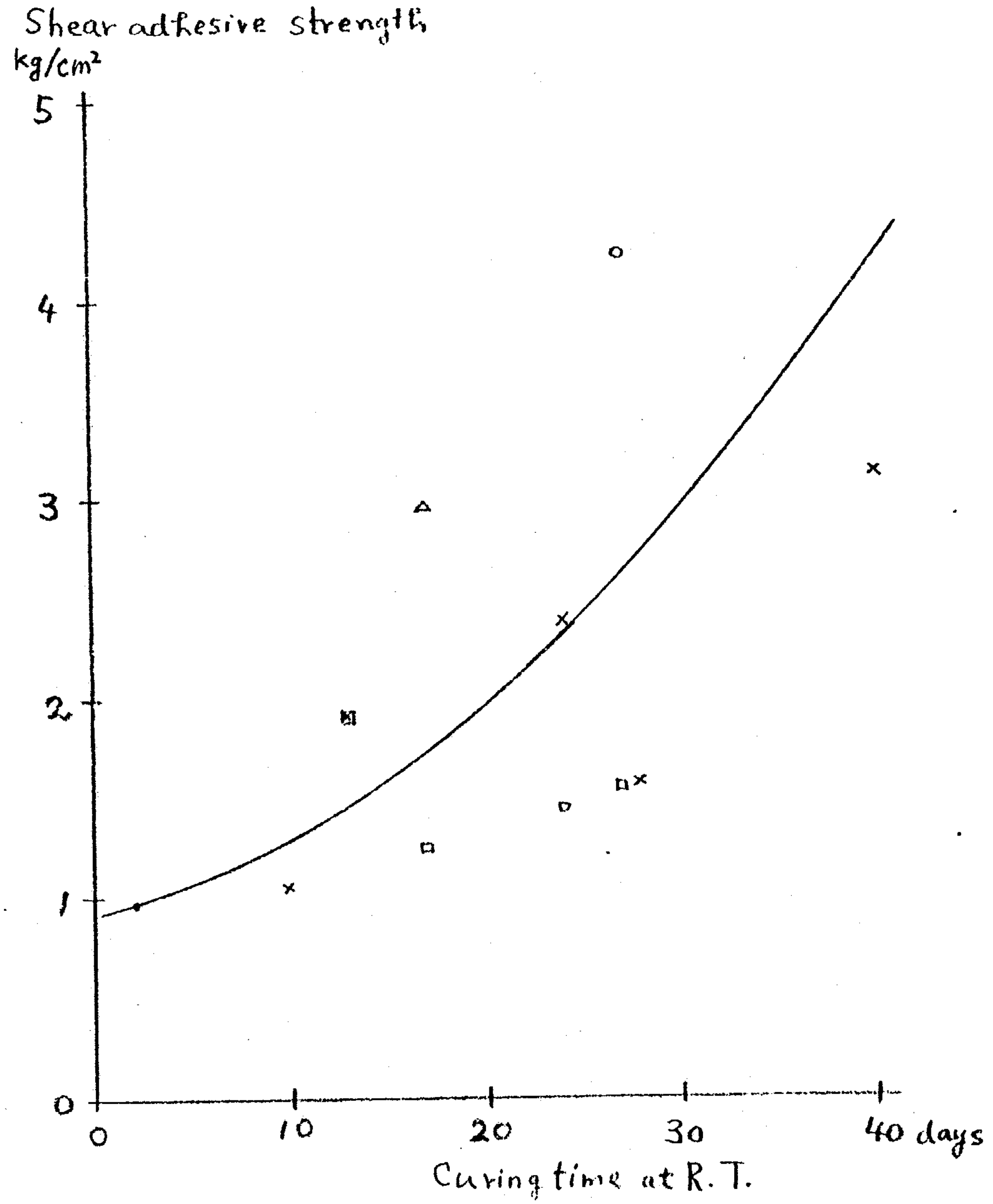

Shear adhesive strength
kg/cm²
5
4
3
2
1
0
0
10
20
30
40 days
Curing time at R.T.

TABLE 64

Samples of RTV and RTV Plus Thomas Oil Coats Coated on Al-Substrate

Sample No.	RTV silicone paste/Thomas silicone oil, by wt.	Coater "clearance", mm
(a) 27.5% by vol. RTV silicone paste solution in toluene		
1	10/0	0.8
2	10/0	0.6
3	10/0	0.6
4	10/0	0.6
5	10/0	0.4
6	10/1	0.4
7	10/2	0.4
8	10/4	0.4
9	10/6	0.4
10	10/8	0.4
11	10/10	0.4
(b) RTV silicone Paste (100% solid)		
12	10/0	0.4
13	10/0	0.6
14	10/0	0.8
15	10/0	1.5

This material proved very promising for de-icing.

2. Shear Adhesive Strength

The adhesive strength of the coats on an Al-substrate to ice was measured as a function of time. RTV-silicone mixed with Thomas silicone oil were tested. The results are listed in tables 64 and 65.

TABLE 65

Ice Shear Adhesive Strength of Samples Listed in Table 64 (-10°C)

lapsed ime after ating; ays	Shear Adhesive Strength, kg/cm^2														
	Sample														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
1		1.53			1.03			0.57	0.47	0.28	0.30	0.26 (Gx3)			0
2			1.89									1.79	0.32	0.26	
3		1.11	1.07	1.08				0.24	0.28	0.11	0.19				
10	1.00					0.86	0.67 (Gx3)								
11	0.60					0.57	0.99								
12	0.56					0.79	0.88					2.01	1.14	1.06	0
13					0.61 (Gx16)							2.08	1.07	0.60	
14	0.60	0.40	0.40	0.51		0.64	0.66					1.35	0.77 (Gx3)	1.02 (Gx16)	
15												1.16	1.33		
16												1.19	1.36	1.15	
24							0.76 (Gx16)								
25							2.87								
82	3.73					3.52	4.08								
85					8.60			2.14	0.97 (Gx16)	0.97	0.64				
86									1.32		0.34				
87									0.90		0.28	3.11	2.74	2.15	
97															
98									0.29	0.11	0.12				

ote: e.g., "Gx16" means "applied water jet for 16 hrs.".

Some remarks are made below concerning the results in Table 65.

(1) Table 65 shows that coats without silicone oil (samples Nos. 1 to 5 and 12 to 15) have smaller adhesive strength with elapsed time than those with silicone oil. The decrease reaches a minimum value within two to three week. Subsequently, the values increase to a high value which is beyond that specified by the sponsor (i.e. 1.76 kg/cm^2).

(2) A dependence of the adhesive strength on coat thickness was not found.

(3) Coats prepared from solution exhibited a number of tiny irregularities on their surface; their shear adhesive strength was somewhat larger than that of coats made from paste. Thus it was thought desirable to carry out tests using a mixed solvent system, so that smooth vaporization could be achieved once the solution was sprayed on the Al-substrate.

(4) Coats containing at least 60% by wt. of silicone oil (Nos. 6 to 11) has low adhesive strengths for at least 98 days; it is expected this would last for a considerably longer time.

(5) The water erosion affected the adhesive strength of the coats; but the values remained within the limits of the specified value for coats containing 60% by wt. of silicone oil.

3. Tensile Strength of RTV Silicone Coats.

Films (coats) prepared from paste were put on various substrates from which they could be easily removed as films. The tensile strength of these films was measured after curing at room temperature for 1, 2, 3 or 5 days. Films of different thickness were obtained by using coaters of different gap-widths. Table 66 gives remark.

TABLE 66

Tensile Strength of RTV Films

Removed From Their Substrates

(Prepared from paste: room temperature)

Elapsed time after coating, days	Tensile modulus, kg/cm^2			
	Film A: Thickness			
	263 ± 8 μm	398 ± 8 μm	578 ± 11 μm	Av. kg/cm^2
1	6.81	7.00	7.38	7.06
2	8.53	7.42	8.84	8.26
3	5.47	7.92	7.99	7.13
6	5.17	6.14	8.12	6.48
7	6.35	6.70	9.66	7.57
Ave. (kg/cm^2)	6.47 ± 1.3	7.04 ± 0.7	8.40 ± 0.9	7.30 ± 0.7
	Film B: Thickness			
	229 ± 6 μm	382 ± 6 μm	529 ± 6 μm	Av. kg/cm^2
1	7.97	6.70	8.78	7.82
2	6.79	8.95	8.84	8.19
3	7.22	7.83	7.82	7.62
6	5.45	6.89	9.22	7.19
7	7.80	8.40	9.75	8.65
Ave. (kg/cm^2)	7.05 ± 1.0	7.75 ± 1.0	8.88 ± 0.7	7.89 ± 0.5

Note: Film A was prepared by coating RTV silicone paste on a glass plate and Film B on polypropylene film, respectively. The former coat could be removed as film by using a razor blade and the latter was easily removed by peeling; the latter film was less damaged.

The average strengths in table 66 increases systematically with film thickness, while the strengths as a function of time do not vary in an orderly way. This indicates that the main effect is due to film thickness while the elapsed time plays a minor role. Sample No. 12 in tables 64 and 65 ($295\mu m$ thick) was measured after 98 days had elapsed; its tensible strength was 8.8 kg/cm^2. This value is larger than the average value of 7.1 ± 1.0 kg/cm^2 (table 64, film B; av. thickness 229 μm). The value is also larger than the av. value for film A, (6.87 ± 1.3 kg/cm^2; 263 m). The elapsed times giving these average values were much shorter than 98 days (i.e. 3.5 days) for sample 1B. A long elapsed time increases the tensible strength. This is due to continued crosslinking taking place in the film (coat). The RTV is still crosslinking after such long time was shown by us using I.R. spectra. Optical densities of O-H bonds ($2.9\mu m$) changing with time were taken as indicators for this crosslinking process.

Final Conclusions

Four coatings suitable for de-icing of oil-drilling platforms have been found whose shear adhesive strength ($-10^\circ C$) lies will within the specified adhesive strength (1.76 kg/cm^2) after "erosion" by a water jet.

(1) Poly(dimethylsiloxane) bisphenol-A polycarbonate block co-polyer LR-5630 (G.E. Co.) with silicone oil SF-1154 (G.E. Co.)

The composition of the "spraying" solution is as follows:

Co-polymer LR-5630 10 g.; SF-1154 5 g., toluene 40 ml. This solution is prepared by dissovling LR-5630 in toluene under stirring and then adding SF-1154 silicone oil. The thickness of the coat was ca. 0.4 mm i.e. 25 ft^2/gal. solution would give such a thickness.

Shear adhesive strength (-10°C) before erosion <0.07 kg/cm^2.

Shear adhesive strength (-10°C) after erosion (16 h) <0.61 kg/cm^2.

(2) Crosslinked PE (polyethylene form), Nalgene 6281 series, thickness 3 mm.

The top surface is coated with "silicone masonry sealer". A "pressure sensitive adhesive" is applied to the bottom surface of the foam, this bottom surface is adhered to the substrate.

Shear adhesive strength before erosion (-10°C) 0.24 kg/cm^2.

Shear adhesive strength after 16 h erosion (-10°C) 0.20 kg/cm^2.

Shear adhesive strength additional 16 h 0.28 kg/cm^2.

The top surface can also be covered with "masonry sealer" for dust-protection (True Value).

(3) Dow Corning 3145 RTV clear adhesive sealant with Thomas silicone oil.

Thickness of coat ca. 0.1 mm.

Solution: 3145 RTV 27.5% by vol. is dissolved in toluene under stirring (room temperature), subsequently silicone oil is added.

Ratio by wt. 3145 RTV/Thomas oil 10/6.

Shear adhesive strength before erosion (10°C) 0.97 kg/cm^2.

Shear adhesive strength after 16 h erosion (-10°C) 1.32 kg/cm^2.

Shear adhesive strength one day after erosion (-10°C) 0.90 kg/cm^2.

Thickness of coat ca. 0.1 mm, i.e. 180 ft^2/gal. solution.

(4) Dow Corning varnish #997.

Curing conditions 200°C, 4.5 h.

Shear adhesive strength before erosion (-10°C) 1.45 kg/cm^2.

Shear adhesive strength 16 h erosion (-10°C) 1.43 kg/cm^2.

Thickness of coat ca. 0.2 mm, i.e. 100 ft^2/gal. solution.

De-icer (1) is the most efficient one while de-icer (2) is easiest in application.

APPENDIX: Preparative Procedure for Most Promising Coatings Including Polyethylene Foam Sheet

1. LR-5630/SF-1154 Coating

Composition of Coating Solution

LR-5630[1)]	50 g
SF-1154[2)]	25 g
Toluene	300 ml

Note: 1) Poly(dimethylsiloxane) bysphenol-A polycarbonate block-co-polymer made by General Electric C.

2) Silicone oil (high phenyl siloxane content) made by General Electric Co.

The ration of LR-5630/SF-1154 = $^{10}/5$.

The solution was coated on a plate by flow coating. The thickness of the coat was ca. 0.25 mm. The surface of the coat was oily with silicone oil which was continuously bled out to the surface for at least several months.

2. Crosslinked Polyethylene (PE) Foam Sheet

Made by Nalge Co. Thickness of the sheet 3 mm.

A plate (3" x 3") was coated with epoxy adhesive (E-POX-E Glue made by Woodhil Permax. Any appropriate adhesive can be used instead of epoxy adhesive). Then a PE sheet 3" x 3" was placed on the adhesive applied surface and applied pressure to adhere the sheet firmly on the plate. After it was allowed to leave at room temperature for three days, Silicone Masonry Sealer (Silicone resin 5% in petroleum thinner; Supplied from True Value) was applied on the PE sheet by using a brush. (A spray would be more convenient for coating it).

3. RTV silicone/Thomas Silicone Oil Coating

RTV silicone: Dow Corning 3145 RTV adhesive/sealant.

Composition of Coating Solution

RTV silicone	90.7 g
Thomas silicone oil[1)]	53 g
Toluene	212 ml.

Note: 1) Dimethylsiloxane oil.

The solution prepared above was coated on plate by dip-coating which was repeated three times. The thickness of the coat was ca. 0.2 mm.

Caution: Since RTV silicone reacts with moisture in air and as a result, it is crosslinked, the solution becomes gel when a bottle of the solution is once opened in air.

4. Modified Dow Corning #997 Varnish

Composition of Coating Solution

#997	200 g
$Me_2Si(OEt)_2$	80 g

The mixture of #997 and $Me_2Si(OE)_2$ was cooked at $120 \pm 1^\circ C$ for two hours. The solution was coated on an iron plate by flow-coating. After it was allowed to leave at room temperature for one day, it was heated in an electrical oven at $200 \pm 1^\circ C$ for two hours. The thickness of the coat was ca. $0.05 \sim 0.1$ mm.