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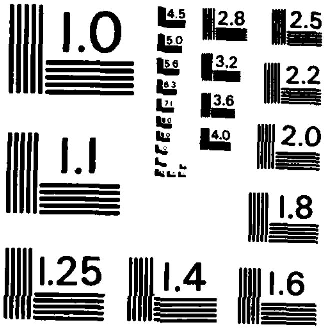

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THE EFFECT OF BARRIER COATINGS ON THE CURE RATE AND FLUID RESISTANCE OF POLYSULPHIDE SEALANTS

by

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THE EFFECT OF BARRIER COATINGS ON THE CURE RATE AND FLUID RESISTANCE OF POLYSULPHIDE SEALANTS

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SUMMARY

Two commercial barrier coating materials based on polyurethane and nitrile (acrylonitrile-butadiene copolymer) were used in conjunction with two of the most commonly used integral fuel tank polysulphide sealants (catalysed with either dichromate or lead dioxide).

The rate and degree of cure were only slightly reduced when either barrier coating was applied. Neither coating appeared to offer any improvement in fuel resistance but significant improvements were noted in the resistance of barrier coated sealants to the ingress of water. After 44 days at 40°C water uptake of dichromate cured sealant was reduced from 126% to 6% by barrier coating with polyurethane. A similar effect was noted with the lead dioxide cured sealant although not to the same degree since this material is inherently more resistant to water than the dichromate cured sealant. There is some doubt about the long term performance of the polyurethane barrier coating as samples appeared to embrittle on ageing.

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1 INTRODUCTION

Liquid polysulphide polymers have been used successfully as integral fuel tank sealants in aircraft for many years. Barrier coatings are often used to give longer service life to sealants by protecting them from attack by aviation fuels and water. They also dry rapidly forming a tough tack-free skin which prevents swarf from subsequent drilling and fitting operations sticking to the sealant surfaces. However, failures do occur causing leaks which have to be repaired 'on site'. The repair consists of removal of old sealant, cleaning the area of the leak, coating it with a layer of sealant and, in most cases, a barrier coating. This form of repair is very time consuming and leads to aircraft being grounded for long periods of time. Some of the sealant formulations require atmospheric moisture to cure satisfactorily[1] and the presence of a barrier coating could impede the ingress of such moisture and thus retard the cure. However, it has been suggested that it may be possible to reduce the time of repair by applying barrier coatings to non-tack-free sealant.

It was decided that work should be carried out to investigate the effects of nitrile and polyurethane barrier coatings on the cure of dichromate and lead dioxide curing polysulphide sealants. It was considered that the effects of applying nitrile barrier coatings to non-tack-free sealants should also be studied. The application of barrier coatings is time consuming and the evolution of volatiles in the confined spaces of integral fuel tanks can cause discomfort to operatives. Thus, it is important to establish whether the use of barrier coatings is necessary.

2 EXPERIMENTAL DETAILS

2.1 Materials

The sealants tested were commercial brushing grade compounds based on thiol terminated liquid polysulphide polymers cured using either dichromate or lead dioxide catalysts.

Barrier coating materials were (a) nitrile, a non-curing compound based on an acrylonitrile-butadiene copolymer and (b) a cureable polyurethane.

2.2 Mixing, curing and barrier coating conditions

The sealant compositions were mixed by hand, care being taken to avoid the inclusion of air and to ensure good dispersion of the curing agent. For the determination of cure, small samples of the mixed sealant were poured onto fluorinated ethylene propylene (FEP) film and allowed to flow to approximately 1 inch diameter. Some of these samples were immediately barrier coated with nitrile (Fig 1) whilst others were left until 'tack free' and then barrier coated with either nitrile or polyurethane (normal coat). To ensure that the coatings were pore free a second coating was applied after the first had dried. A large sheet approximately 25 cm × 5 cm was formed from the remaining mixed sealant and used for tests on uncoated materials and for fluid immersion tests on coated materials. All of the samples were left to cure at 26°C and 65% relative humidity. Barrier coating for immersion tests was carried out after 45 days to ensure that the underlying sealant was fully cured. The coatings were left to dry/cure for 7 days before commencement of tests.

2.3 Determination of cure

2.3.1 Uncoated material

For each sealant small samples (≏ 0.2 g) were taken from the large sheet at regular intervals during a 42 day period of cure, weighed accurately, and immersed in an excess of toluene at 26°C. After a period of 72 hours, when swelling equilibrium had been reached, each sample was withdrawn, surface dried, and weighed in a stoppered bottle. Each sample was then dried at room temperature to constant weight. The extent of cure is indicated by the amount of soluble material (initial weight-final dry weight/initial weight) and by the degree of swelling at equilibrium (swelling ratio = swollen weight/final dry weight).

2.3.2 Barrier coated materials

Small samples were cut from the centre of each individual test specimen, care being taken to remove all of the barrier coating material. Tests were carried out as in section 2.3.1.

2.4 Fluid immersion

Tests were carried out in distilled water and aviation fuel (AVTUR). Small samples (≏ 0.2 g) of uncoated and coated sealant were weighed and immersed in an excess of fluid at 26°C and 40°C. They were then withdrawn at regular intervals, surface dried and re-weighed before replacing in the fluid. Uptake of fluid was expressed as a percentage of the initial dry weight of the sample.

3 RESULTS AND DISCUSSION

3.1 Effects of barrier coatings on the cure rate of dichromate and lead dioxide catalysed sealants

The effects of barrier coatings on the cure rate of the sealants are shown in Figs 2, 2a&b. The solvent swell ratio is a sensitive measure of the degree of crosslinking in rubbers and together with information on the percentage of soluble material present (Fig 3) it gives a good indication of the state of cure. Detailed test results of coated and uncoated sealants are given in Appendices A and B.

There was little difference between the rate of cure of the uncoated and barrier coated sealants after the first 24 hours (Figs 2, 2a&b). However, the uncoated materials had the lowest percentage of soluble material (Fig 3) possibly indicating that there is (a) a retardation of cure or (b) solvent retention when a barrier coating is applied.

It was noted that when a nitrile barrier coat was applied immediately (*ie* when the sealant was still wet) considerable flow took place caused by the solvent migrating from the barrier coat into the underlying sealant. This is very undesirable in practice as it would affect the non-sag properties of the sealant and cause it to flow on vertical and overhead surfaces.

3.2 Effects of barrier coatings on water resistance of sealants

3.2.1 Water absorption by sealants and coatings

Table 1

Percentage weight change of materials immersed in water at 26°C and 40°C

Time days	Polyurethane barrier coating		Nitrile barrier coating		Dichromate cured polysulphide sealant		Lead dioxide cured polysulphide sealant	
	26°C	40°C	26°C	40°C	26°C	40°C	26°C	40°C
1	2.4	2.4	3.4	0.6	2.5	5.1	1.1	2.3
2	3.0	2.0	3.1	0.6	3.9	8.3	1.6	3.2
3	3.0	2.0	3.4	1.3	-	-	-	-
4	2.7	1.8	3.0	-	6.3	14.0	2.3	4.7
7	-	-	-	3.9	8.8	22.0	3.3	6.8
8	2.2	1.7	3.0	-	-	-	-	-
9	-	-	-	-	10.6	27.4	3.8	8.2
11	-	-	-	-	12.0	32.7	4.2	9.3
13	-	-	-	7.9	-	-	-	-
14	1.9	1.7	3.4	-	-	-	-	-
16	-	-	-	-	15.8	45.7	5.4	12.2
21	1.4	1.4	4.1	9.4	-	-	-	-
22	-	-	-	-	19.8	61.2	6.5	15.2
27	-	-	-	-	-	-	-	-
28	1.2	0.9	4.7	12.9	-	-	-	-
29	-	-	-	-	24.6	83.0	7.8	19.1
34	-	-	-	14.9	-	-	-	-
35	1.2	0.9	5.2	-	-	-	-	-
36	-	-	-	-	28.9	98.8	8.8	21.6
41	-	-	-	16.3	-	-	-	-
42	1.0	0.8	5.9	-	-	-	-	-
44	-	-	-	-	34.0	125.7	10.3	25.7

Polyurethane coatings appear to have excellent water resistance at 26°C and 40°c (Table 1, Fig 4). However the steady decrease in weight after 2 days suggests the presence of soluble material which is being dissolved. Table 1 and Fig 5 show that the water resistance of nitrile coatings is fairly good at 26°C but is relatively poor at 40°C, *eg* 16% H_2O was taken up after 41 days at 40°C and equilibrium was not attained. Dichromate cured polysulphide sealant, owing mainly to its curing system, is known to absorb substantial amounts of water[1]. This was confirmed in the present work, *eg* dichromate cured sealant absorbed 126% H_2O after 44 days at 40°C and 34% after 44 days at 26°C. Lead dioxide cured polysulphide sealant exhibited better water resistance than dichromate cured sealant. Percentage uptake after 44 days at 40°C was 26% and at 26°C, 10%. However, these values are poor by comparison with most other elastomers.

3.2.2 Water resistance of dichromate and lead dioxide catalysed sealants barrier coated with polyurethane

Table 2

Percentage weight change of barrier coated sealants immersed in water at 26°C and 40°C

Polysulphide sealant	Dichromate cured		Dichromate cured		Lead dioxide cured		Lead dioxide cured	
Barrier coat	Polyurethane		Nitrile		Polyurethane		Nitrile	
Temperature Time, days	26°C	40°C	26°C	40°C	26°C	40°C	26°C	40°C
1	0.9	1.2	0.8	1.3	0.7	1.0	0.4	0.8
2	1.2	1.6	0.9	1.4	0.9	1.1	0.6	0.8
3	1.3	1.8	-	-	1.0	1.2	-	-
4	1.3	1.8	1.2	2.3	1.1	1.0	0.9	1.2
7	1.5	2.0	1.6	3.5	1.2	1.0	1.0	1.7
9	1.5	2.3	1.7	4.2	1.2	1.0	1.1	2.0
11	1.4	2.3	2.0	5.1	1.3	0.9	1.2	2.3
16	1.5	2.9	2.4	7.4	1.4	1.2	1.3	3.1
22	1.5	3.5	2.9	9.7	1.4	1.4	1.7	4.0
29	1.7	4.3	3.5	12.9	1.6	1.8	2.0	4.9
36	2.1	5.2	4.1	15.7	1.6	2.2	2.2	5.7
44	2.0	6.0	5.0	19.6	1.6	2.6	2.6	7.1

Polyurethane provided a very effective barrier coat against water for both dichromate and lead dioxide cured sealants (Tables 1 and 2 and Fig 6), for example, water uptake of dichromate cured sealant immersed for 44 days at 40°C was reduced from 126% to 6% and at 26°C, from 34% to 2%. Similarly, water absorption by the lead dioxide cured sealant was reduced from 26% to 3% at 40°C and from 10% to 2% at 26°C.

3.2.3 Water resistance of dichromate and lead dioxide catalysed sealants barrier coated with nitrile

Although nitrile was not as effective a barrier coat against water as polyurethane (Table 2 and Fig 7), a significant reduction in water uptake was achieved. Thus for dichromate cured sealant the water uptake after 44 days at 40°C was reduced from 126% to 20% and at 26°C from 34% to 5%. For lead dioxide cured sealant the water uptake after 44 days at 40°C was reduced from 26% to 7%, and at 26°C from 10% to 3%.

3.3 Effects of barrier coatings on fuel resistance of sealants

3.3.1 Fuel resistance of barrier coatings

Table 3

Percentage weight change of materials immersed in AVTUR at 26°C and 40°C

Time days	Polyurethane barrier coating		Nitrile barrier coating		Dichromate cured polysulphide sealant		Lead dioxide cured polysulphide sealant	
	26°C	40°C	26°C	40°C	26°C	40°C	26°C	40°C
1	2.0	3.2	0.4	-1.8	0.9	1.4	0.6	0.5
2	3.0	4.2	0.4	-2.8	1.1	1.4	0.5	0.3
3	3.8	4.9	0.0	-3.3	-	-	-	-
4	4.2	5.0	-0.2	-4.4	1.4	1.3	0.4	-0.3
7	-	-	-	-	1.5	1.3	0.1	-0.7
8	5.4	5.3	-0.4	-5.4	-	-	-	-
9	-	-	-	-	1.5	1.1	0.0	-0.8
11	-	-	-	-	1.4	1.1	0.0	-0.9
14	5.9	4.7	-0.8	-4.7	-	-	-	-
16	-	-	-	-	1.2	1.0	-0.5	-1.1
21	6.0	4.3	-1.3	-5.1	-	-	-	-
22	-	-	-	-	1.2	1.0	-0.7	-1.1
28	6.1	4.1	-1.4	-5.3	-	-	-	-
29	-	-	-	-	1.2	1.0	-0.9	-1.2
35	6.2	4.0	-1.5	-5.0	-	-	-	-
36	-	-	-	-	1.1	1.0	-1.0	-1.3
42	5.9	3.8	-1.1	-5.7	-	-	-	-
44	-	-	-	-	1.1	1.0	-1.0	-1.2

The polyurethane barrier coating reached an equilibrium swell of ≃6% weight increase at 26°C after approximately 14 days immersion (Table 3 and Fig 4). The effect of raising the temperature to 40°C was to increase the rate of weight change during the first 5 days but thereafter small weight losses were observed, probably due to the loss of soluble material. This reduction in weight was even more pronounced in the nitrile coating, particularly at the higher temperature (Table 3, Fig 5). Both dichromate and lead dioxide cured sealants showed excellent resistance to swelling, but here again there was some indication of the loss of soluble material which was not very dependent on temperature and more marked in the lead dioxide cured sealant (Table 3 and Fig 8).

3.3.2 Fuel resistance of dichromate and lead dioxide catalysed sealants barrier coated with polyurethane and nitrile

Table 4

Percentage weight change of barrier coated sealants immersed in AVTUR at 26°C and 40°C

Sealant	Dichromate cured polysulphide sealant		Dichromate cured polysulphide sealant		Lead dioxide cured polysulphide sealant		Lead dioxide cured polysulphide sealant	
Barrier coat	Polyurethane		Nitrile		Polyurethane		Nitrile	
Temperature / Time, days	26°C	40°C	26°C	40°C	26°C	40°C	26°C	40°C
1	0.2	0.0	0.2	0.0	0.2	0.0	0.1	0.1
2	0.2	-	0.1	0.0	0.2	-0.1	0.1	0.1
3	0.2	0.2	-	-	0.2	-0.1	-	-
4	0.5	0.1	0.3	0.1	0.3	-0.1	0.2	0.2
7	0.5	0.0	0.5	0.3	0.3	-0.4	0.3	0.1
9	0.3	-0.5	0.3	0.4	0.3	-0.5	0.3	-0.1
11	0.3	-0.7	0.5	0.3	0.2	-0.8	0.3	-0.2
16	0.2	-0.9	0.5	0.2	0.2	-1.0	0.5	-0.6
22	0.2	-1.3	0.5	0.2	0.2	-1.4	0.5	-0.8
29	0.0	-1.4	0.5	-0.1	0.1	-1.6	0.5	-1.0
36	-0.1	-1.5	0.6	-1.4	0.0	-1.8	0.5	-1.2
44	-0.2	-1.6	1.0	-1.5	0.0	-2.0	0.5	-1.2

No significant improvements in fuel resistance due to barrier coating of the polysulphide sealants were indicated by the weight change data obtained on immersion in AVTUR at 26°C and 40°C for up to 44 days (see Tables 3 and 4 and Figs 8 and 9). Further work involving longer periods of immersion and a wider temperature range is required in order to more fully assess the effects of the polyurethane and nitrile barrier coatings on fuel resistance.

4 CONCLUSIONS

(1) The application of barrier coatings lowers the initial cure rate and the final level of cure of dichromate cured polysulphide sealants but the effect on mechanical properties is probably relatively small. Barrier coating did not seem to inhibit the cure of lead catalysed sealant. Sealants must be sufficiently cured before application of the barrier coat, otherwise the non-sag properties of the sealant will be seriously affected.

(2) Polysulphide sealants, particularly those cured with dichromate, can absorb large quantities of water at nominally low temperatures and the amount absorbed is temperature dependent.

(3) Of the two barrier coats tested the polyurethane was far more resistant to water than the nitrile and when applied to both polysulphides it proved an effective barrier against water ingress. Despite its high water absorption at 40°C the nitrile material, although inferior to the polyurethane, markedly enhanced the water resistance of both polysulphides.

(4) The weight change data obtained for the two barrier coating materials indicated that solubility in AVTUR was more pronounced for the unvulcanised nitrile than for the cross-linked polyurethane. Although the results suggest that equilibrium was attained for both materials when they were immersed in AVTUR at 26°C and 40°C for 42 days, longer term confirmatory tests are required.

(5) At temperatures up to 40°C both polysulphide sealants appear to have good fuel resistance. However, at aircraft operating temperatures it has been found in practice that lead cured sealants are not sufficiently fuel resistant and a barrier coat is necessary.

(6) Although the present work has indicated that the polyurethane material shows promise as a barrier coating there are indications from examination of old material removed from aircraft fuel tanks that it eventually embrittles and cracks, especially in thick sections formed by flow to the lowest point (sumping). The long term ageing characteristics of this material therefore require further study before its real value as a barrier coating in integral fuel tanks can be assessed.

Appendix A

SOLUBILITY AND SWELLING OF SEALANTS IN TOLUENE AT 26°C
DICHROMATE CURED SEALANT

Percentage soluble in toluene

Immersion time Days	Uncoated	Nitrile immediate coat	Nitrile normal coat	Polyurethane normal coat
1	15	19	19	19
2	11	15	17	18
3	11	16	16	17
4	10	13	14	15
7	9	13	13	12
14	7	11	11	9
22	6	9	10	9
28	6	8	9	9
35	6	10	10	9
42	6	10	10	8

Swell ratio in toluene

Immersion time Days	Uncoated	Nitrile immediate coat	Nitrile normal coat	Polyurethane normal coat
1	1.70	1.74	1.75	1.77
2	1.65	1.69	1.72	1.65
3	1.64	1.68	1.70	1.72
4	1.65	1.67	1.68	1.70
7	1.60	1.64	1.66	1.66
14	2.56	1.60	1.64	1.62
22	1.55	1.59	1.61	1.61
28	1.56	1.57	1.60	1.59
35	1.55	1.59	1.61	1.61
42	1.53	1.57	1.60	1.58

Appendix B

SOLUBILITY AND SWELLING OF SEALANTS IN TOLUENE AT 26°C
LEAD DIOXIDE CURED SEALANT

Percentage soluble in toluene

Immersion time Days	Uncoated	Nitrile immediate coat	Nitrile normal coat	Polyurethane normal coat
1	17	24	20	20
2	16	20	18	20
3	18	22	21	22
4	17	28	19	20
7	16	20	20	19
15	14	20	17	18
21	15	21	18	17
28	15	20	19	17
35	16	17	17	16
42	15	20	19	17

Swell ratio in toluene

Immersion time Days	Uncoated	Nitrile immediate coat	Nitrile normal coat	Polyurethane normal coat
1	2.29	2.21	2.32	2.29
2	2.26	2.21	2.26	2.26
3	2.25	2.13	2.20	2.20
4	2.22	2.15	2.21	2.19
7	2.18	2.11	2.14	2.15
15	2.13	2.07	2.12	2.10
21	2.10	2.00	2.07	2.07
28	2.14	2.12	2.11	2.13
35	2.08	2.05	2.07	2.08
42	2.07	2.01	2.06	2.07

REFERENCE

No.	Author	Title, etc
1	J. Day D.K. Thomas	Polysulphide sealants. RAE Technical Report 75104 (1975)

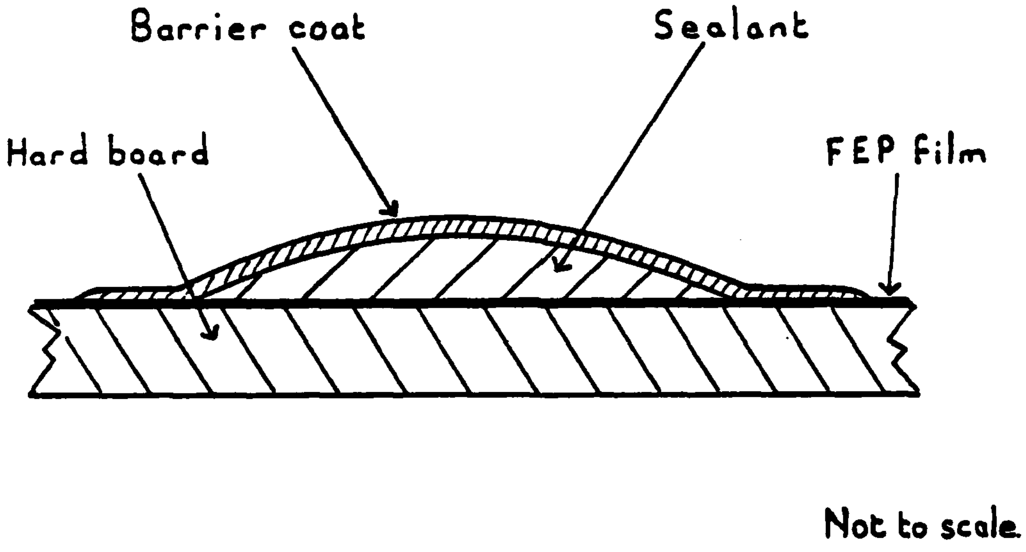

Fig 1 Cross section of a barrier coated test specimen for determination of cure

Fig 2

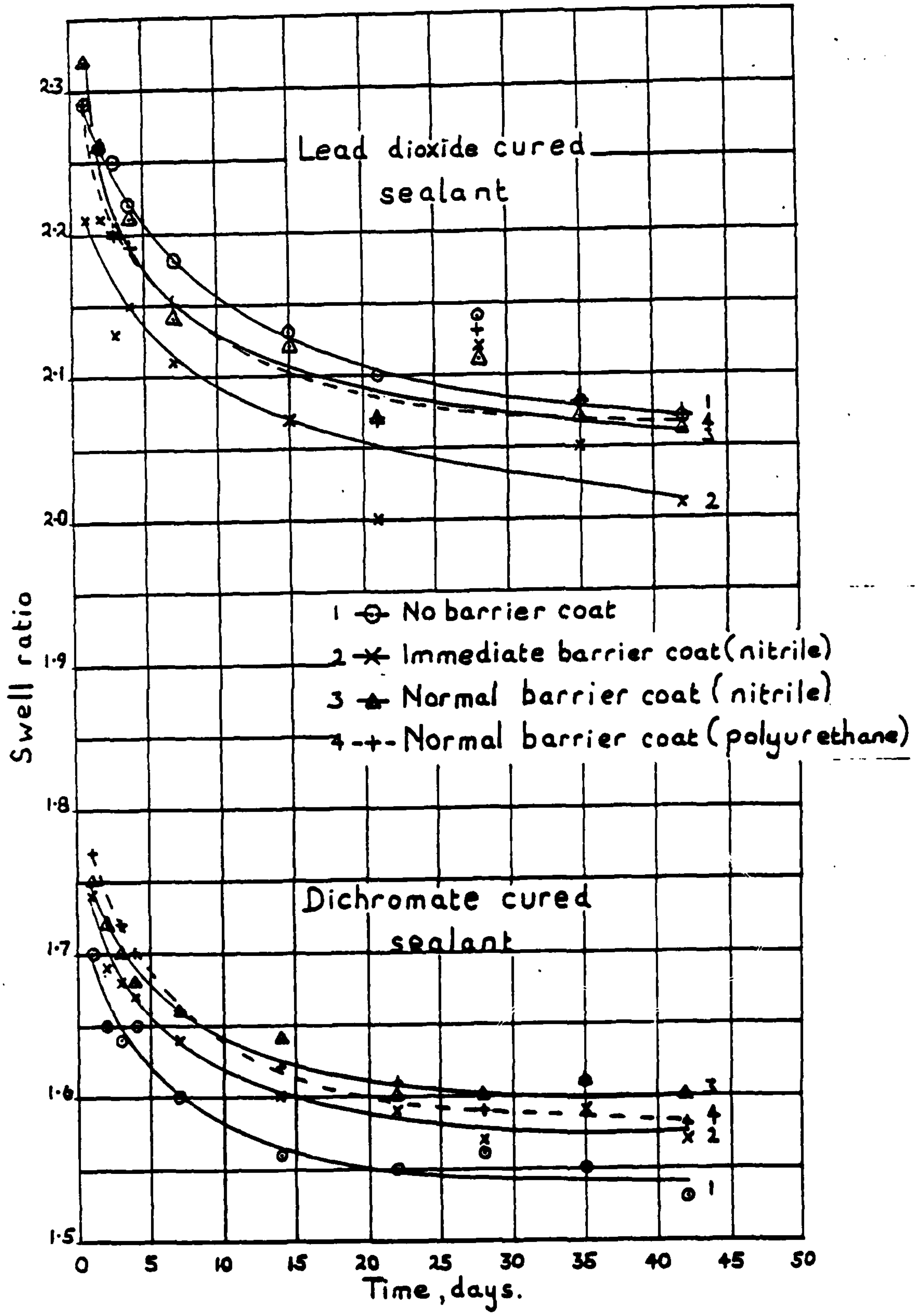

Fig 2 Swell ratios of uncoated and barrier coated sealants

Fig 2a

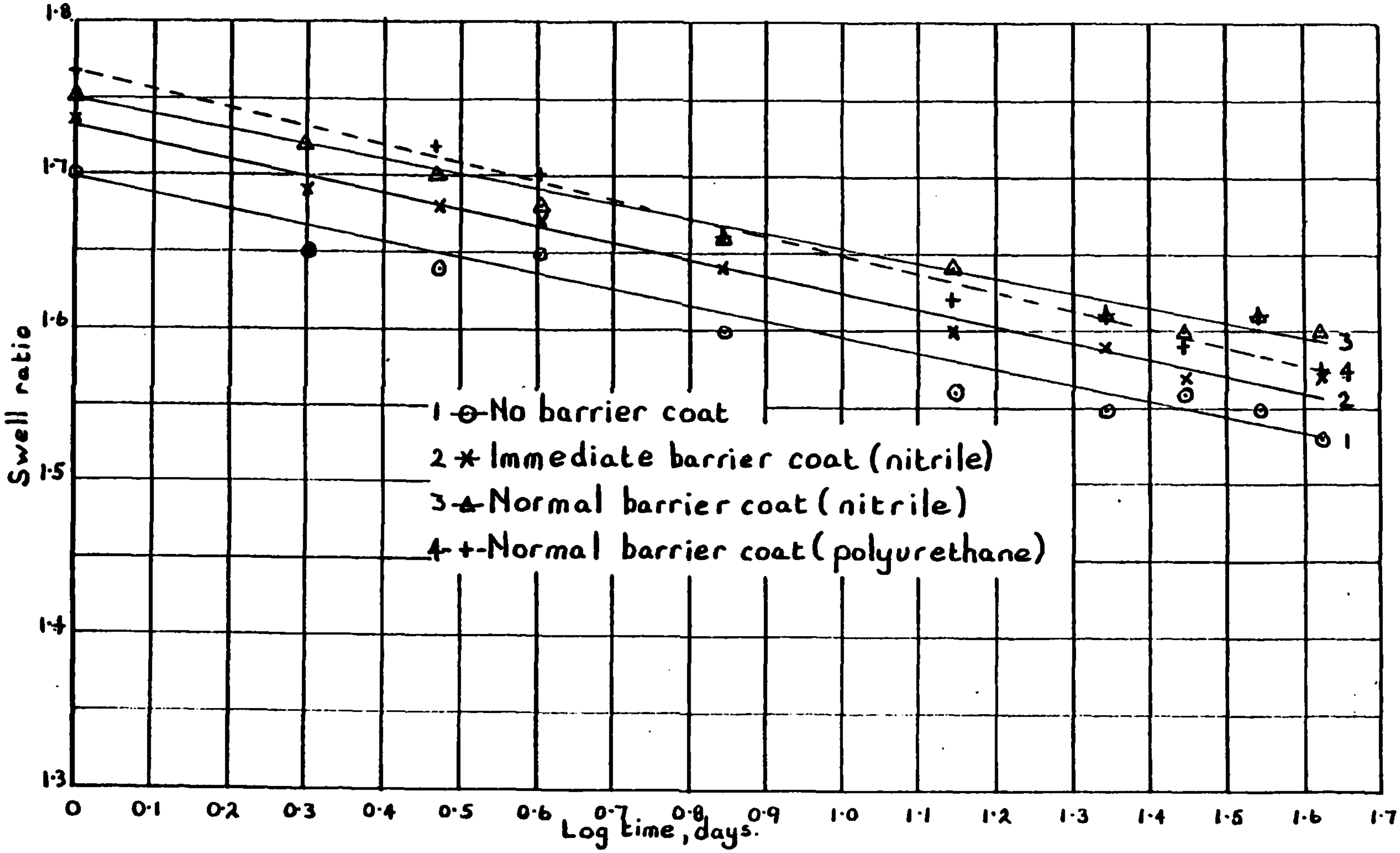

Fig 2a Swell ratios of uncoated and barrier coated dichromate cured sealant

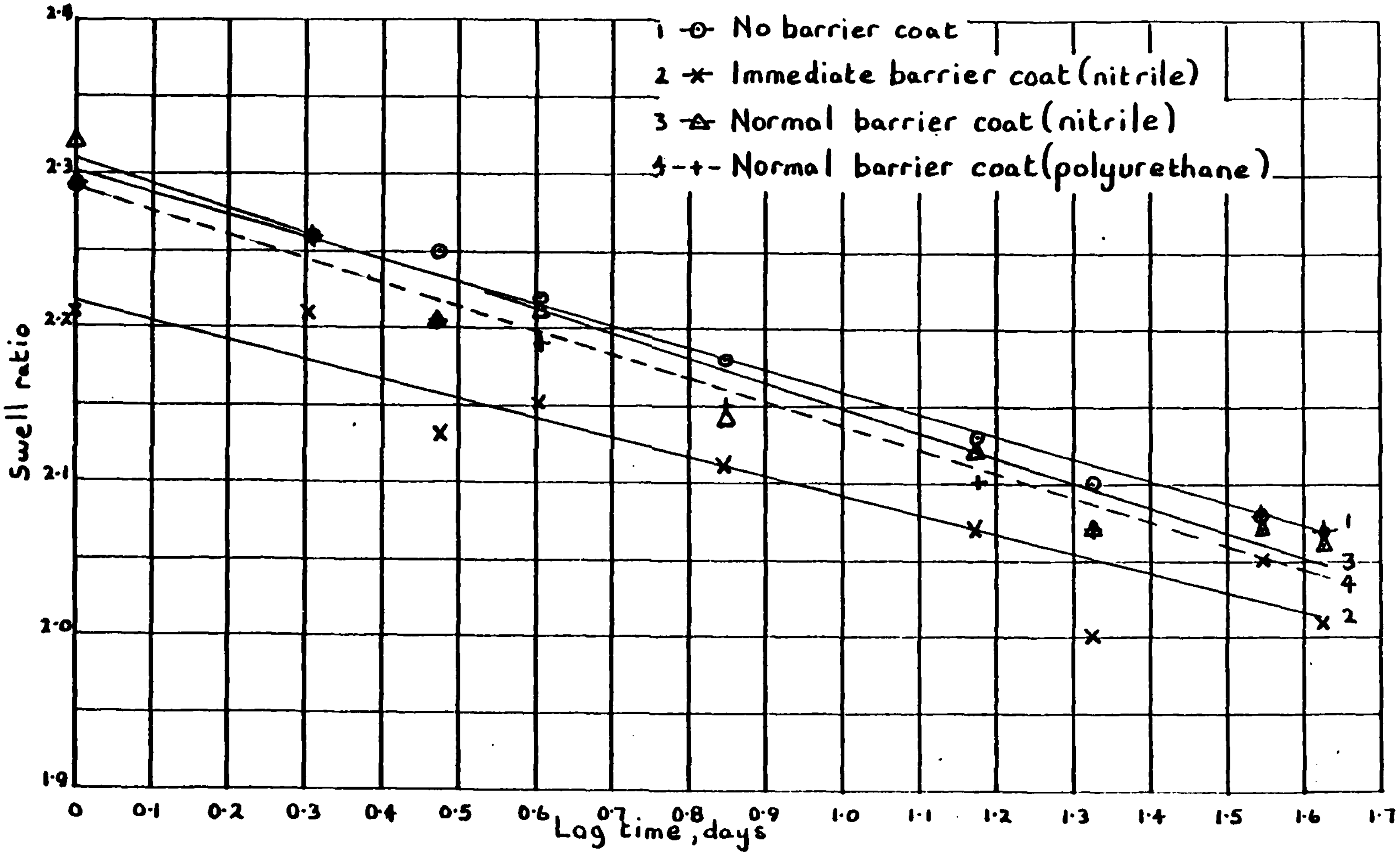

Fig 2b Swell ratios of uncoated and barrier coated lead dioxide cured sealant

Fig 3

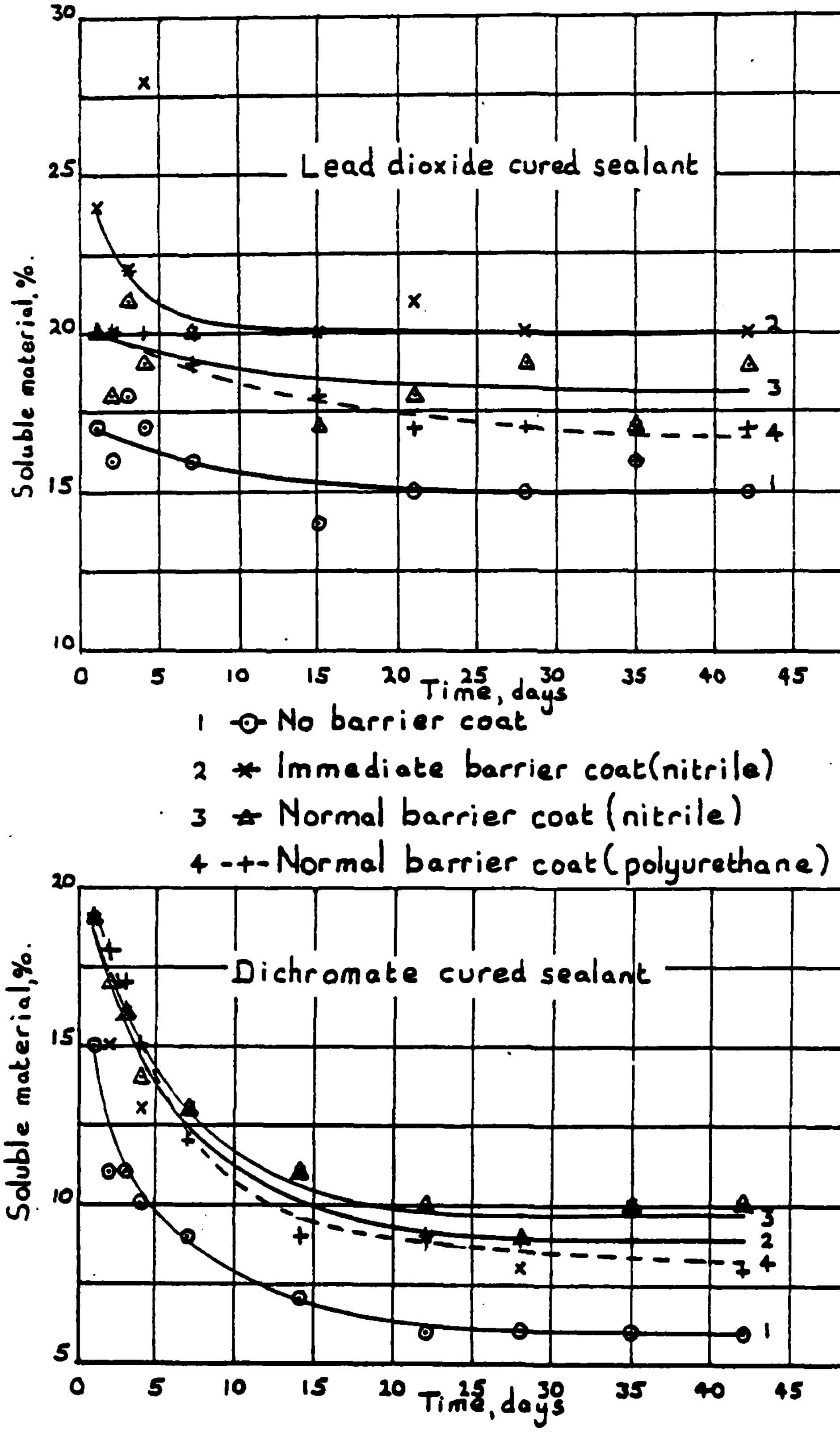

Fig 3 Percentage of soluble material in uncoated and barrier coated sealants

Fig 4

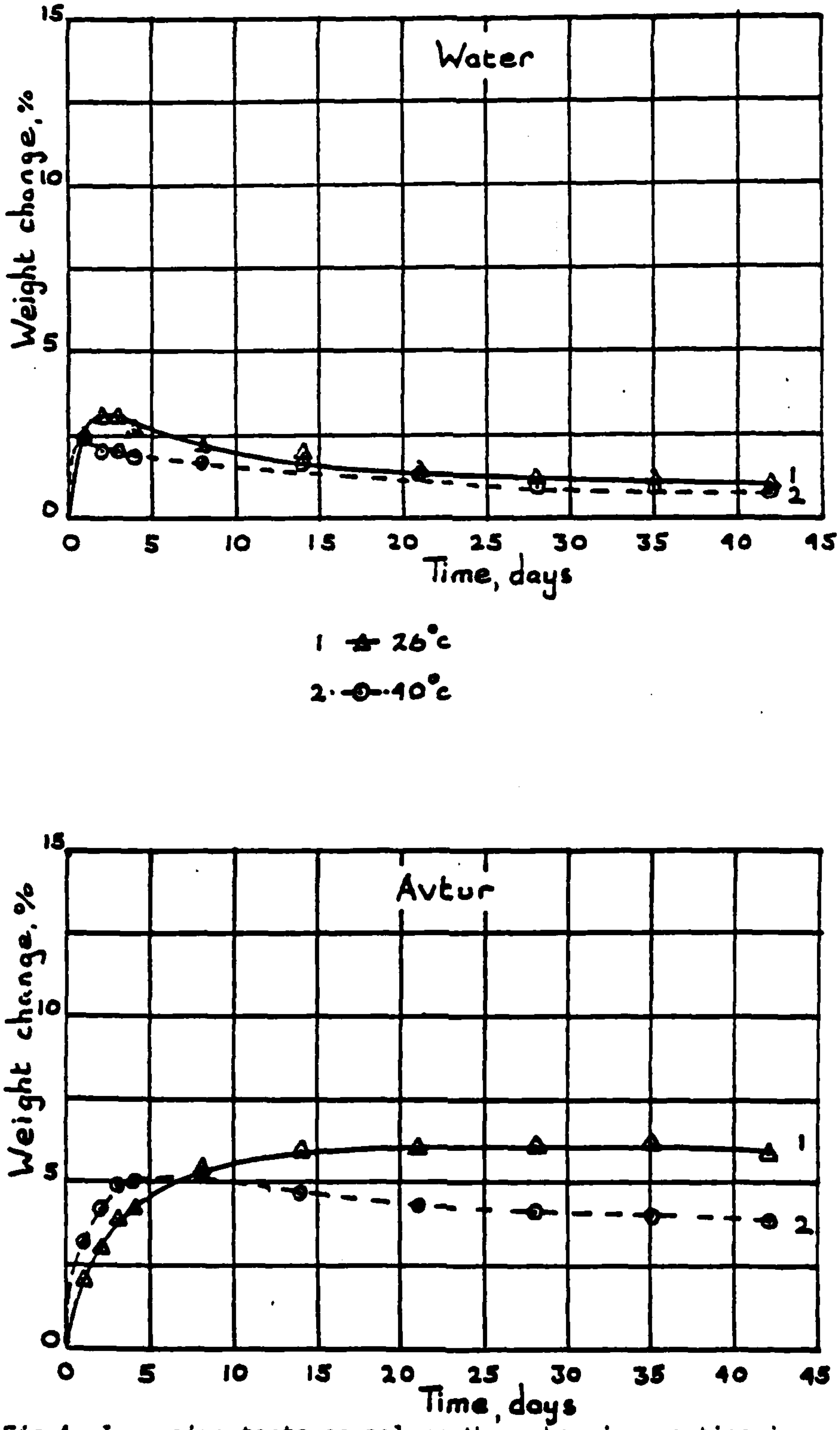

Fig 4 Immersion tests on polyurethane barrier coating in water and AVTUR (26°C and 40°C)

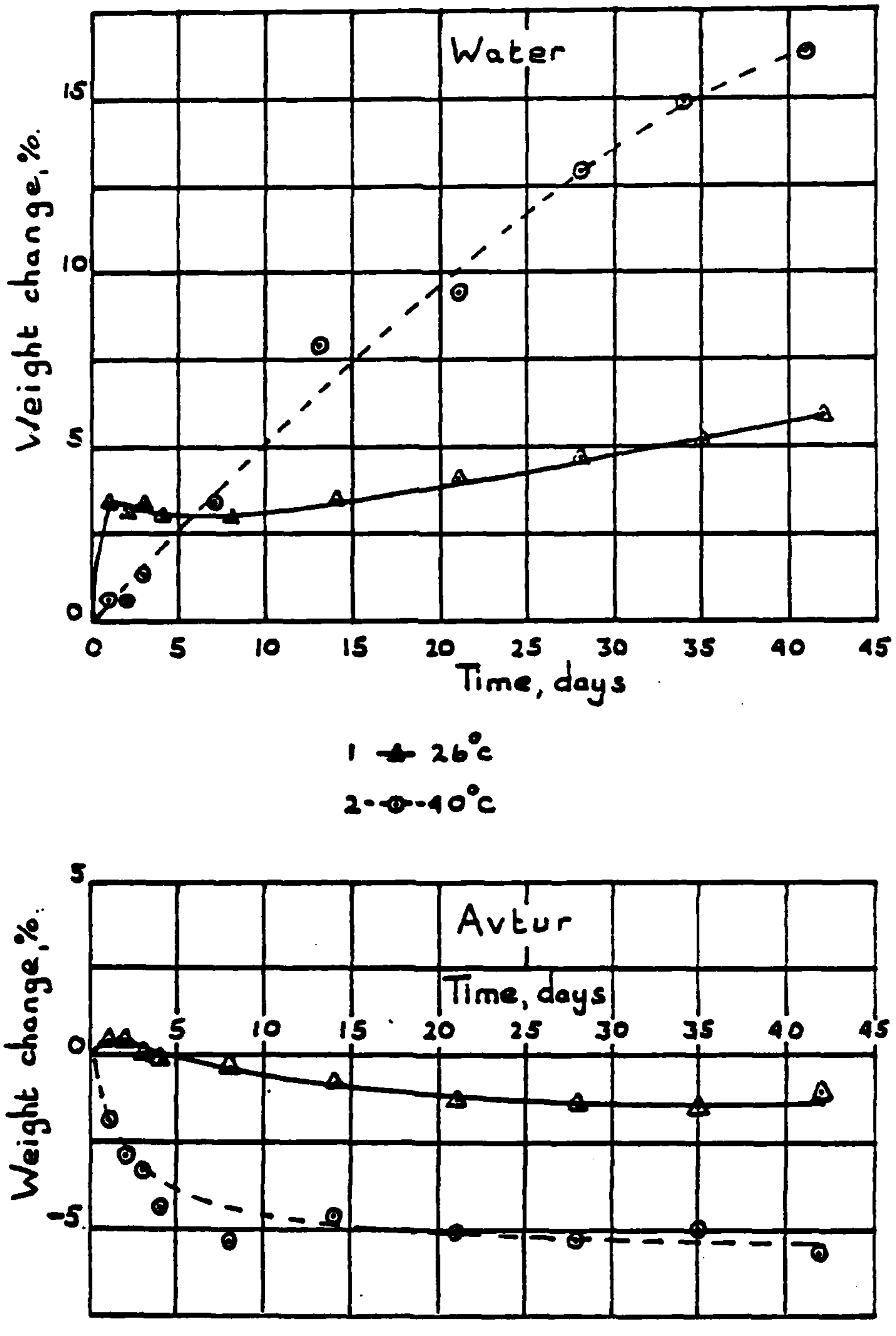

Fig 5 Immersion tests on nitrile barrier coating in water and AVTUR (26°C and 40°C)

Fig 6

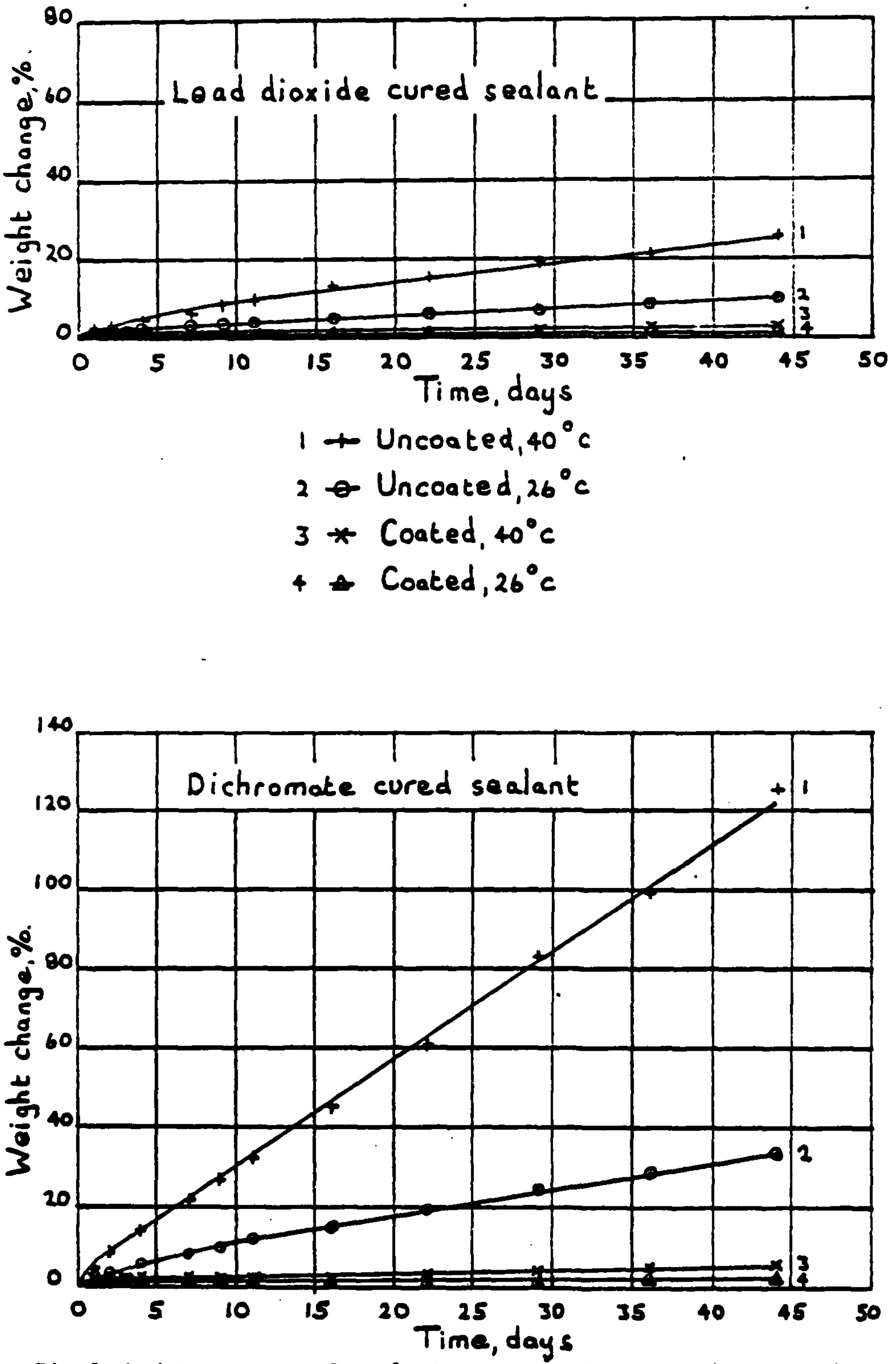

Fig 6 Weight change of sealants, uncoated and barrier coated with polyurethane, immersed in water at 26°C and 40°C

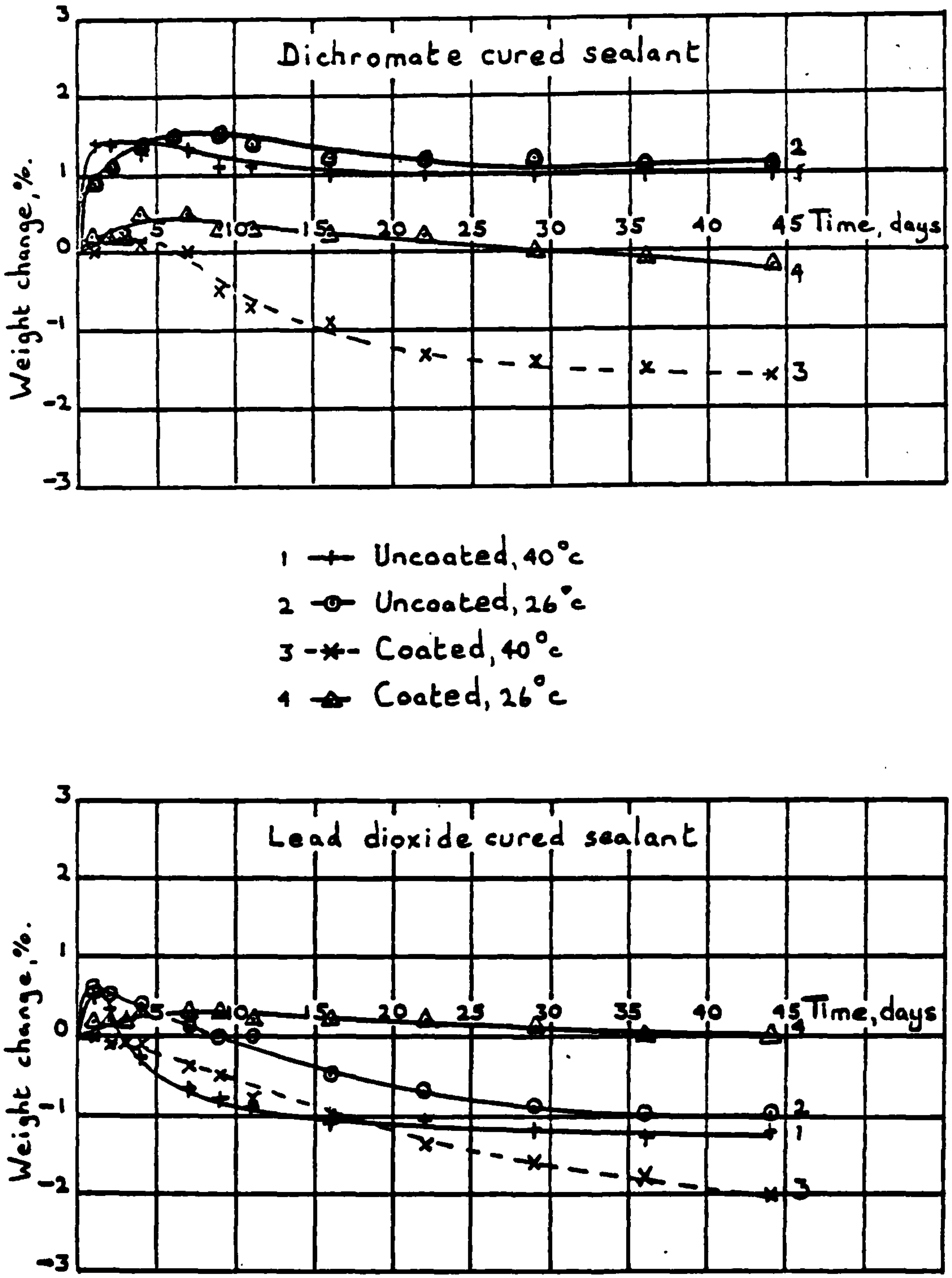

Fig 8 Weight change of sealants, uncoated and barrier coated with polyurethane, immersed in AVTUR at 26°C and 40°C

Fig 7

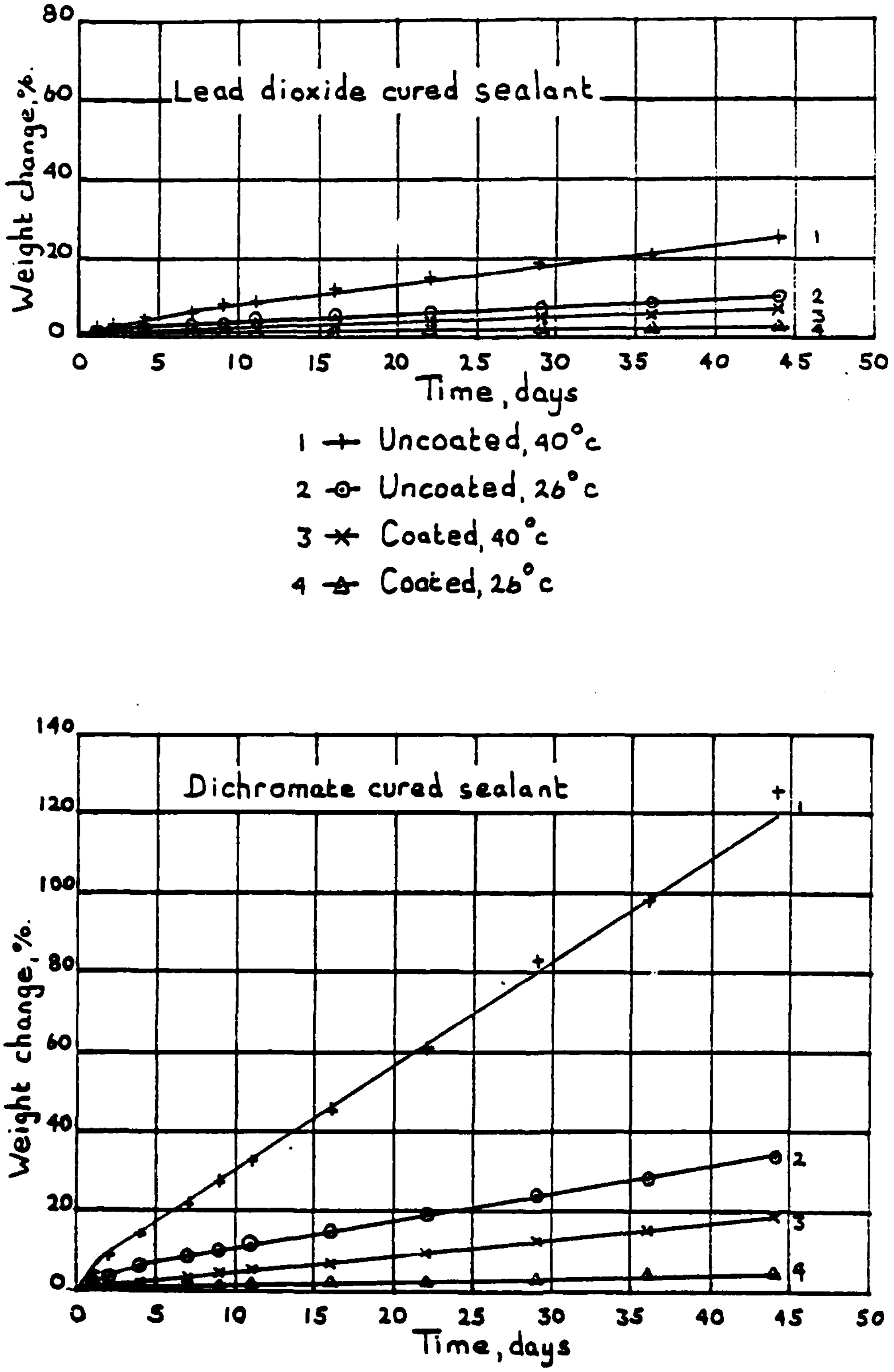

Fig 7 Weight change of sealants, uncoated and barrier coated with nitrile, immersed in water at 26°C and 40°C

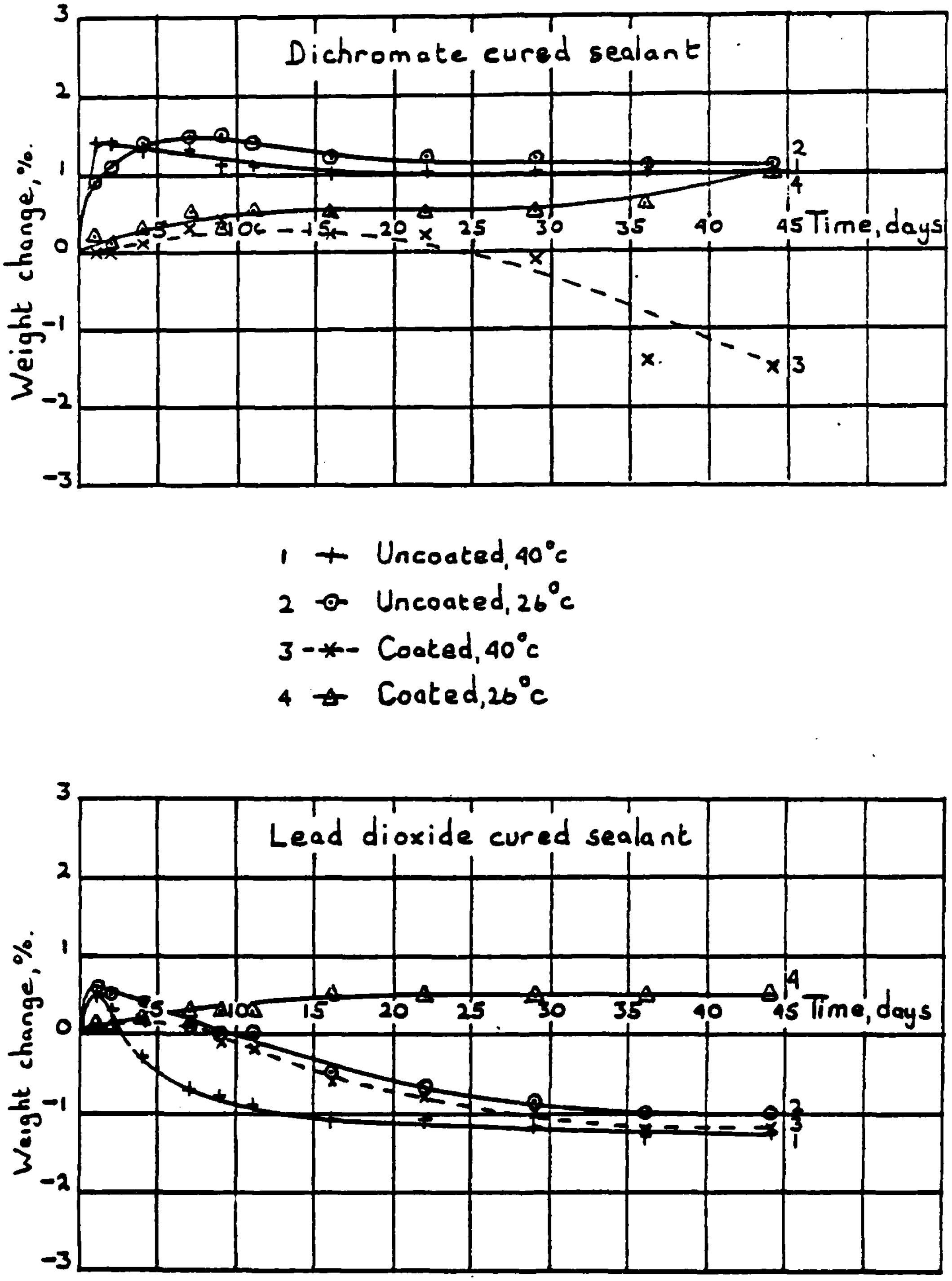

Fig 9 Weight change of sealants, uncoated and barrier coated with nitrile, immersed in AVTUR at 26°C and 40°C

REPORT DOCUMENTATION PAGE

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Polysulphide sealants. Cure rate. Fluid resistance. Nitrile and polyurethane barrier coats.

17\. Abstract

Two commercial barrier coating materials based on polyurethane and nitrile (acrylonitrile-butadiene copolymer) were used in conjunction with two of the most commonly used integral fuel tank polysulphide sealants (catalysed with either dichromate or lead dioxide).

The rate and degree of cure were only slightly reduced when either barrier coating was applied. Neither coating appeared to offer any improvement in fuel resistance but significant improvements were noted in the resistance of barrier coated sealants to the ingress of water. After 44 days at 40°C water uptake of dichromate cured sealant was reduced from 126% to 6% by barrier coating with polyurethane. A similar effect was noted with the lead dioxide cured sealant although not to the same degree since this material is inherently more resistant to water than the dichromate cured sealant. There is some doubt about the long term performance of the polyurethane barrier coating as samples appeared to embrittle on ageing.

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