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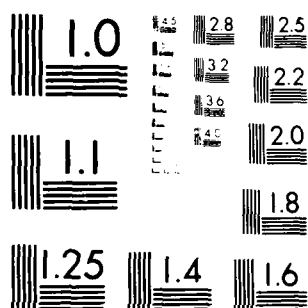
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ROYAL AIRCRAFT ESTABLISHMENT

OZONE AGEING OF SILICONE RUBBER AND THE EFFECTS OF ANTI-OXIDANTS
ON THE OZONE AGEING OF NITRILE RUBBER

by

S. T. Smith

April 1981

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OZONE AGEING OF SILICONE RUBBER AND THE EFFECTS OF ANTI-OXIDANTS
ON THE OZONE AGEING OF NITRILE RUBBER

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SUMMARY

Work done by others suggested that a rapid loss of physical properties could occur in silicone rubbers when subjected to high concentrations of ozone. Experiments have now been carried out using a Hampden P3 C6 ozone cabinet to evaluate the significance of this evidence when the material is used in the face masks worn by RAF air-crews at high altitudes, where the ozone concentration can reach relatively high levels. No loss of physical properties was found over the duration of the experiment.

The effect of ozone attack on nitrile rubber was also investigated. The effectiveness of four anti-oxidants used as anti-ozonants at an ozone concentration of 50 pphm (parts per hundred million) was studied together with a commercial nitrile rubber seal material. It was found that the anti-oxidants were effective anti-ozonants when compared with the unprotected rubber, whereas the commercial formulation had relatively poor resistance to ozone. The effect of varying the tensile strain applied to the samples was also considered and indicated that in general a lower strain resulted in a smaller drop in physical properties. The effect was not very marked. ←

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1 INTRODUCTION

Originally RAF air crews of non-pressurised, high altitude aircraft were equipped with natural rubber oxygen masks. The use of natural rubber in the face masks became a cause for major concern due to the dermatitis it produced when in contact with the skin. An alternative to natural rubber was sought by the RAE and found in the form of silicone rubber. This rubber was shown not to cause mask dermatitis when in contact with the face, and had the added advantage of being ozone resistant. Natural rubber masks were found to have comparatively short useful lives due to the effects of ozone around areas of high strain such as across the bridge of the nose and the fold of the face seal. Silicone rubber had the added bonus of being more aesthetically pleasing than the all black natural rubber.

However, in 1976 L.S. Fel'dshtein, L.E. Doll', V.G. Muradora and L.G. Angert reported rapid changes in the physical properties of silicone rubbers subjected to high concentrations of ozone¹. To clarify the situation it was decided to study the effects of long term exposure of the mask material to ozone at a level of concentration appropriate to high altitude flying².

Attack by ozone becomes a problem when one considers fluid systems in aircraft. Seals are usually elastomeric and many of them are made from nitrile rubbers, which resist attack by fuels and hydraulic fluids based on mineral oil (this is purely a military use as the hydraulic fluids used in civil aircraft attack nitrile rubbers). In general a fluid seal will have part of its surface exposed to air and its ozone resistance must therefore be taken into account. Nitrile rubbers are not ozone resistant and will tend to crack at relatively low tensile strains and ozone concentrations. The effectiveness of a range of anti-oxidants used as anti-ozonants in nitrile rubbers has been studied and also the performance of a commercial formulation based on nitrile rubber commercially used for fluid seals in aircraft.

2 EXPERIMENTAL DETAILS

The experimental details are given below under appropriate headings.

2.1 Materials

The mask material is a commercial product based on methyl-vinyl-silicone.

Four anti-oxidants were used in the tests on nitrile rubber. Two of these were commercial products; PBN (phenyl β naphthylamine) and TMQ (Poly 2, 2, 4 - trimethyl - 1, 2 - dihydroquinoline); and two were RAE polymeric anti-oxidants, BQ/PPD (benzoquinone/para-phenylene diamine reaction product) and BQ/PAD (benzoquinone/para-amino diphenylamine reaction product).

The anti-oxidants were present in concentrations of 2.0% and 0.5% of the weight of polymer in the mix. A medium nitrile rubber (Breon 1042) was used. The formulation contained 50 parts of FEF black and five parts of propylene adipate and was cured with a semi EV system. Tests were also carried out on the nitrile rubber containing no anti-oxidant and on a commercial seal material.

2.2 Compounding

100 g of silicone rubber were milled on a small 300 mm × 100 mm mill to break down the crêpe hardening that occurs in the raw stock. 4 g of a peroxide curing agent (Varox) 2, 5 - dimethyl - 2, 5 - (ditertiary butyl peroxy) hexane, were then added to the rubber and the two were milled for a period of time sufficient to give good dispersion.

The rubber was then cured in a hot press at 160°C for 30 min and post cured at 200°C for 4 h.

The nitrile rubbers were supplied in a pre-mixed form and therefore only required to be weighed out (65 g per sheet) and milled into a usable form before being press cured. The curing was carried out at 160°C for 40 min.

2.3 Test pieces

Tensile measurements were made on dumbbells cut using a BS type 2 die from the 2 mm sheets of silicone rubber. Crescent test pieces cut with an ASTM D624 die A were also taken from the silicone rubber sheets for tear strength measurements.

Dumbbells of the type used for the silicone rubber were also used for the tensile measurements on the nitrile rubbers.

2.4 Ozone exposure

The test specimens were exposed to ozone in a P3 C6 Hampden automatic ozone cabinet³. This cabinet enables ozone concentration, temperature and humidity to be automatically controlled within close limits.

The temperature control in the P3 C6 operates over a range from 25°C to 60°C (±1°C). The cabinet was kept at a standard test temperature of 30°C for all the experiments as recommended in BS 903 part A23. Ozone concentration could be varied over a range from 0 to 500 pphm of air (±5%). A value of 400 pphm was selected for the silicone rubber experiments (see Introduction) to simulate atmospheric conditions at high altitude². Due to the high susceptibility of nitrile rubbers to ozone attack a much lower level of 50 pphm was selected so as to ensure that ozone attack occurred at a reasonable rate.

The humidity control system was not used in either set of experiments. The rate of air flow through the cabinet could be varied between 50 and 500 l/min and was set at 100 l/min in both sets of experiments. In the P3 C6 ozone is generated by means of an ultra violet lamp and is monitored by means of an electro-chemical cell.

The silicone rubber test pieces were mounted in a Hampden mobile test piece carrier and positioned in the ozone cabinet. They were not strained in any way and were made to circulate in the ozone atmosphere. Sets of three test pieces were removed after appropriate intervals of time. When all the samples had been removed they were tested on a 'Monsanto' Tensometer 500 for tensile strength, elongation at break, modulus at 100% elongation and tear strength.

A solution made from Hypalon dissolved in methyl-ethyl-ketone and toluene was used to coat the two ends of each nitrile rubber test piece. This was to protect the areas of rubber in contact with the carrier grips.

The nitrile rubber test pieces were then mounted in the mobile test carrier under a 30% tensile strain and exposed to the ozone atmosphere at 50 pphm. The procedure was the same as for silicone rubber but on a much shorter time scale. After the first run had been completed the process was repeated at 20% tensile strain.

The silicone and the nitrile rubbers were viewed under a microscope (at a magnification of $\times 70$) to observe any cracks which occurred due to ozone attack. This was carried out before tensile tests were undertaken on the tensometer.

3 RESULTS AND DISCUSSION

3.1 Cracks

The normal method for determining the degree of ozone attack is by examination of the cracks found in the test pieces⁴. In vulcanisates such as the nitrile rubbers the ozone cannot penetrate to any appreciable depth beneath the surface and therefore ozone attack is restricted to the surface layer and appears in the form of small cracks which increase in size and depth with increased exposure. However silicone rubber has a high permeability with respect to gases and therefore ozone attack is unlikely to be confined to the surface. For this reason it was decided that examination of the cracks would not be a definitive way of correlating the degradation of the rubbers particularly in the case of silicone rubber. The samples were however studied under a microscope and as expected no cracks were found in any of the silicone rubber test pieces. But on examining the nitrile rubber samples it was found that even after only 2 h in the cabinet the cracks were too numerous to count with any degree of accuracy even in an area of 1 mm^2 .

3.2 Silicone rubber

In attempting to achieve rapid results, the Soviet scientists had used extremely high concentrations of ozone (up to 40000 pphm; all ozone concentrations are quoted in parts per hundred million for ease of comparison). They were able to achieve very significant changes in physical properties after tests of only 29 h.

The experiment carried out at the RAE used an ozone concentration of 400 pphm. The tensile results are recorded in Table 1a and graphically represented in Figs 1, 2 and 3. It can be seen from the results that over the 347 h of the experiment the methyl-vinyl-silicone used in the face masks suffered no loss in physical properties. A very slight change in colour was seen to take place and to become more noticeable with time but this was considered to be a bleaching effect. Each sample was observed under a microscope at a magnification of $\times 70$ and as previously stated no cracks were found. A slight but insignificant increase in tensile strength was found but no change was observed in the other properties. The results of the tear strength tests are recorded in Table 2a and shown graphically in Fig 4.

Table 1a

Physical properties of silicone rubber after different periods of exposure ($O_3 = 400$ pphm)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	640	9.9	1.2
65	645	10.5	1.2
138	655	10.5	1.2
192	635	10.5	1.4
248	640	10.4	1.2
298	630	10.7	1.2
347	640	10.8	1.2

Table 2a

Tear strength of silicone rubber after different periods of exposure ($O_3 = 400$ pphm)

Time in ozone (h)	0	65	138	192	248	298	347
Tear strength (kN/m)	21.5	20.3	21.0	20.0	22.2	20.5	22.0

3.3 Nitrile rubber

Nitrile rubber can be considered to be quite permeable to molecular oxygen (O_2). For this reason oxidation of the rubber can take place throughout its bulk. Anti-oxidants operate by combining with the oxygen and stabilising it chemically. They are required to be fairly immobile in the nitrile rubber. The RAE polymeric anti-oxidants were developed to have increased thermal stability over commercial products and to be less soluble in fluids especially the hydraulic fluids used in RAF aircraft.

It was decided to study their capabilities as anti-ozonants even though lack of mobility might be expected to detract from their effectiveness in this respect as ozone attacks at the surface. Two commercial materials were included for comparison. The results of the ozone exposure tests at 50 pphm are recorded in Tables 1 to 21, and graphically in Figs 5 to 22. From the graphs it is evident that all the rubber samples experienced a relatively rapid drop in tensile strength and elongation at break in the first 10 h. This is followed by a slow but noticeable levelling off until the decline is almost halted. The 'plateau' is maintained until the sample is almost at breaking point (the recorded results are of the first 40 h but three samples of each anti-oxidant formulation were allowed to run to failure which occurred at approximately 80 h; the same was true for the unprotected rubber).

The results show that all the vulcanisates were affected in the same way by the ozone, the graphs follow a characteristic curve of ozone attack on rubber. Table 1 is

a representation of the retention of physical properties of the rubbers after 40 h of ozone exposure.

From the table it can be seen that, in the case of the TMQ formulation, there is no significant difference in the retention of tensile strength and elongation at break at 20% and 30% strain. This is seen with both the 0.5% and the 2.0% concentrations; the same is true when comparing the 0.5% with the 2.0% concentration for the tensile strength. However the elongation at break and the M100 show a slight increase in retention with the 2.0% concentration compared with the 0.5%. The retention of tensile strength at the 2.0% and 0.5% concentrations was markedly better than that of the unprotected rubber. The elongation at break and M100 did not show a significant effect at 20%, though at 30% the M100 of TMQ showed a greater retention than the unprotected rubber.

The BQ/PPD formulation retained a greater proportion of its physical properties at 20% strain than at 30% strain in all cases except for the elongation at break for 2.0% of anti-oxidant (here the change was negligible) and the M100 at 2.0% concentration which actually showed an increase to a level above the initial value. There was no significant difference between the 0.5% and the 2.0% concentrations for 20% strain but a slight improvement was seen at 2.0% for the 30% strain. Again the retention of tensile strength of the protected rubber was far better than that of the unprotected, but a reverse in the trend could be found with elongation at break. The M100s showed no significant change.

The results for BQ/PAD show a negligible strain effect on both tensile strength and modulus. However the high strain produced a bigger reduction in elongation. When comparing the 0.5% and 2.0% concentrations, both the tensile strength and the elongation at break show an improved retention with higher concentration. The M100s show a reverse to this trend.

For the PBN formulation it can be seen that in all cases the test pieces strained to 20% retained a significantly higher proportion of their physical properties than those strained to 30%. However when considering the difference in retention between the 0.5% and 2.0% concentrations, the elongation at break at 2.0% is vastly superior to that at 0.5% but the tensile strength and M100 show a slight decrease in retention at 2.0% concentration when compared with 0.5%. PBN at 2.0% concentration seems to be superior to the unprotected rubber in retention of physical properties in every case. With the 0.5% concentration the tensile strength and M100 are superior but the elongation at break is markedly lower at 0.5% than for the unprotected rubber.

The unprotected rubber itself shows a greater degree of retention of physical properties at 20% strain than at 30% strain. It fared quite favourably compared with the protected rubbers in retention of elongation at break and M100 at 20% strain but showed a far lower retention of tensile strength.

The commercial formulation showed slightly better retention of tensile strength and elongation at break at 30% strain than at 20% strain. It was not possible to give M100 result as the elongation was less than 100% before 40 h were reached. The commercial formulation fared considerably worse than all the other rubber formulations.

All the anti-oxidants have a marked effect on retention of tensile strength, BQ/PPD and PBN are the most effective at 20% strain whereas at the 30% strain level BQ/PAD is marginally the best. There is a much smaller effect on elongation at break, only PBN at the 2% concentration level showing any benefit. No significant difference can be found in the modulus at 20% strain except in the BQ/PPD formulation at both concentrations where at 2.0% there is actually an increase in modulus. At 30% strain the anti-oxidant formulations show better retention of modulus than the unprotected rubber the best being TMQ at 0.5% and again BQ/PPD at 2.0% showing a marked increase in modulus.

4 CONCLUSIONS

From the results of the experiments carried out we can arrive at the following conclusions:

- (1) Methyl-vinyl-silicone rubber is not affected by ozone when subjected to concentrations of 400 pphm over prolonged periods of time.
- (2) Nitrile rubber containing the anti-oxidants TMQ, BQ/PPD, BQ/PAD and PBN has a higher resistance to ozone than nitrile rubber containing no anti-oxidant.
- (3) In most cases by reducing the tensile strain on the test pieces a smaller loss in the physical properties is produced in the rubber over a particular time interval.
- (4) The nitrile rubber containing the anti-oxidants and the unprotected rubber were more resistant to attack by ozone than the commercial seal material (also based on a nitrile rubber).
- (5) The anti-oxidants do seem to act as anti-ozonants in nitrile rubber, but even so the degradation of the rubber due to ozone attack is still rapid at concentrations of 50 pphm when strained to levels of 20% and 30%.
- (6) There is virtually no difference between the anti-oxidants as anti-ozonants, however the PBN formulation seems to be marginally better in retaining elongation at the 2% level.

Table 1

RETENTION OF PHYSICAL PROPERTIES FOR NITRILE RUBBER
AFTER 40 h IN OZONE AT A CONCENTRATION OF 50 pphm

Strain Anti-oxidant	Tensile strength		Elongation at break		M100	
	20%	30%	20%	30%	20%	30%
0%	38%	23%	61%	50%	86%	57%
0.5% TMQ	52%	50%	51%	49%	84%	100%
0.5% BQ/PPD	60%	50%	48%	42%	100%	88%
0.5% BQ/PAD	48%	47%	56%	46%	88%	88%
0.5% PBN	61%	48%	48%	42%	84%	80%
2.0% TMQ	47%	49%	54%	57%	80%	77%
2.0% BQ/PPD	57%	44%	49%	50%	115%	125%
2.0% BQ/PAD	53%	52%	63%	58%	83%	83%
2.0% PBN	55%	46%	70%	64%	80%	75%
Commercial formulation	10%	13%	34%	37%	-	-

Table 2

PHYSICAL PROPERTIES OF NITRILE RUBBER CONTAINING TMQ
AT 0.5% CONCENTRATION (30% STRAIN)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	355	22.0	3.8
2	320	20.0	4.5
5	300	18.5	4.0
10	270	16.0	4.0
15	260	13.0	3.0
20	240	13.0	3.0
25	220	12.0	4.0
30	200	11.5	4.0
35	180	11.0	4.0
40	175	11.0	3.8

Table 3

PHYSICAL PROPERTIES OF NITRILE RUBBER CONTAINING TMQ
AT 0.5% CONCENTRATION (20% STRAIN)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	355	22.0	3.8
2	340	21.5	4.0
5	315	19.0	4.0
10	285	15.5	3.5
15	275	13.5	3.8
20	240	12.3	3.0
25	230	12.0	3.0
30	210	11.8	3.0
35	195	11.5	3.2
40	180	11.5	3.2

Table 4

PHYSICAL PROPERTIES OF NITRILE RUBBER CONTAINING TMO
AT 2.0% CONCENTRATION (30% STRAIN)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	370	22.3	3.5
2	350	21.0	3.5
5	320	17.8	4.0
10	300	17.0	3.5
15	280	14.5	4.0
20	260	12.7	2.7
25	220	11.0	3.0
30	240	11.0	3.0
35	220	10.8	3.0
40	210	11.0	2.7

Table 5

PHYSICAL PROPERTIES OF NITRILE RUBBER CONTAINING TMO
AT 2.0% CONCENTRATION (20% STRAIN)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	370	22.3	3.5
2	365	21.0	3.3
5	345	19.5	4.0
10	320	14.0	4.0
15	295	13.5	3.9
20	280	13.0	3.7
25	260	12.8	4.0
30	225	12.0	3.0
35	210	11.0	3.0
40	200	11.0	2.8

Table 6

PHYSICAL PROPERTIES OF NITRILE RUBBER CONTAINING BQ/PPD
AT 0.5% CONCENTRATION (30% STRAIN)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	325	21.0	4.0
2	290	18.5	4.5
5	280	16.7	4.0
10	260	15.2	4.0
15*	225	12.2	4.0
20	210	12.5	3.8
25	205	11.5	3.8
30	180	10.5	3.8
35	160	10.7	3.6
40	135	10.5	3.5

Table 7

PHYSICAL PROPERTIES OF NITRILE RUBBER CONTAINING BQ/PPD
AT 0.5% CONCENTRATION (20% STRAIN)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	325	21.0	4.0
2	310	20.5	4.5
5	290	19.2	4.5
10	270	15.0	4.3
15	245	13.7	4.2
20	230	12.2	4.2
25	210	13.0	4.0
30	185	13.0	4.0
35	180	13.0	4.0
40	155	12.7	4.0

Table 8

PHYSICAL PROPERTIES OF NITRILE RUBBER CONTAINING BQ/PPD
AT 2.0% CONCENTRATION (30% STRAIN)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	370	22.3	3.0
2	315	20.5	4.5
5	395	17.7	4.0
10	280	17.0	4.0
15	260	15.5	4.0
20	250	12.5	3.3
25	230	11.3	3.0
30	220	10.8	3.5
35	210	11.0	3.5
40	185	10.0	3.5

Table 9

PHYSICAL PROPERTIES OF NITRILE RUBBER CONTAINING BQ/PPD
AT 2.0% CONCENTRATION (20% STRAIN)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	370	22.3	3.0
2	360	21.5	4.8
5	315	19.2	4.6
10	300	16.5	4.6
15	275	15.0	4.5
20	265	13.2	4.5
25	230	13.0	4.0
30	220	13.2	4.0
35	205	13.2	3.8
40	180	12.5	4.0

Table 10

PHYSICAL PROPERTIES OF NITRILE RUBBER CONTAINING BQ/PAD
AT 0.5% CONCENTRATION (30% STRAIN)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	390	23.0	4.5
2	320	18.5	4.5
5	305	18.0	4.0
10	270	14.5	3.5
15	250	12.5	4.0
20	240	13.0	4.0
25	210	11.2	3.5
30	215	11.0	4.0
35	195	11.0	3.5
40	180	10.7	4.0

Table 11

PHYSICAL PROPERTIES OF NITRILE RUBBER CONTAINING BQ/PAD
AT 0.5% CONCENTRATION (20% STRAIN)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	390	23.0	4.5
2	345	22.0	3.5
5	315	19.7	3.0
10	295	16.2	3.7
15	270	13.7	4.0
20	260	13.0	4.0
25	250	12.2	3.5
30	245	12.2	3.7
35	240	11.7	4.0
40	220	11.0	4.0

Table 12

PHYSICAL PROPERTIES OF NITRILE RUBBER CONTAINING BQ/PAD
AT 2.0% CONCENTRATION (30% STRAIN)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	430	25.0	4.2
2	360	22.0	4.0
5	310	19.2	3.5
10	280	17.0	4.0
15	265	14.5	3.7
20	270	13.5	4.0
25	260	13.7	3.5
30	250	14.5	3.5
35	245	12.7	3.5
40	250	13.0	3.5

Table 13

PHYSICAL PROPERTIES OF NITRILE RUBBER CONTAINING BQ/PAD
AT 2.0% CONCENTRATION (20% STRAIN)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	430	25.0	4.2
2	385	23.2	4.0
5	355	19.2	4.0
10	325	16.7	4.0
15	305	15.5	4.0
20	280	15.0	3.7
25	275	14.2	3.2
30	275	13.5	3.5
35	280	13.2	3.5
40	270	13.2	3.5

Table 14

PHYSICAL PROPERTIES OF NITRILE RUBBER CONTAINING PBN
AT 0.5% CONCENTRATION (30% STRAIN)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	380	22.0	5.0
2	310	20.0	4.5
5	310	17.5	3.5
10	250	15.5	4.0
15	255	13.0	3.5
20	235	13.7	4.0
25	215	13.0	3.8
30	200	12.0	3.8
35	160	12.0	4.0
40	160	10.5	4.0

Table 15

PHYSICAL PROPERTIES OF NITRILE RUBBER CONTAINING PBN
AT 0.5% CONCENTRATION (20% STRAIN)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	380	22.0	5.0
2	360	21.0	5.0
5	330	20.5	4.5
10	310	18.5	4.0
15	285	16.2	4.0
20	260	15.0	4.5
25	240	14.2	3.7
30	230	13.7	4.0
35	220	13.5	4.0
40	185	13.5	4.2

Table 16

PHYSICAL PROPERTIES OF NITRILE RUBBER CONTAINING PBN
AT 2.0% CONCENTRATION (30% STRAIN)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	390	24.0	4.0
2	310	20.0	3.5
5	315	18.5	4.0
10	310	18.0	3.5
15	280	15.0	3.5
20	260	13.5	3.0
25	270	13.2	3.0
30	280	11.2	2.4
35	245	11.0	3.0
40	250	11.0	3.0

Table 17

PHYSICAL PROPERTIES OF NITRILE RUBBER CONTAINING PBN
AT 2.0% CONCENTRATION (20% STRAIN)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	390	24.0	4.0
2	340	23.0	3.5
5	335	21.2	3.2
10	320	20.0	3.0
15	300	18.0	4.0
20	300	16.0	3.5
25	310	15.5	3.5
30	280	14.2	3.2
35	275	14.0	3.0
40	275	13.2	3.2

Table 18

PHYSICAL PROPERTIES OF THE UNPROTECTED NITRILE RUBBER
(30% STRAIN)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	320	18.5	3.5
2	280	16.0	4.0
5	250	12.7	3.5
10	240	11.7	3.2
15	230	10.0	3.2
20	220	9.0	3.0
25	195	8.2	3.0
30	190	6.2	2.2
35	170	5.2	2.2
40	160	4.2	2.0

Table 19

PHYSICAL PROPERTIES OF THE UNPROTECTED NITRILE RUBBER
(20% STRAIN)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	320	18.5	3.5
2	300	17.2	4.0
5	285	14.5	3.2
10	265	13.0	3.2
15	250	11.5	3.2
20	255	10.7	2.5
25	225	9.7	2.7
30	225	9.0	2.7
35	210	8.2	2.5
40	195	7.0	3.0

Table 20

PHYSICAL PROPERTIES OF THE COMMERCIAL NITRILE RUBBER
FORMULATION (30% STRAIN)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	190	15.0	8.2
2	140	10.8	8.0
5	120	8.8	7.0
10	105	6.5	6.4
15	100	5.9	5.9
20	100	5.5	5.5
25	105	4.9	4.8
30	100	3.9	3.9
35	85	2.7	-
40	70	1.9	-

Table 21

PHYSICAL PROPERTIES OF THE COMMERCIAL NITRILE RUBBER
FORMULATION (20% STRAIN)

Time in ozone (h)	Elongation at break (%)	Tensile strength (MN/m ²)	M100 (MN/m ²)
0	190	15.0	8.2
2	140	9.0	7.0
5	130	9.7	6.4
10	120	6.0	5.2
15	110	4.6	4.4
20	105	3.6	3.5
25	100	2.8	2.8
30	95	2.6	-
35	75	1.7	-
40	60	1.5	-

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- | <u>No.</u> | <u>Author</u> | <u>Title, etc</u> |
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Fig 1

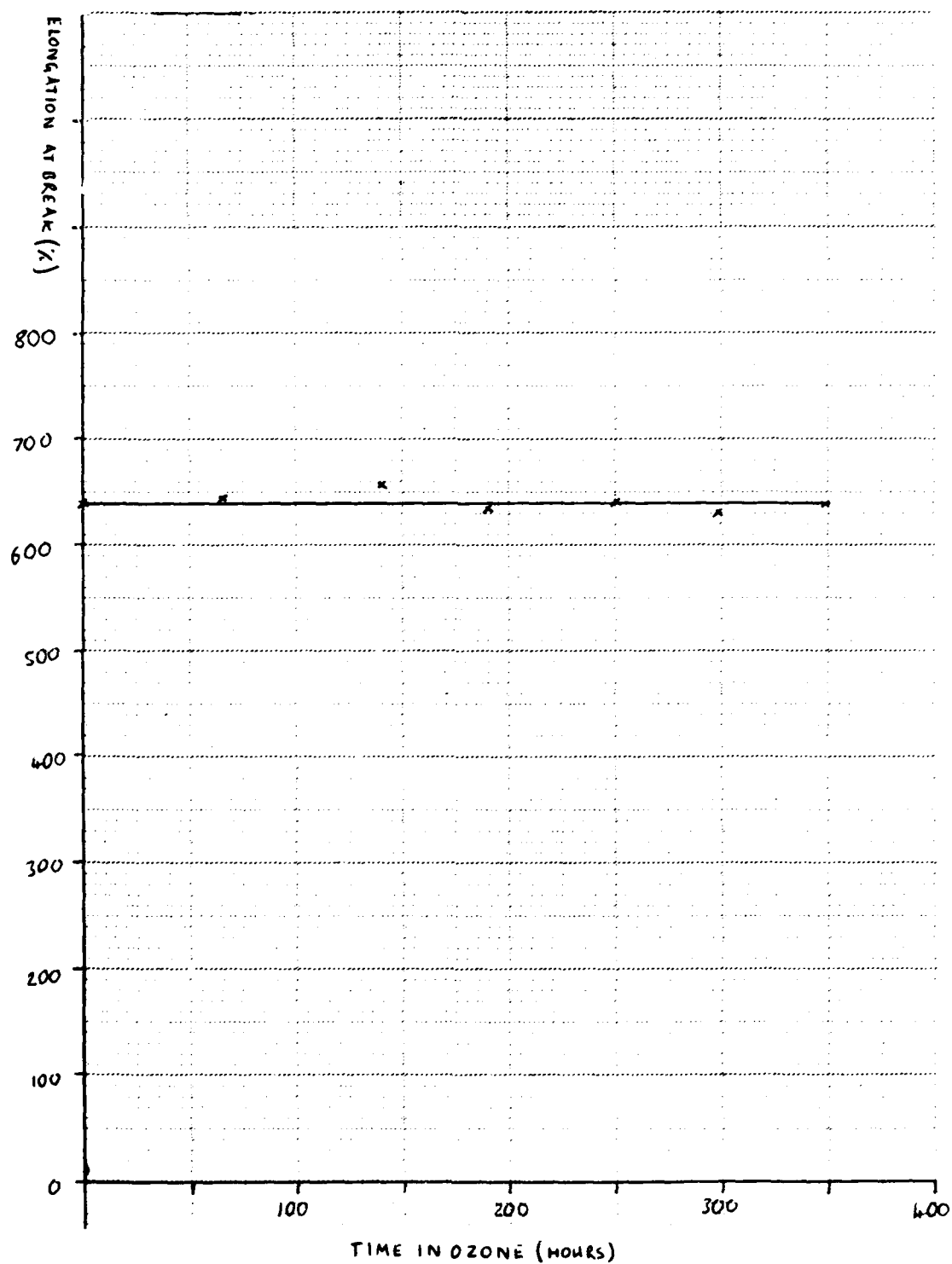


Fig 1 Elongation at break vs time in ozone for silicon rubber (400 ppm)

Fig 2

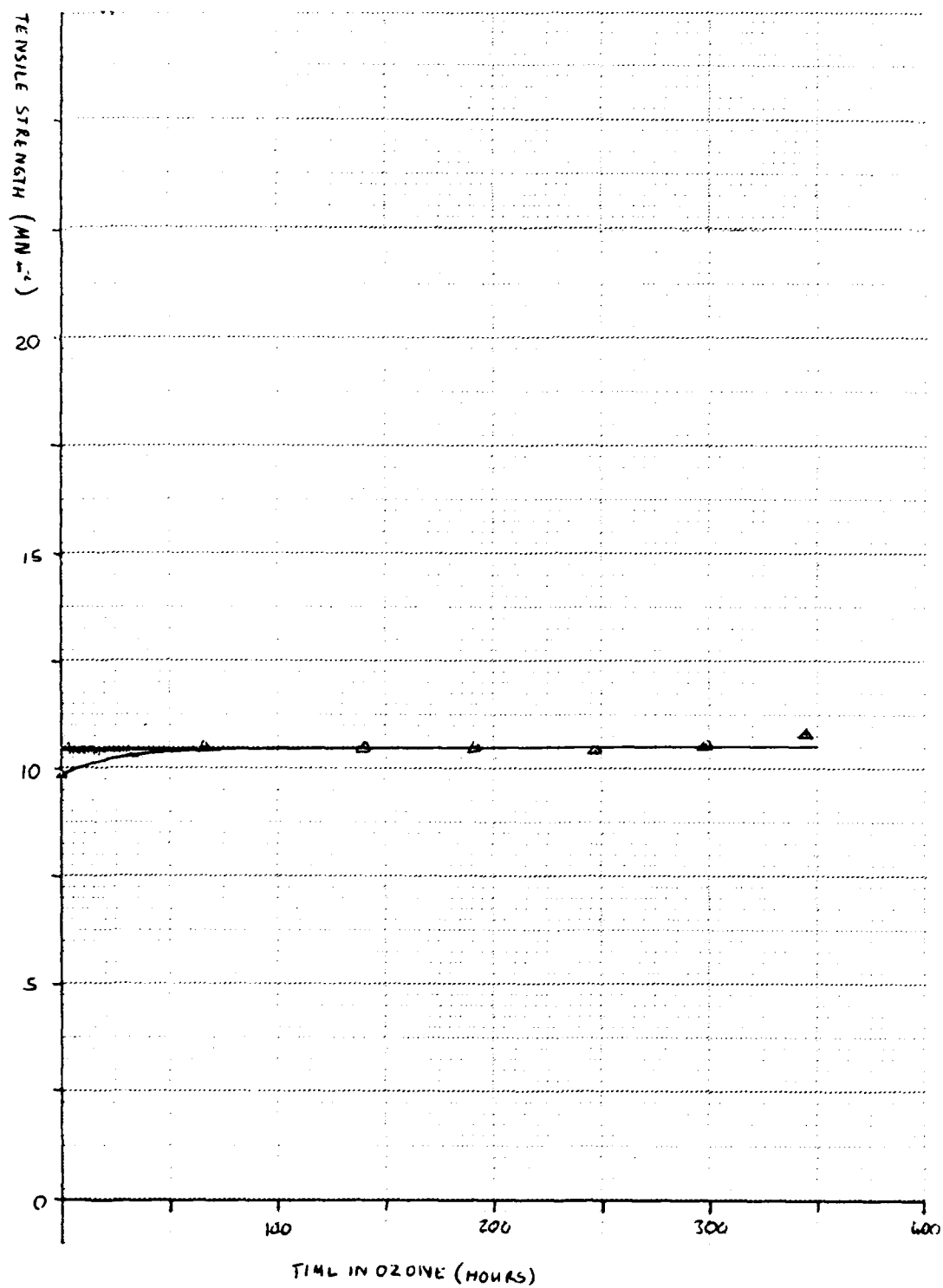


Fig 2 Tensile strength vs time in ozone for silicone rubber (400 ppm)

Fig 3

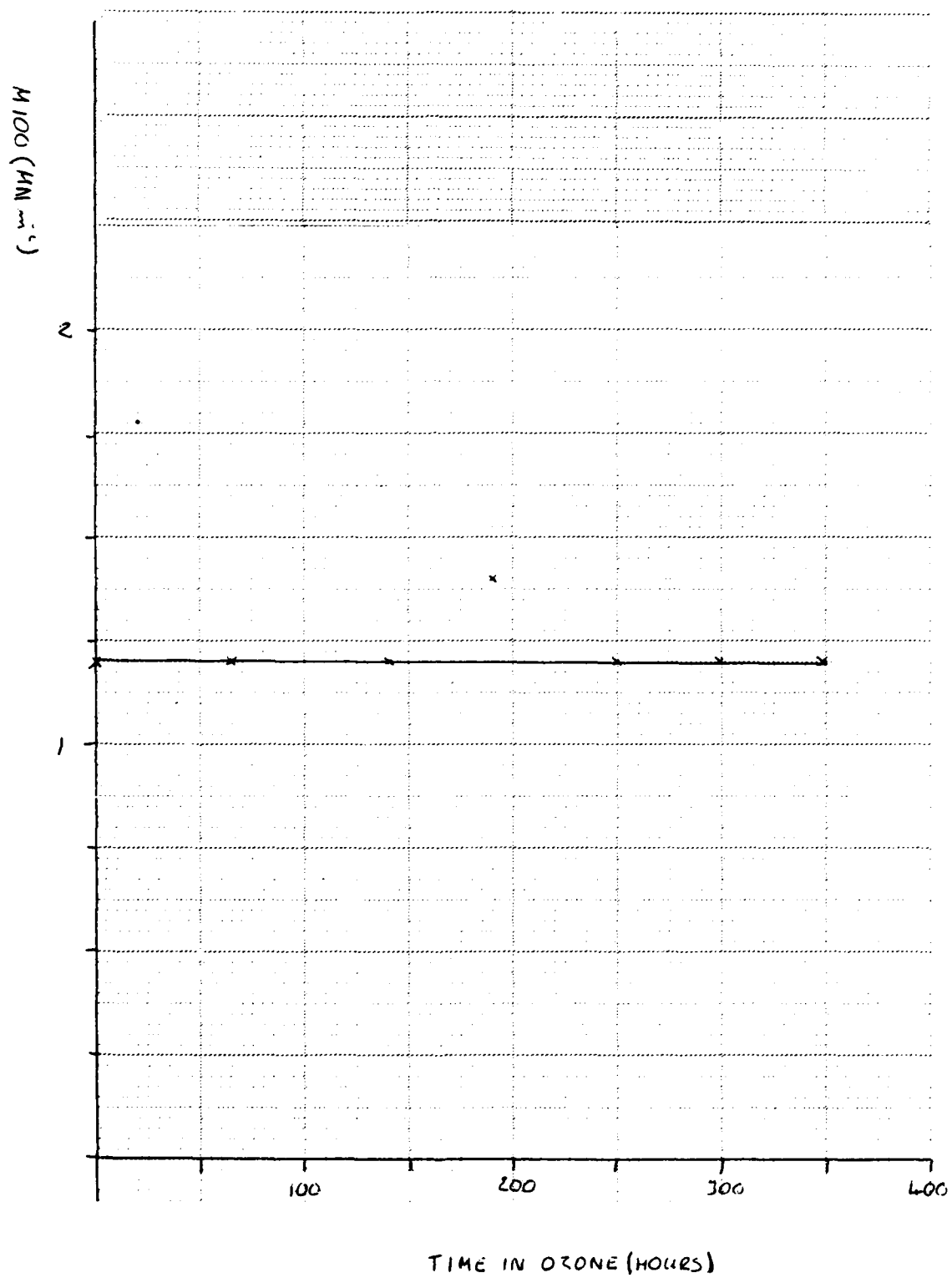


Fig 3 M100 vs time in ozone for silicone rubber (400 ppm)

Fig 4

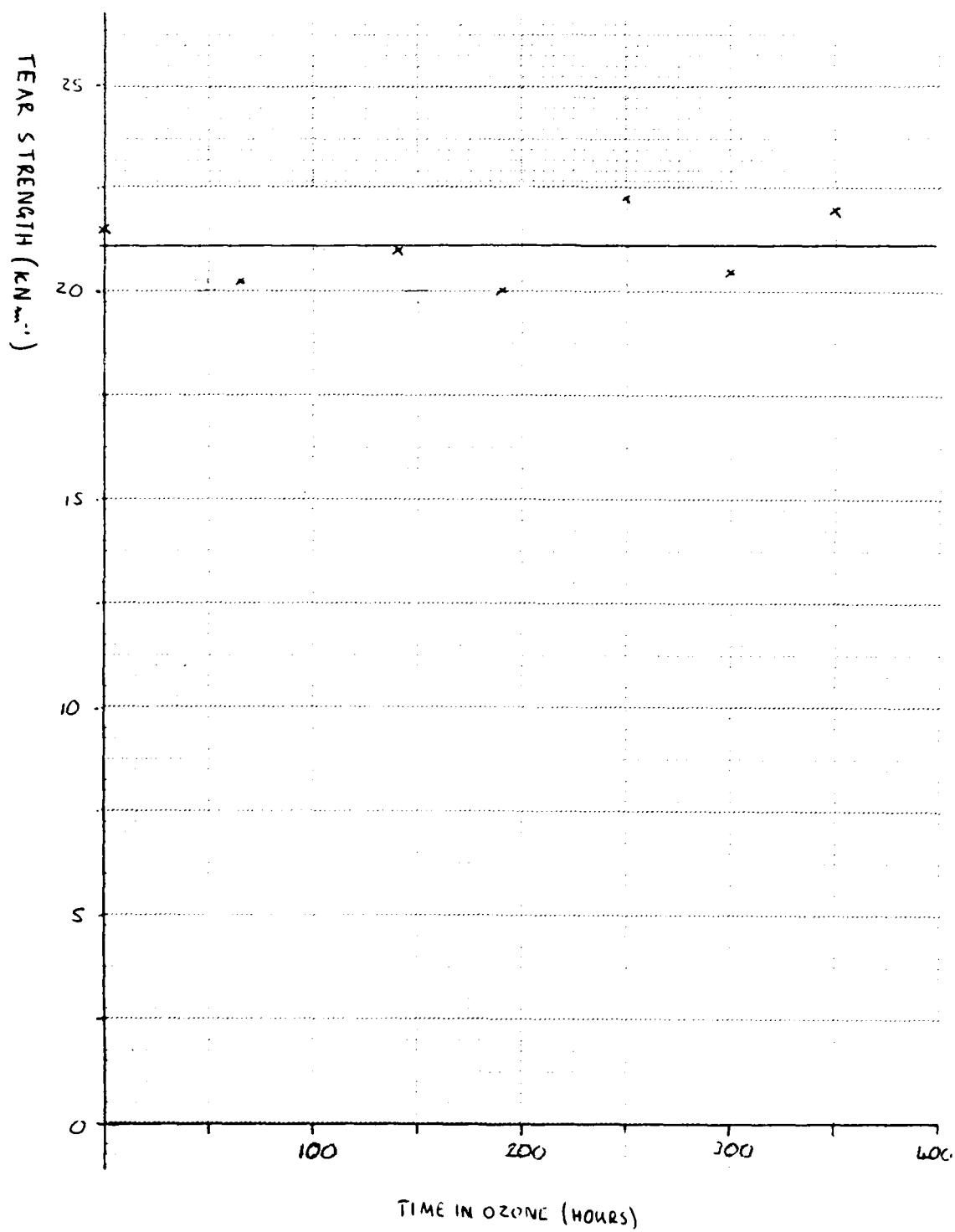


Fig 4 Tear strength vs time in ozone for the silicone rubber (400 ppm)

Fig 5

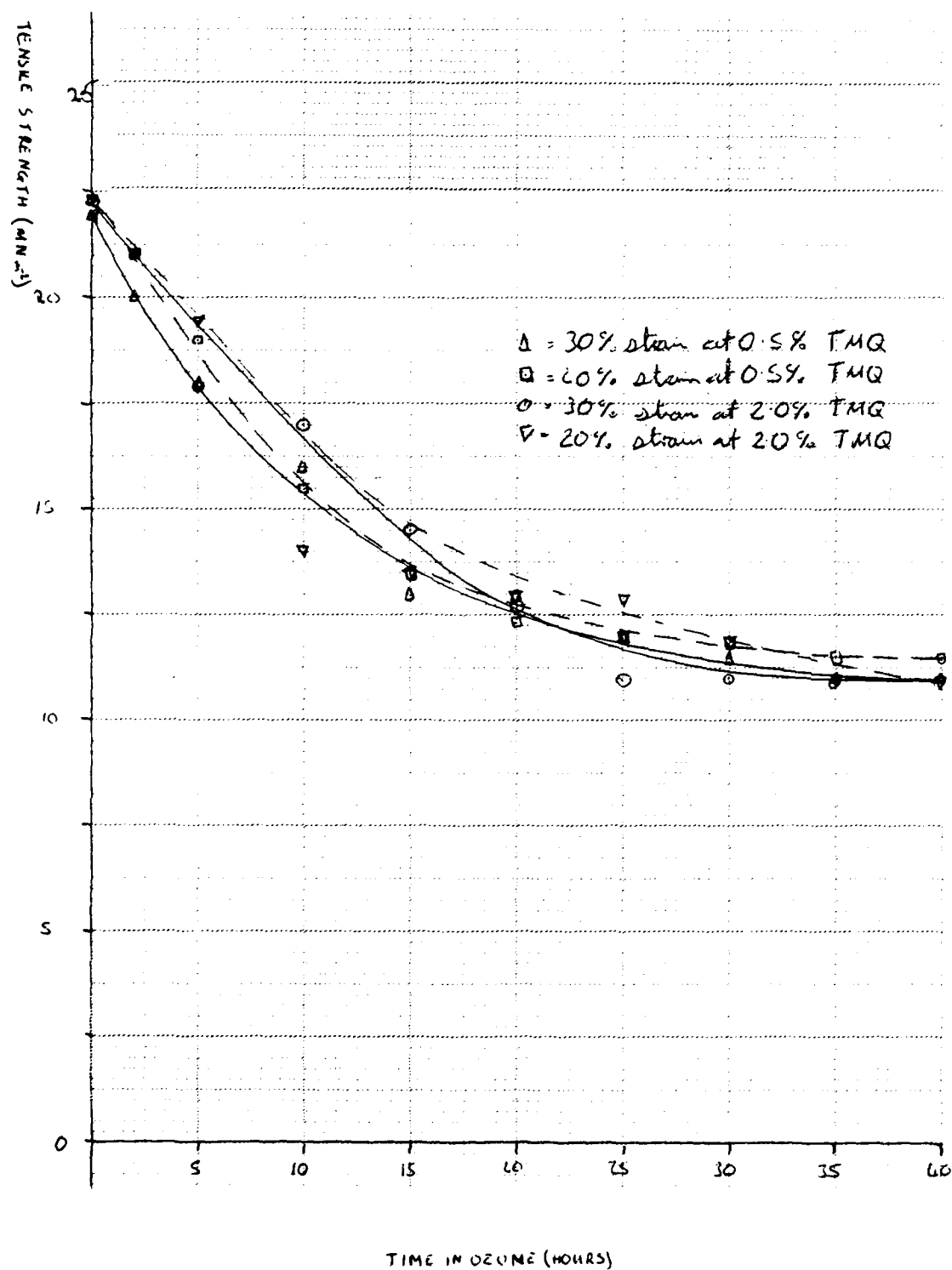


Fig 5 Tensile strength vs time in ozone for the nitrile TMQ formulation.
Ozone at 50 pphm

Fig 6

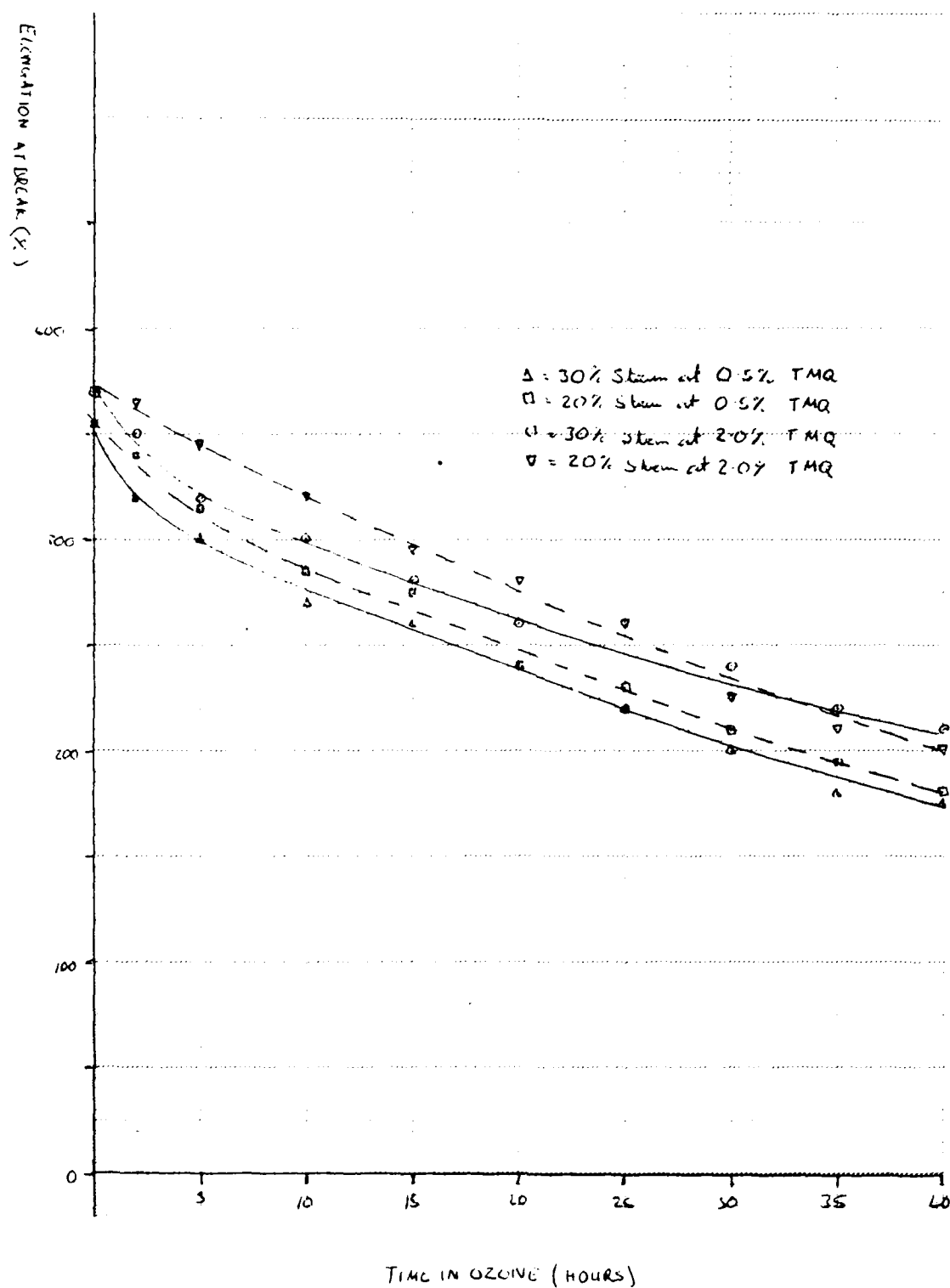


Fig 6 Elongation at break vs time in ozone for the nitrile TMQ formulation. Ozone at 50 ppm

Fig 7

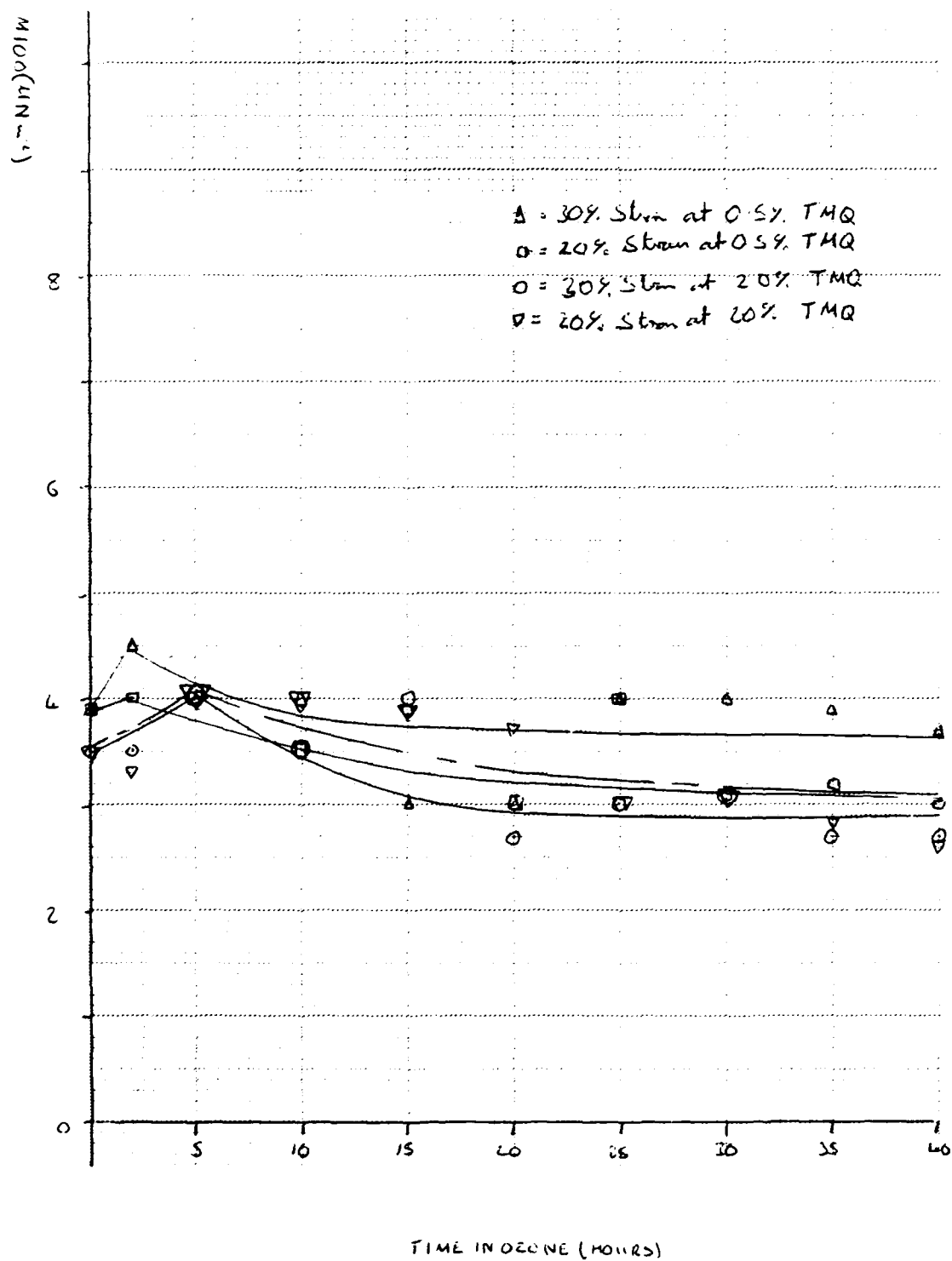


Fig 7 M100 vs time in ozone for the nitrile TMQ formulation.
Ozone at 50 pphm

Fig 8

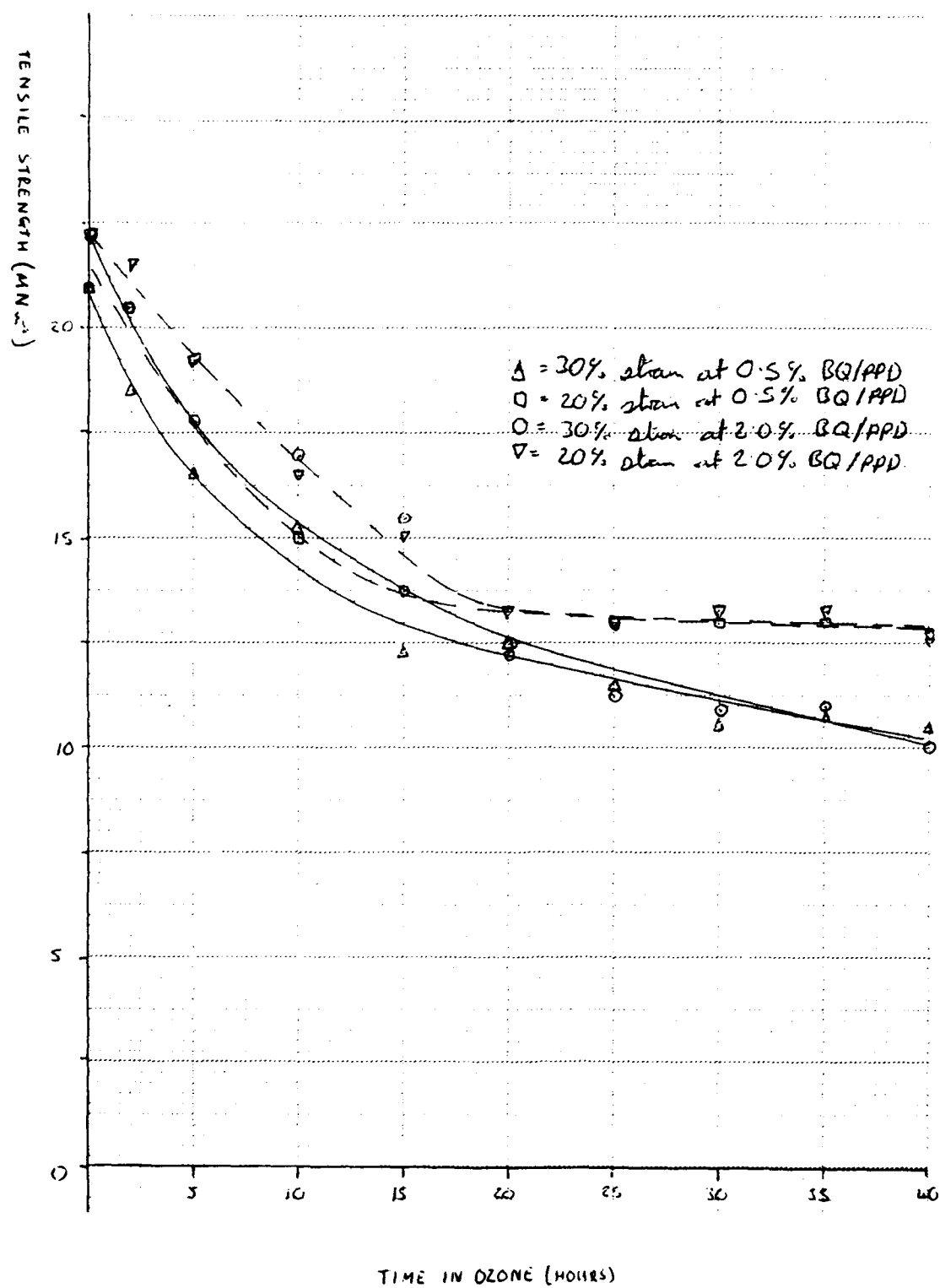


Fig 8 Tensile strength vs time in ozone for the nitrile BQ/PPD formulation. Ozone at 50 pphm

Fig 9

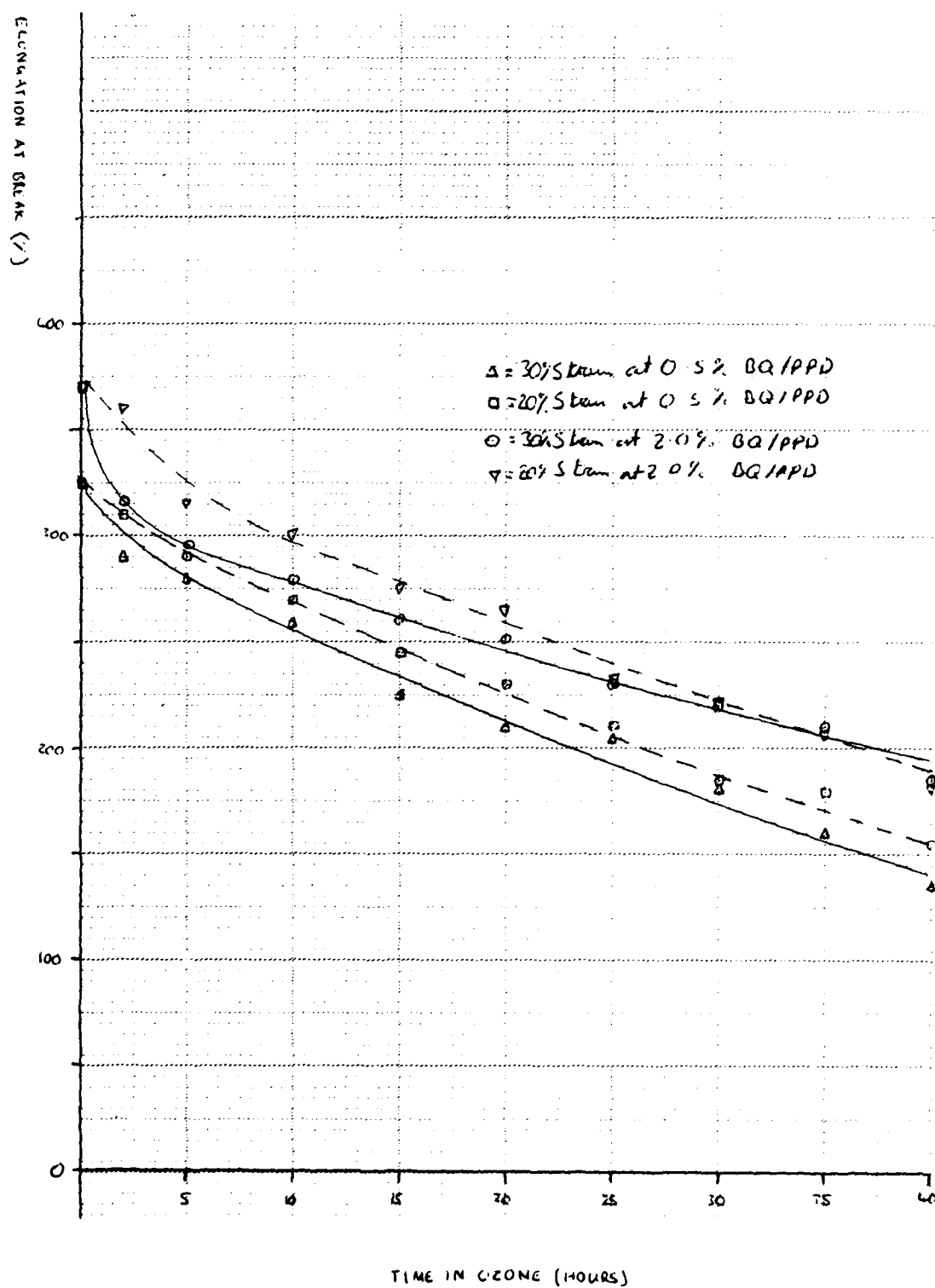


Fig 9 Elongation at break vs time in ozone for the nitrile BQ/PPD formulation. Ozone at 50 ppm

Fig 10

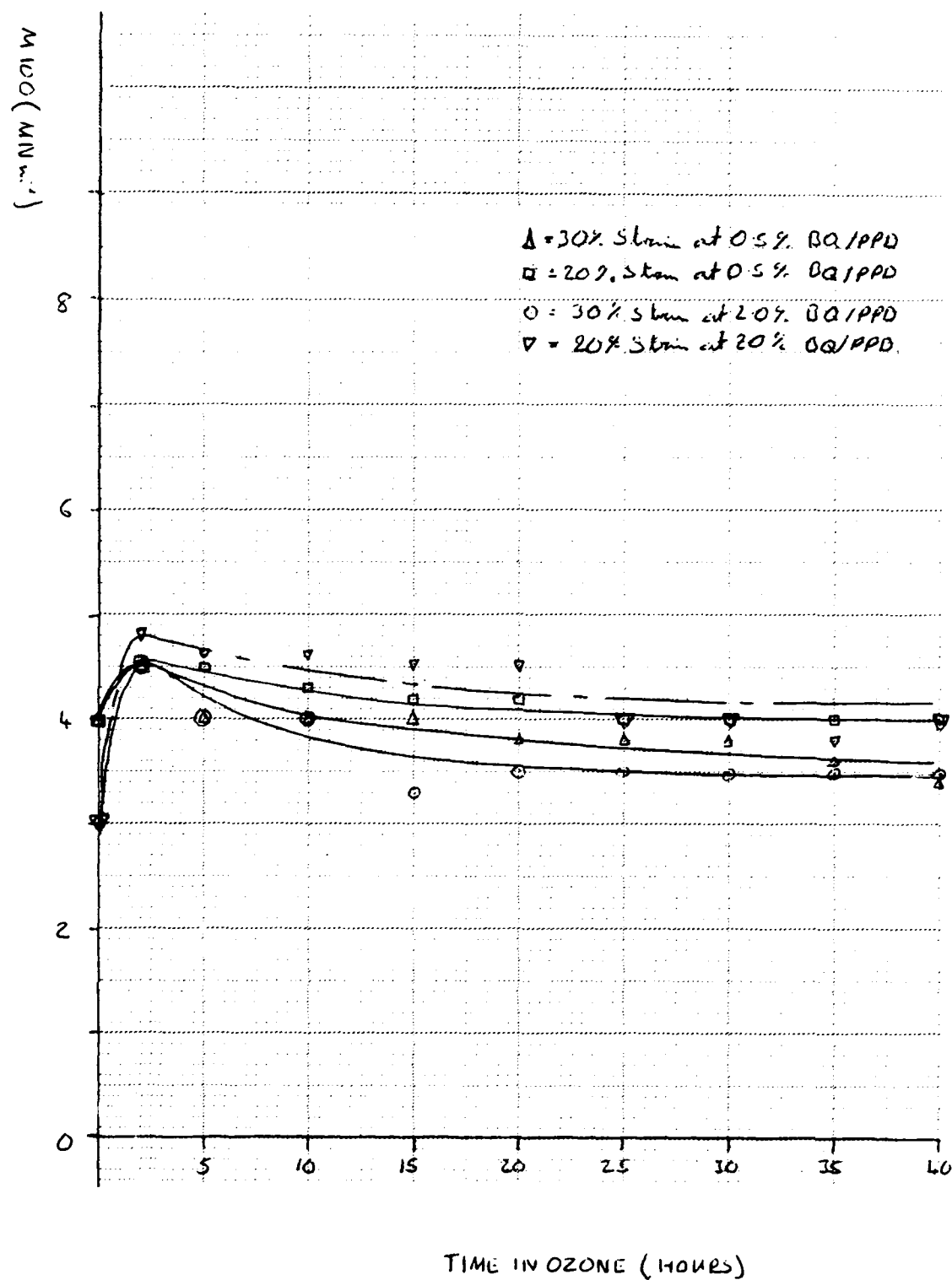


Fig 10 M100 vs time in ozone for the nitrile BQ/PPD formulation.
Ozone at 50 ppm

Fig 11

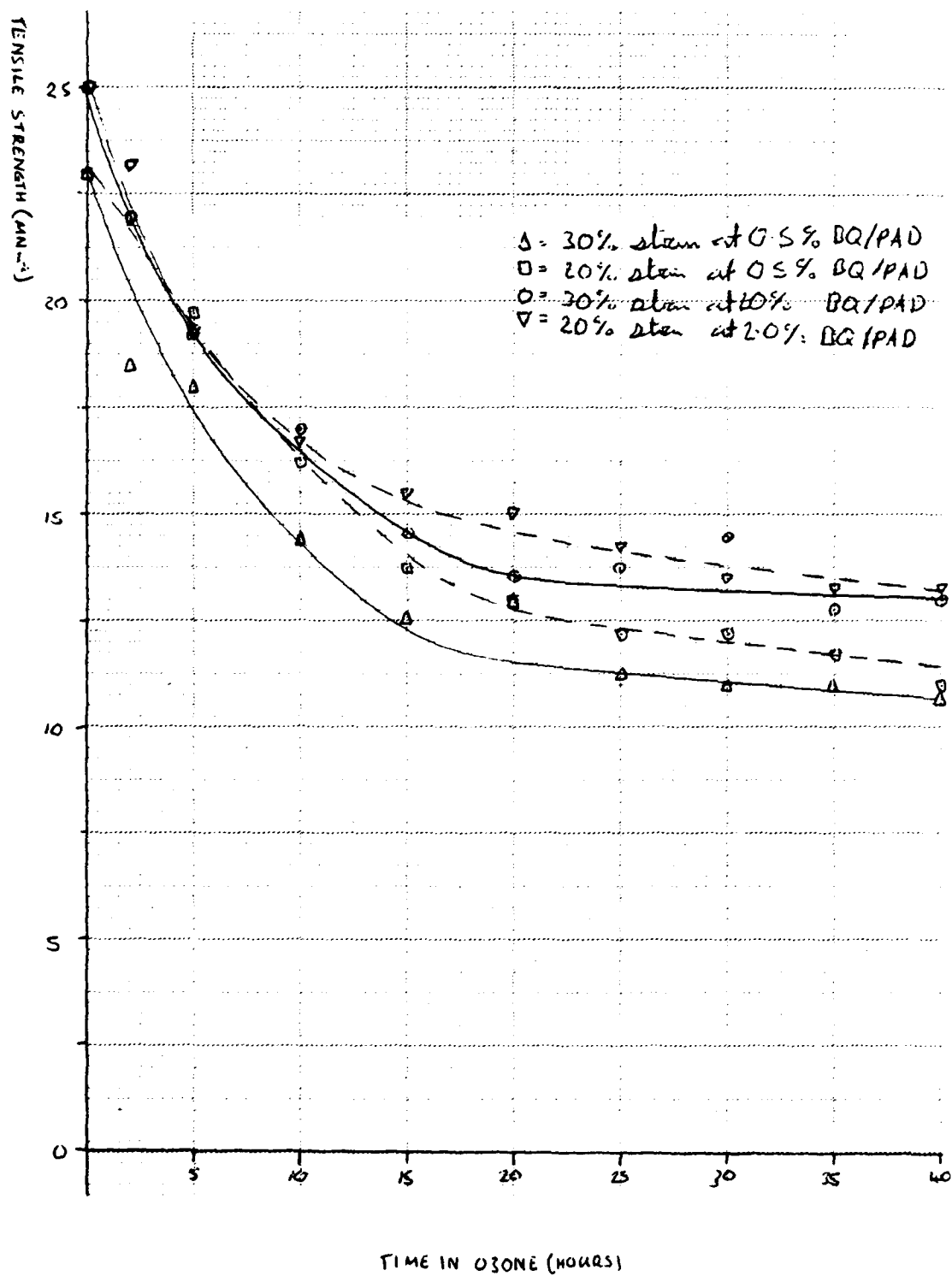


Fig 11 Tensile strength vs time in ozone for the nitrile BQ/PAD formulation.
Ozone at 50 ppm

Fig 12

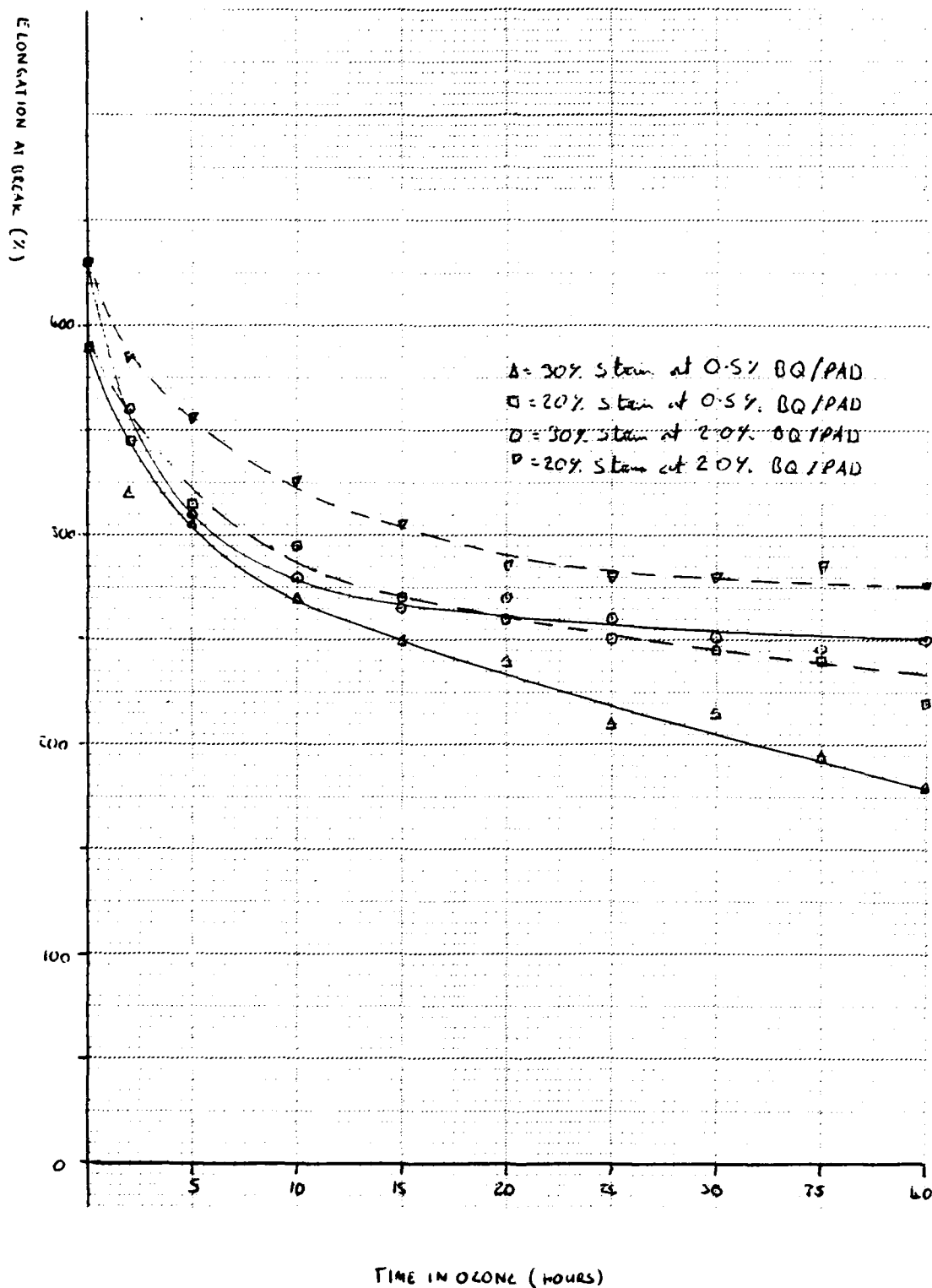


Fig 12 Elongation at break vs time in ozone for the nitrile BQ/PAD formulation. Ozone at 50 ppm

Fig 13

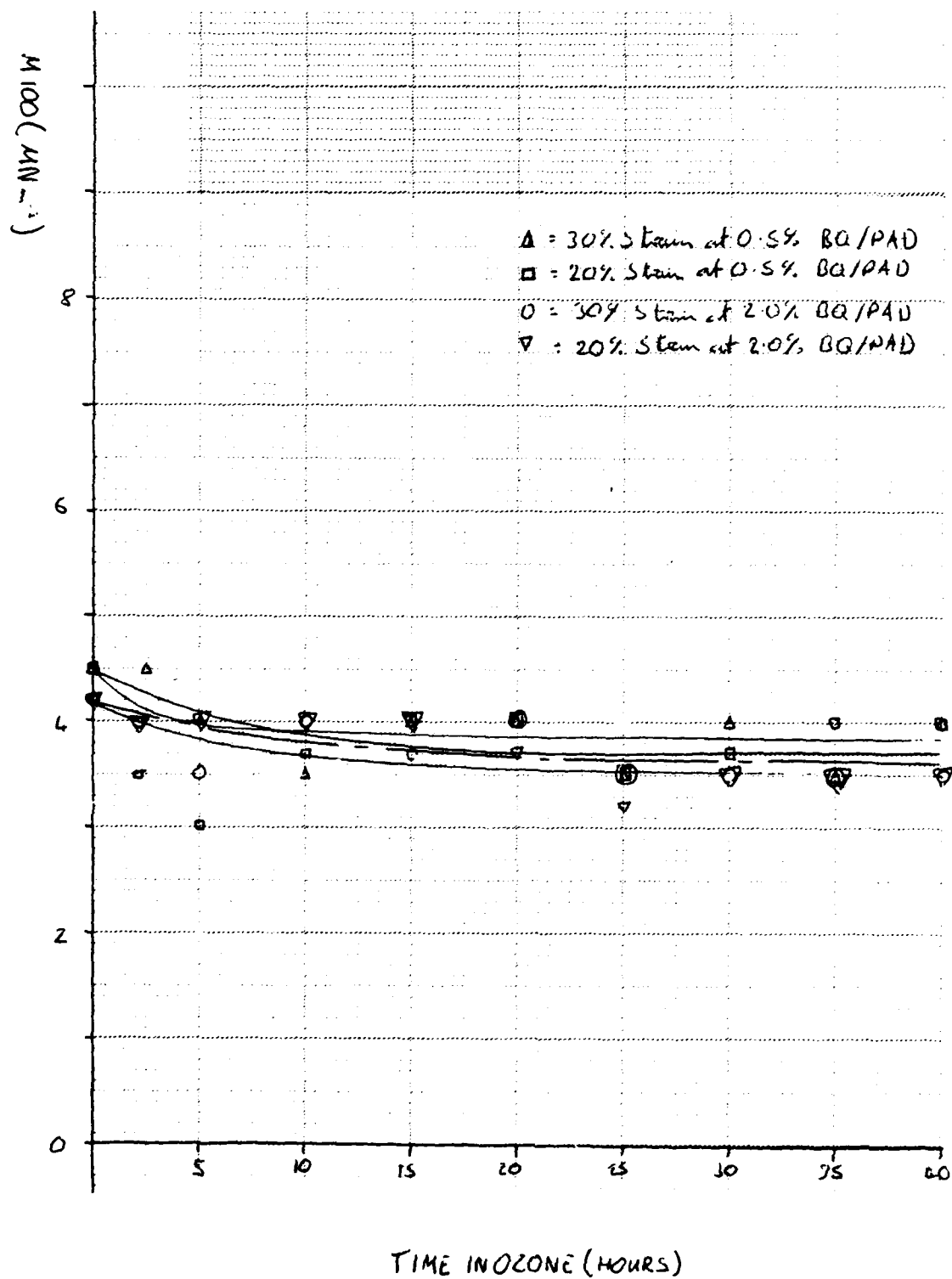


Fig 13 M100 vs time in ozone for the nitrile BQ/PAD formulation.
Ozone at 50 ppm

Fig 14

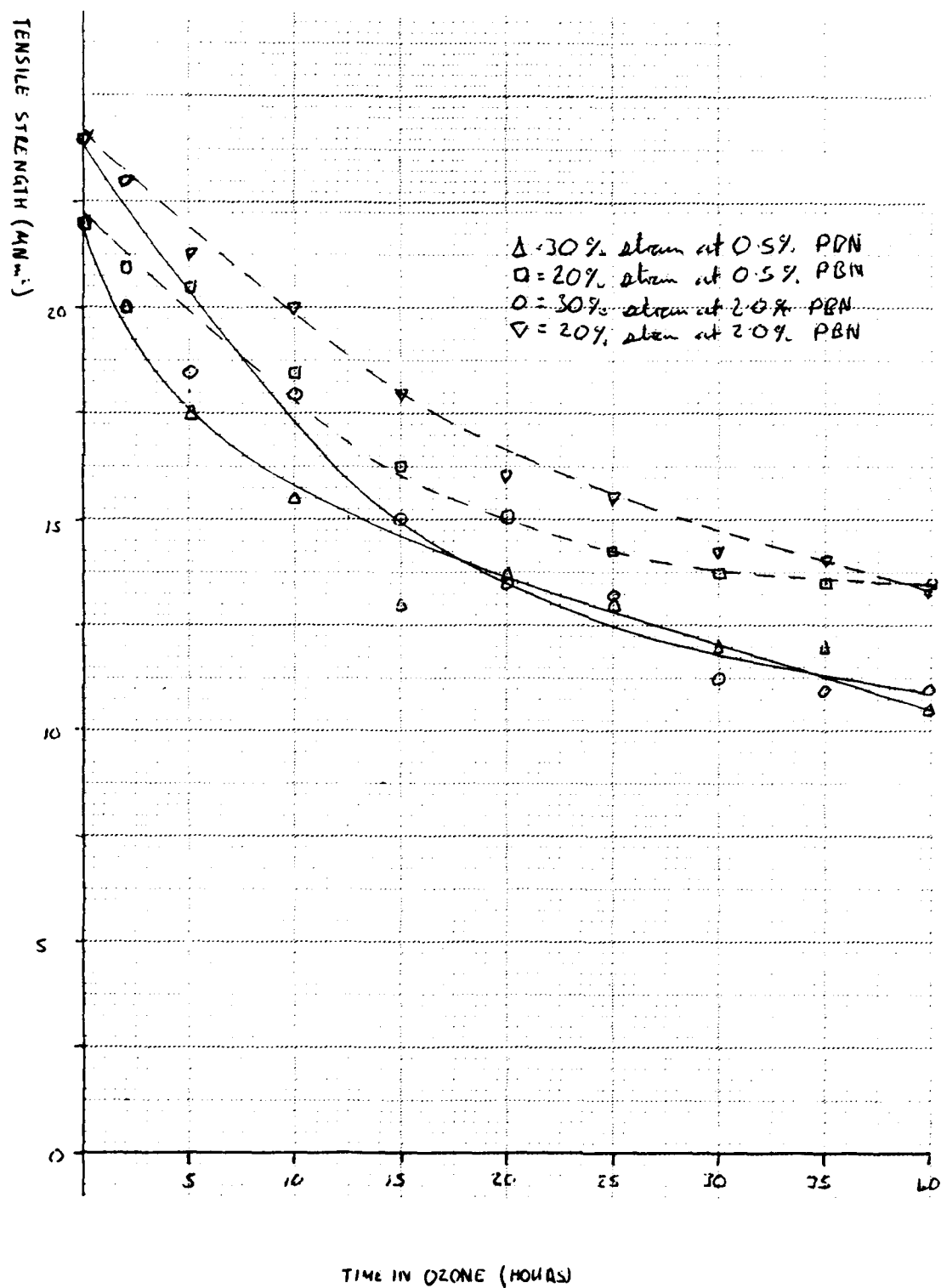


Fig 14 Tensile strength vs time in ozone for the nitrile PBN formulation.
Ozone 50 ppm

Fig 15

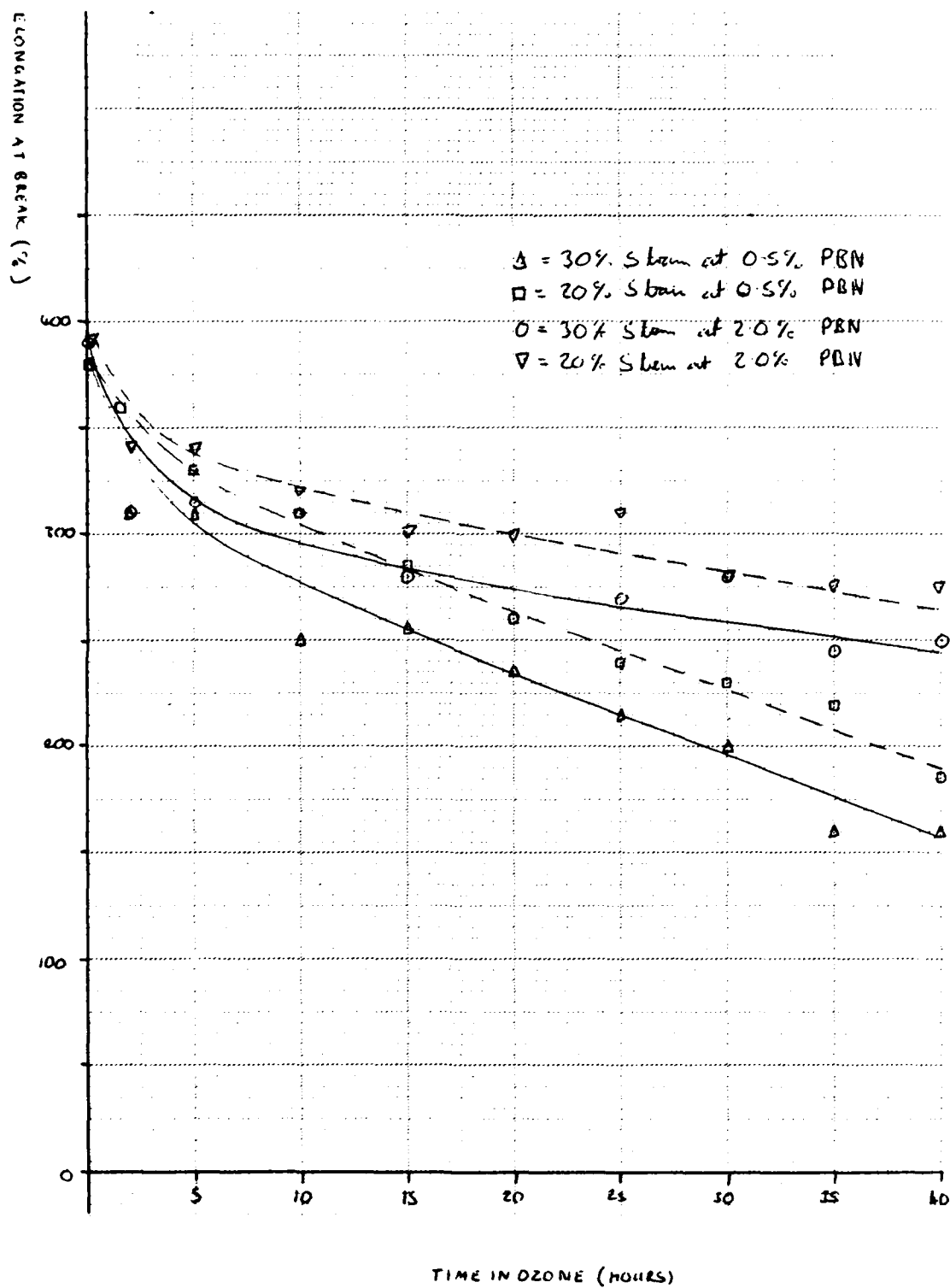


Fig 15 Elongation at break vs time in ozone for the nitrile PBN formulation.
Ozone at 50 ppm

Fig 16

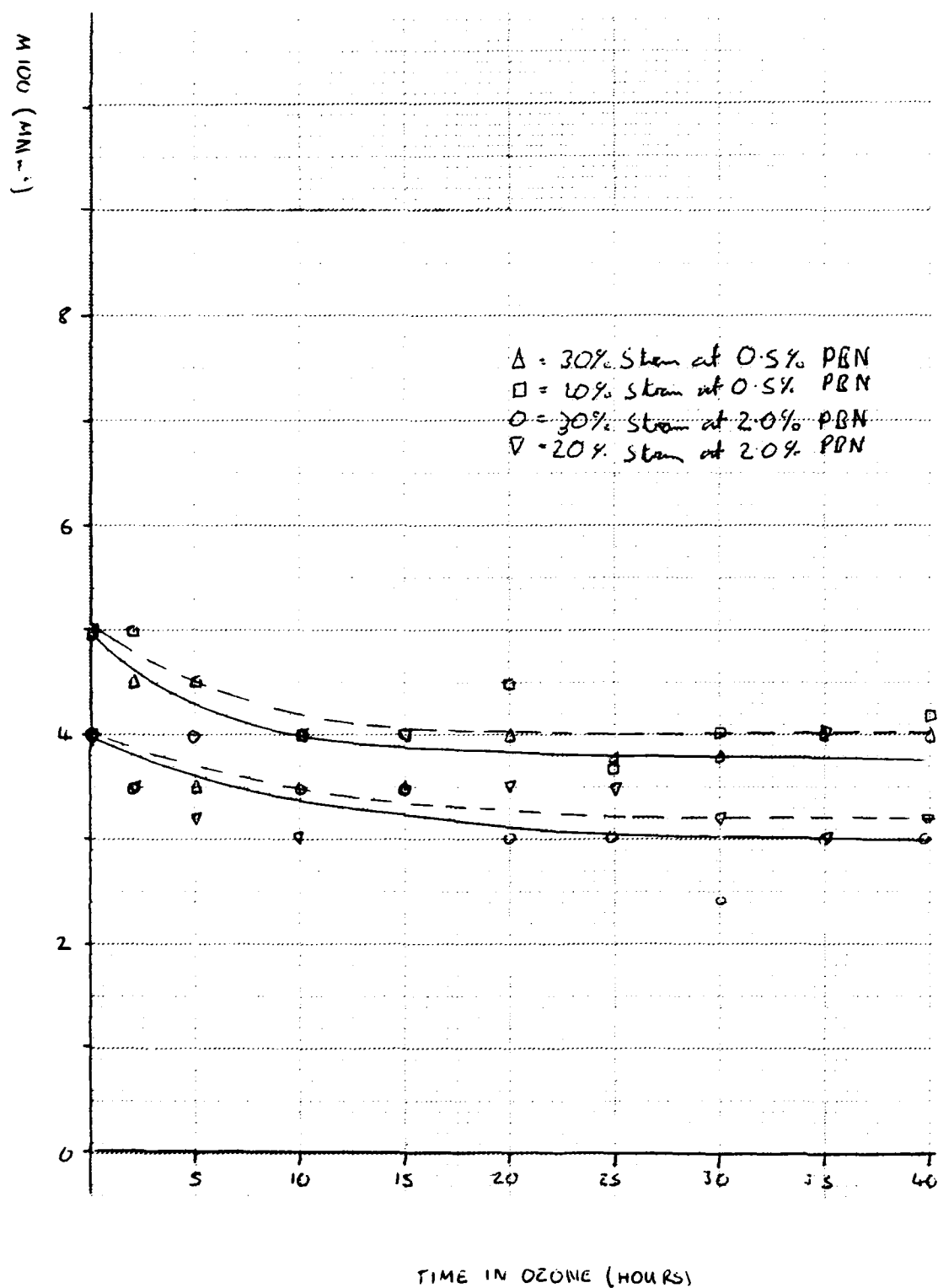


Fig 16 M100 vs time in ozone for the nitrile PBN formulation.
Ozone at 50 ppm

Fig 17

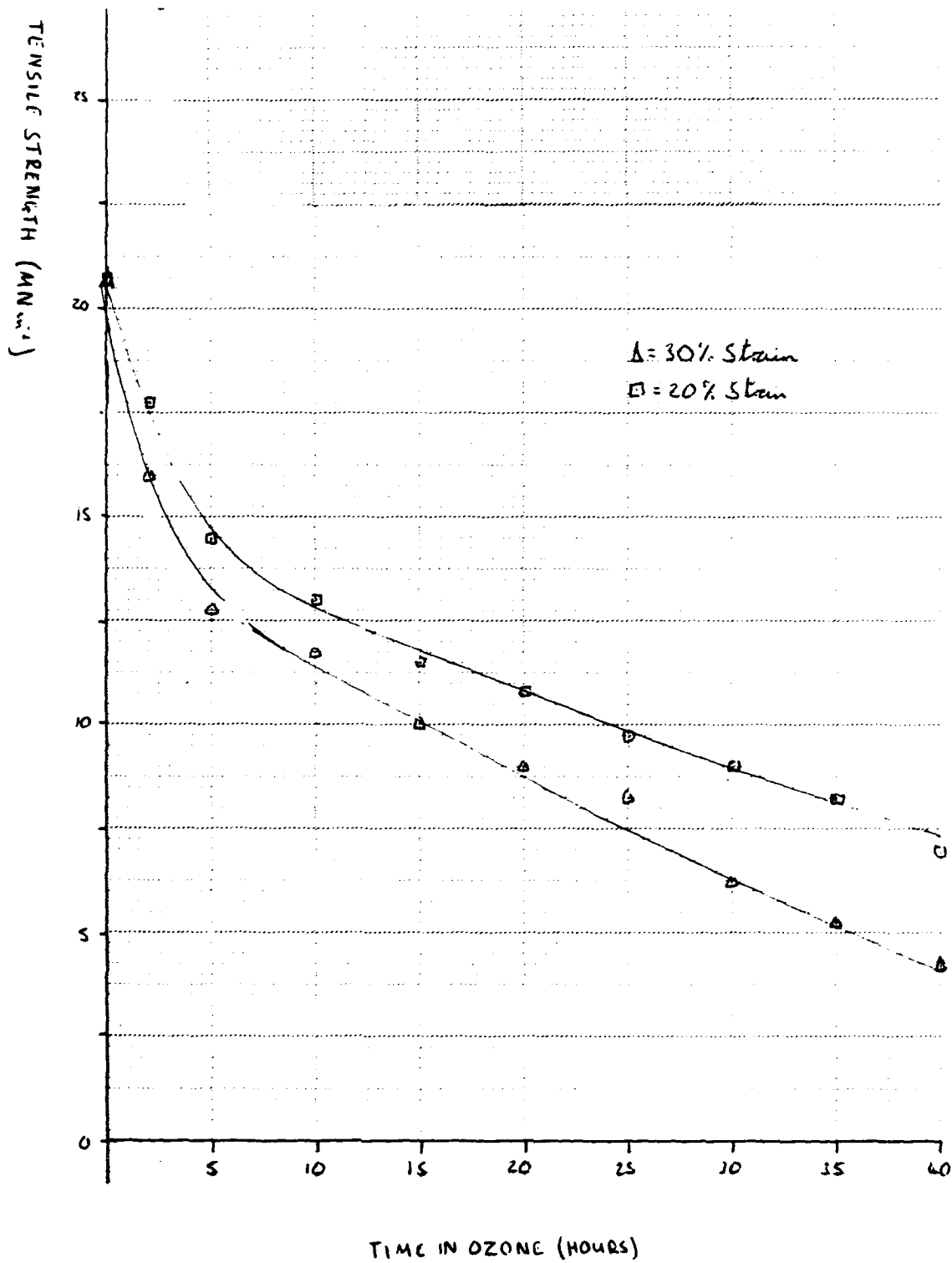


Fig 17 Tensile strength vs time in ozone for nitrile rubber containing no anti-oxidant (50 ppm)

Fig 18

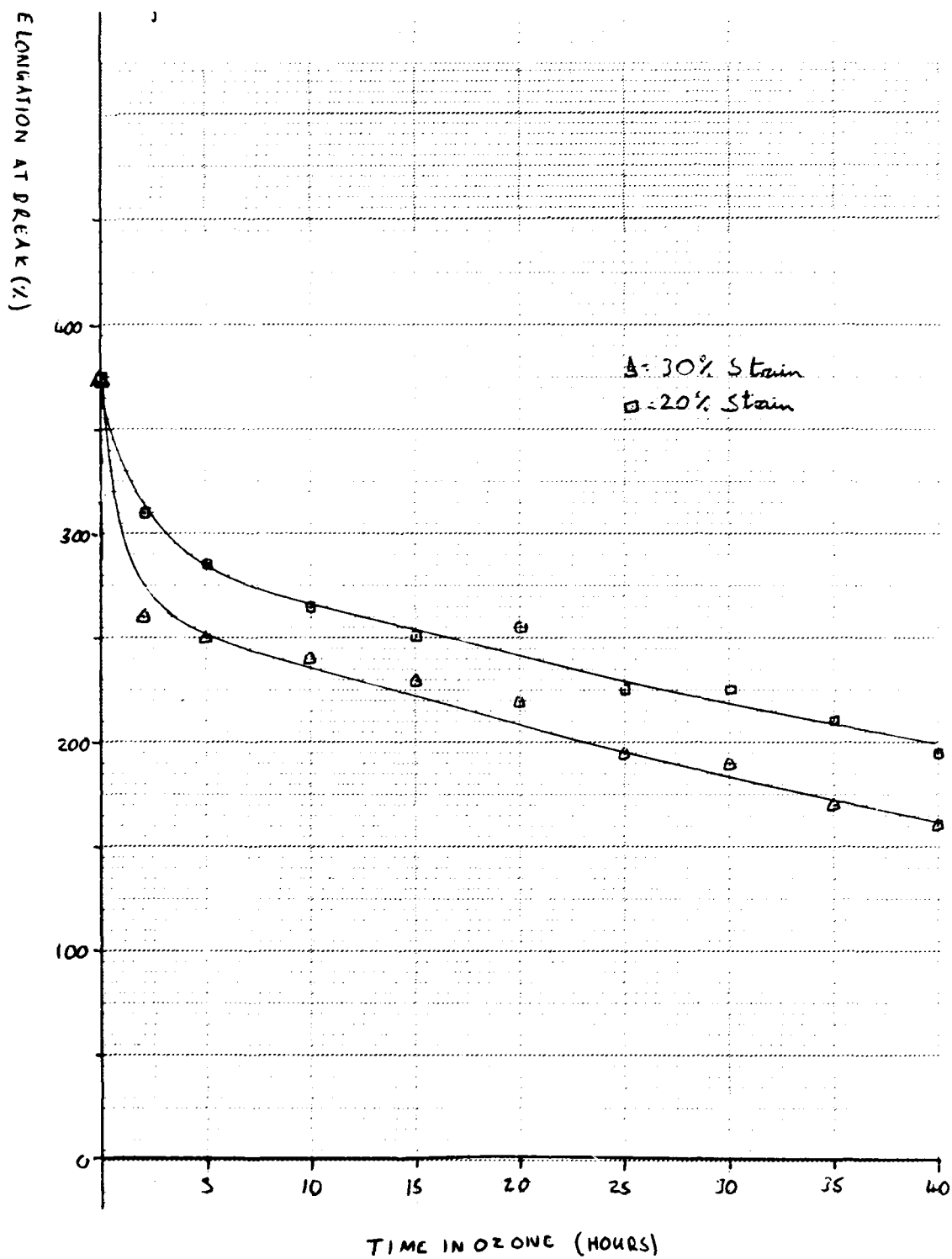


Fig 18 Elongation at break vs time in ozone for nitrile rubber containing no anti-oxidant (50 pphm)

Fig 19

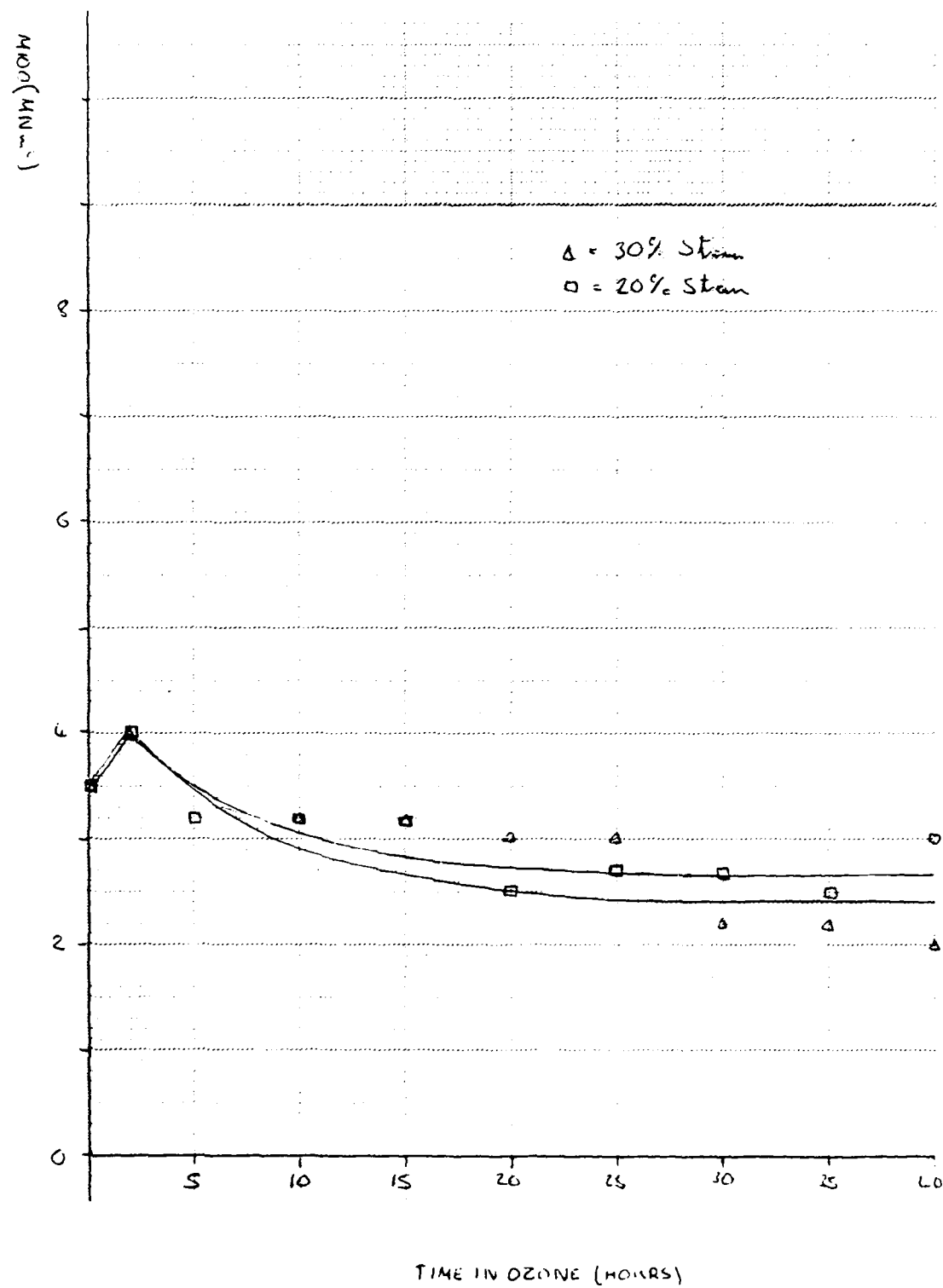


Fig 19 M100 vs time in ozone for nitrile rubber containing no anti-oxidant (50 ppm)

Fig 20

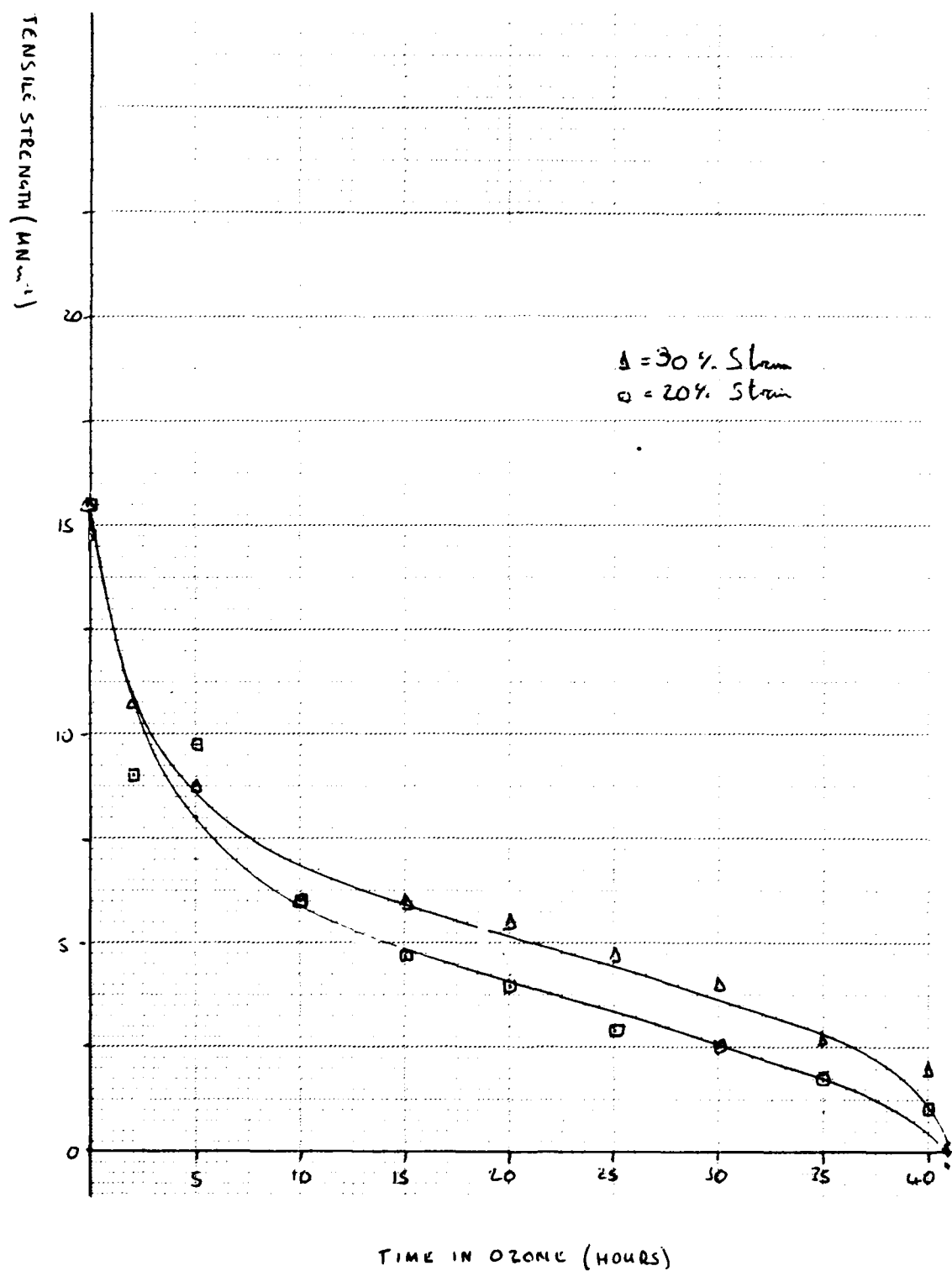


Fig 20 Tensile strength vs time in ozone for the nitrile rubber (commercial formulation). Ozone at 50 pphm

Fig 21

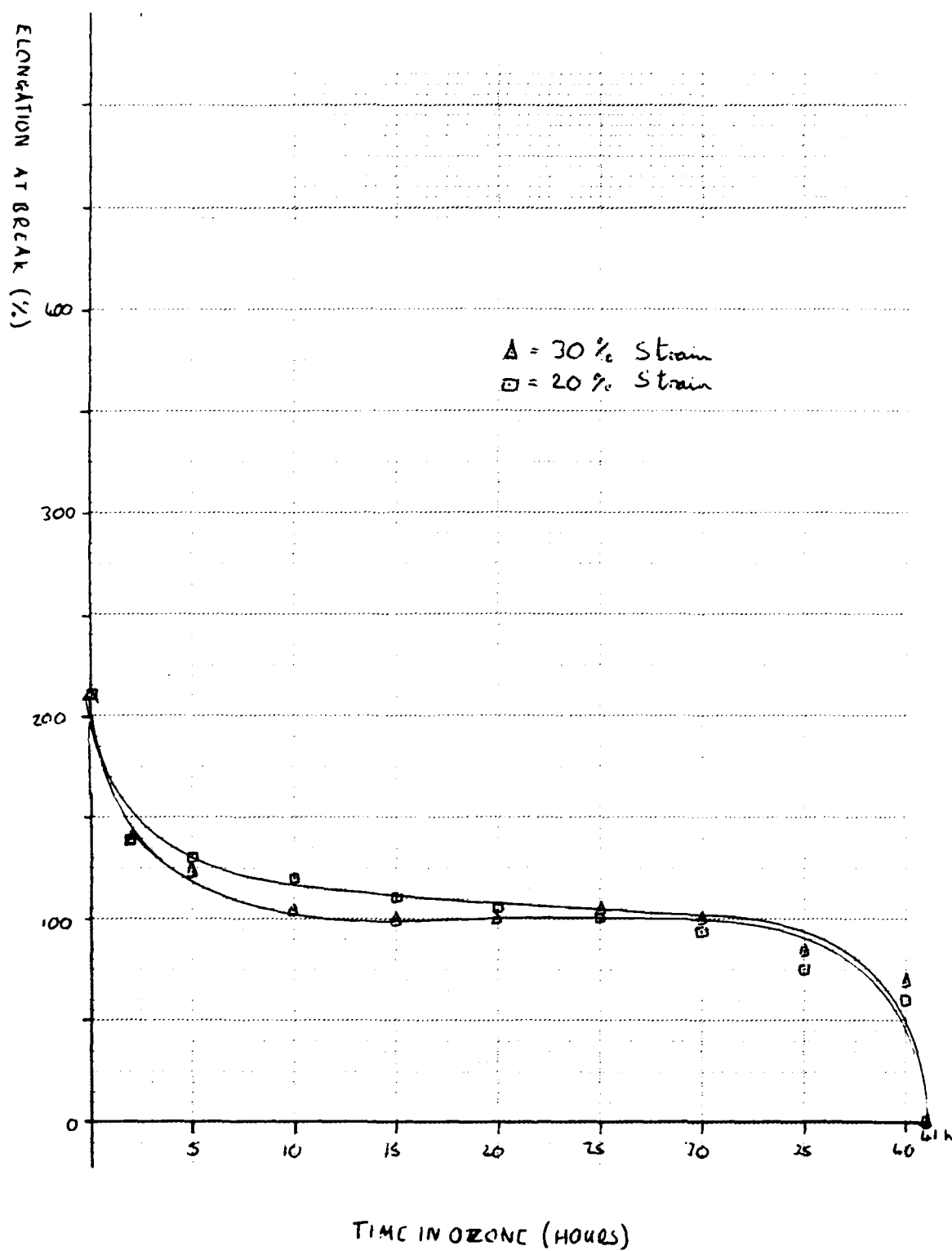


Fig 21 Elongation at break vs time in ozone for nitrile rubber (commercial formulation). Ozone at 50 ppm

Fig 22

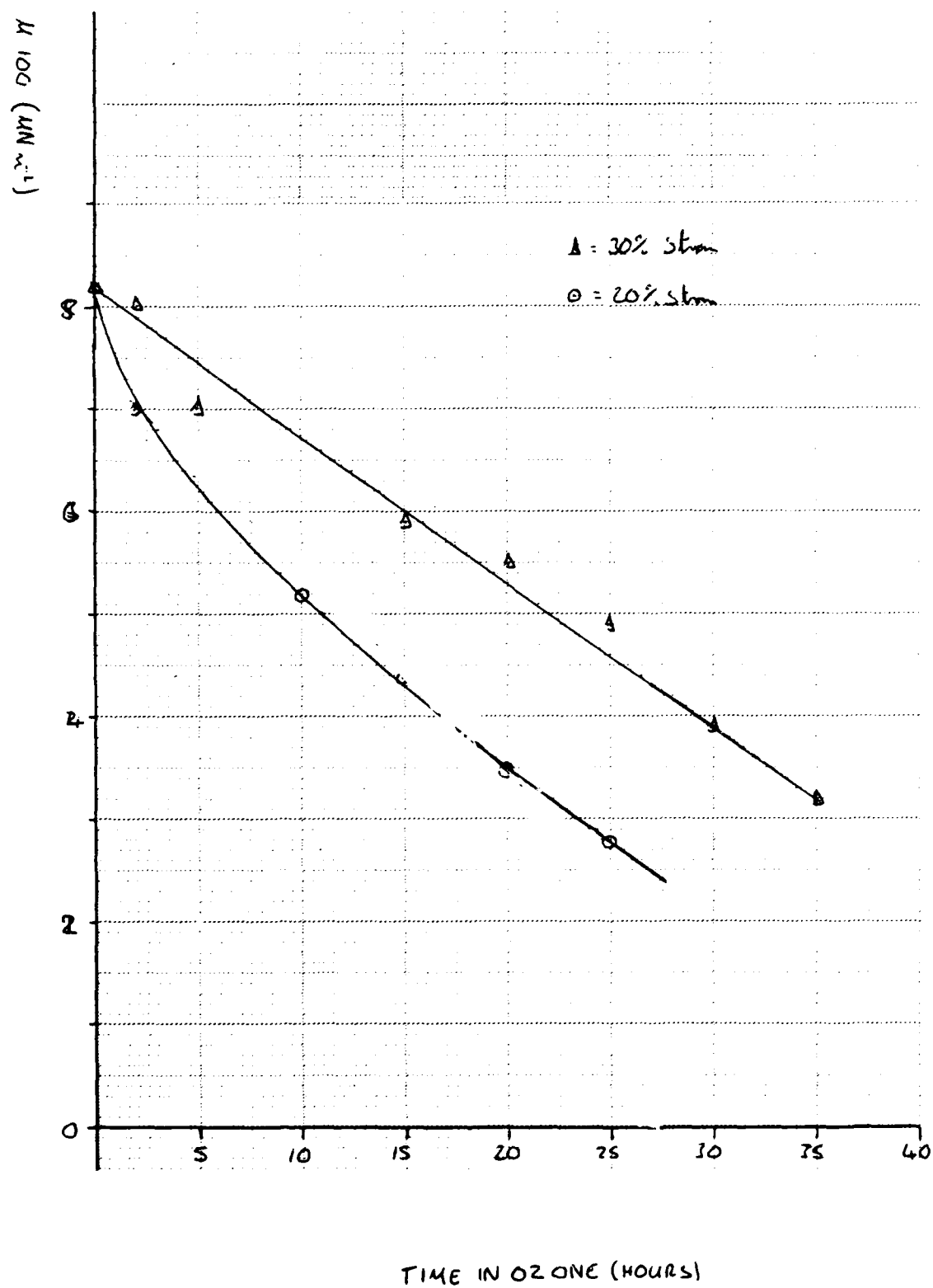


Fig 22 M100 vs time in ozone for nitrile rubber (commercial formulation). Ozone at 50 ppm

REPORT DOCUMENTATION PAGE

Overall security classification of this page

UNLIMITED

As far as possible this page should contain only unclassified information. If it is necessary to enter classified information, the box above must be marked to indicate the classification, e.g. Restricted, Confidential or Secret.

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7b. (For Conference Papers) Title, Place and Date of Conference					
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				Refs. 4	
11. Contract Number N/A	12. Period N/A	13. Project		14. Other Reference Nos.	
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16. Descriptors (Keywords) (Descriptors marked * are selected from TEST) Ozone resistance. Silicone rubber. Nitrile rubber.					
17. Abstract Work done by others suggested that a rapid loss of physical properties could occur in silicone rubbers when subjected to high concentrations of ozone. Experiments have now been carried out using a Hampden P3 C6 ozone cabinet to evaluate the significance of this evidence when the material is used in the face masks worn by RAF air-crews at high altitudes, where the ozone concentration can reach relatively high levels. No loss of physical properties was found over the duration of the experiment. The effect of ozone attack on nitrile rubber was also investigated. The effectiveness of four anti-oxidants used as anti-ozonants at an ozone concentration of 50 ppm (parts per hundred million) was studied together with a commercial nitrile rubber seal material. It was found that the anti-oxidants were effective anti-ozonants when compared with the unprotected rubber, whereas the commercial formulation had relatively poor resistance to ozone. The effect of varying the tensile strain applied to the samples was also considered and indicated that in general a lower strain resulted in a smaller drop in physical properties. The effect was not very marked.					

