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**COMPRESSION
SET RESISTANCE IN
SILICONE RUBBERS**

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SUMMARY

It is common practice in silicone rubber technology to give rubber articles a long high temperature post cure in air in order to achieve maximum resistance to compression set. In the present work it is proposed that this is necessary to destroy hydroperoxide groups established in the rubber during vulcanisation. Systems are described in which maximum resistance to compression set can be achieved without post cure.

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1 INTRODUCTION

Polydimethyl silicone rubbers became available commercially in 1945; in their original form they were vulcanised by a peroxide initiated free radical process. These rubbers had exceptional heat stability as shown by conventional heat aging tests but were relatively poor in resistance to compression set at temperatures as low as 160°C. This led, initially, to the introduction of additives for improving compression set resistance. These additives were principally metallic oxides, the most favoured being mercuric or mercurous oxide and cadmium oxide. Such systems required a relatively long heat treatment at 250°C in order to develop low compression set and they never proved entirely satisfactory.

Vulcanisation of polydimethyl silicones with organic peroxides is an inefficient process and in an effort to speed up cure a low concentration of vinyl groups (~ 0.2 mole per cent) was introduced at random along the polymer chains. This not only had the desired effect but also produced a marked improvement in compression set resistance but it was still found necessary to give a relatively long high temperature treatment in order to achieve maximum performance. Recently it has been found that certain curatives¹, when used with vinyl-containing polymers, give rise to rubbers which do not require such a heat treatment in order to develop optimum compression set resistance. This represents an important advance in silicone rubber technology.

In the present work the mechanism of curing and heat ageing in vinyl and non-vinyl polymers is reviewed and reconciled with their resistance to compression set. A rational explanation is provided for the effects of high temperature post cure on compression set, and for the existence of no-post-cure systems based on the vinyl containing polymers.

2 EXPERIMENTAL

2.1 Materials

Polymers used were a methyl-vinyl silicone containing 0.2 mole per cent of vinyl groups and a methyl-phenyl silicone containing 0.1 mole per cent of phenyl groups. Vulcanisation was carried out with bis 1.4 dichlorobenzoyl peroxide and 2.5 dimethyl-2.5 di-tert ary butyl peroxy hexane.

2.2 Compounding and vulcanisation

Polymer and vulcanising agent were mixed on a laboratory roll mill. Thin sheets of thickness 0.010 inch were produced for swelling measurements and blocks 0.25 inch thick for compression set tests.

All compounds were heated under pressure for a time sufficient to completely decompose the peroxide; this amounted to at least eight half-lives.

2.3 Swelling measurements

About 0.2 g of vulcanisate was weighed accurately and immersed in an excess of benzene at 28°C. After a period of 48 hours the rubber had reached its equilibrium swollen state, and was then withdrawn, surface dried, and weighed in a stoppered bottle. Finally it was dried to constant weight at 40°C. The volume of rubber in the swollen vulcanisate was calculated using values of 1.08 and 0.876 for the density of polymer and benzene respectively.

2.4 Compression testing

Compression set measurements were made at 160°C according to B.S.903 PtA.6. After release from compression the specimens were allowed to recover for 10 minutes at 160°C and 10 minutes in water at room temperature before being measured.

3 DISCUSSION

The compression set resistance of silicone gum vulcanisates at elevated temperatures will be controlled by three factors:-

- (a) main chain stability
- (b) cross-link density
- (c) cross-link stability.

The stability of the main chain polymer is determined principally by its chemical structure, although it can sometimes become modified through side reactions occurring during vulcanisation. The cross-link density and cross-link stability are governed by the cross-linking reagent used and the conditions of temperature, time, and environment in which vulcanisation is carried out.

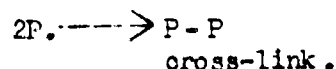
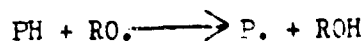
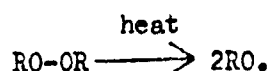
It is common practice to use a two-stage process when vulcanising silicone rubbers. The first stage - called the press cure - involves heating the compound in a closed mould under pressure for a time sufficient to decompose almost all of the peroxide curative. The second stage - called the post cure - involves heating the already vulcanised rubber in the open in an air oven for periods of up to 24 hours at 250°C. It is thought that post cure gets rid of volatile by-products of vulcanisation which might have a harmful effect on the heat stability of the rubber².

3.1 Main chain stability

In polydimethyl and polymethyl-vinyl silicones at temperatures up to 250°C, there are two reactions which can occur in the main polymer chain and lead to structural changes in gum vulcanisates. One is a hydrolytic reaction leading to scission of -Si-O- bonds and the other is an oxidative reaction at methyl side groups leading to the formation of cross-links³. Once stable cross-links have been established the compression set resistance will be governed by these two reactions. Under such circumstances one means of improving resistance to compression set is by the use of chemical additives capable of inhibiting or retarding hydrolysis and oxidation. Another possibility is to produce structural modifications in the base polymers which will make them less susceptible to hydrolytic and oxidative attack.

3.2 Press cure

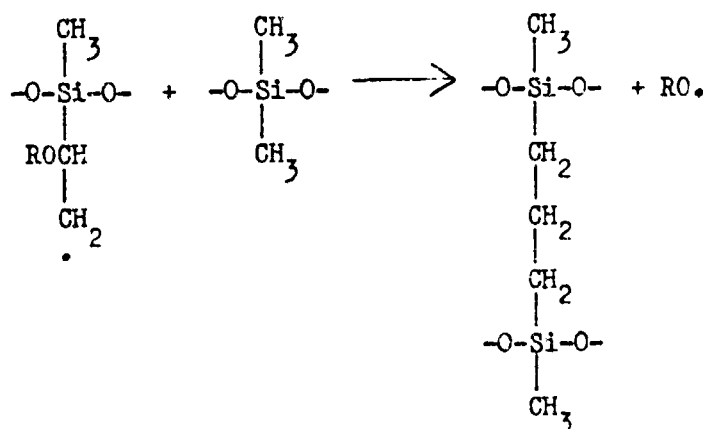
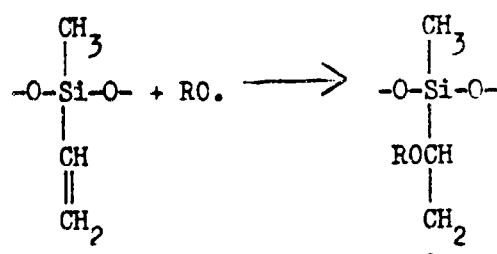
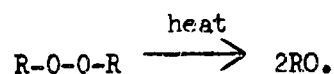
Silicone rubbers are invariably cross-linked with organic peroxides. In principle the reaction is simple



In practice it is found that different peroxides can react with a given base polymer to produce vulcanisates of quite different stability¹.

By way of illustration consider the vulcanisation of a polymethyl vinyl polymer with bis 1.4 dichlorobenzoyl peroxide (DCBP) and 2.5 dimethyl-2.5 ditertiary butyl peroxy hexane (VX). Vulcanisates were prepared by press-curing compounds containing different levels of peroxide and the elastic constants derived from equilibrium swelling measurements. The variation of elastic constant (C_1), which is directly proportional to cross-link density, with molar concentration of each peroxide is shown in Fig.1. It can be seen that both peroxides produce cross-links with the same efficiency and that a plateau is reached which represents the maximum cross-link density attainable with this base polymer. The level of C_1 represented by the plateau is determined by the concentration of vinyl groups in the unvulcanised polymer. In the absence of vinyl groups the VX peroxide would fail to produce a measurable number of cross-links. This confirms that the cross-link density achieved in vinyl containing

polymers arises entirely from reaction at vinyl groups. It is thought that the reaction proceeds as follows:-



At the optimum concentration of peroxide (as shown by the dotted line in Fig.1) both the DCBP and VX vulcanisates contain equal numbers of cross-links of identical structure. It seems reasonable to suppose, therefore, that they would possess a closely similar resistance to compression set. The results in Table 1 show that this is not so. Also shown in Table 1 are values of the continuous stress-relaxation rate constants (k) for the two vulcanisates in moist air at 160°C.

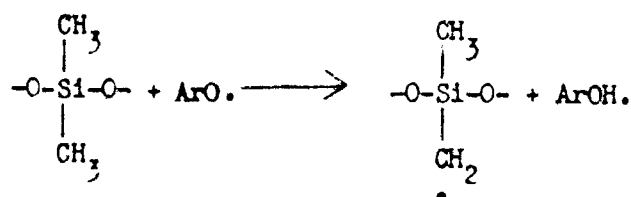
Table 1

Stability of press-cured methyl-vinyl silicone vulcanisates
in air at 160°C

Curative	Concentration	% compression set in 24 hr at 160°C	Continuous relaxation rate constant k in moist air at 160°C
DCBP	1.5 per cent	51	2.5×10^{-4}
VX	2.0 per cent	23	1.6×10^{-4}

The compression set results show a substantial difference in stability between the DCBP and VX vulcanisates. The stress-relaxation results also show significant differences in the rates of network scission. Previous studies of network stability in silicone rubbers in the temperature range from 120 to 250°C showed that scission observed at 160°C was due to hydrolytic reactions in the main polymer chain³. It is possible, therefore, that the poor resistance to compression set of DCBP vulcanisates is due to an increased rate of hydrolytic scission in such systems.

The results of Fig.1 show that both DCBP and VX are cross-linking with a low efficiency in the methyl-vinyl polymer. If cross-linking efficiency were defined as the ratio of the number of cross-links formed to the number of radicals produced by the initiator the values for DCBP and VX at optimum conditions would be about 20 per cent. In both cases there are, therefore, large numbers of radicals available to engage in side reactions. It is known that DCBP and VX differ notably in their reactivity towards primary hydrogen atoms; for example DCBP will cross-link a non-vinyl silicone fairly readily whilst VX will not (see Fig.2). In the methyl-vinyl polymer both peroxides react readily with the vinyl groups which subsequently produce cross-links. When VX is used there will be no further reaction between polymer and initiating radicals, whereas with DCBP there will be a substantial amount of reaction between aryloxy radicals and primary hydrogen atoms on the polymer.



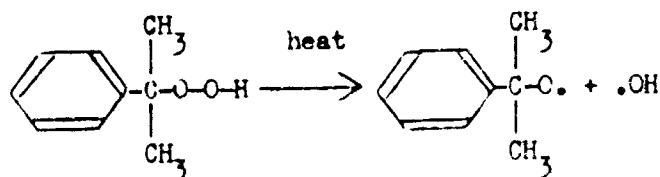
The rate of dimerisation of the resulting radicals is always low in a polydimethyl silicone; in the present system it will be especially low since they are being produced in a three dimensional network structure already established by reaction at the vinyl groups. There is every likelihood, therefore, of their participating in side reactions which do not result in cross-linking. One such reaction could be with oxygen to give a hydroperoxide.

The presence of hydroperoxide groups on the rubber could provide an explanation for the compression set and stress-relaxation results. Thermal decomposition of these groups during a high temperature test would lead to the production of water in the vulcanisate and this in turn would lead to an

increased rate of hydrolytic scission. This mechanism would also account for the poor resistance to compression set shown by polydimethyl silicones cross-linked with DCBP and benzoyl peroxide.

It is often stated that the poor compression set resistance of press-cured DCBP vulcanisates is due to the presence of 1,4 dichlorobenzoic acid formed during vulcanisation^{2,4}. This acid is readily soluble in benzene and solvent extraction of the vulcanisates should, therefore, result in an improved resistance to compression set and a lower rate of continuous stress-relaxation. In practice a long benzene extraction failed to change the results from those shown in Table 1.

If hydroperoxide groups on the polymer can produce network instability it should be possible to do the same by the introduction of other organic hydroperoxides. In this context an attempt was made to vulcanise a polymethyl vinyl silicone with cumene hydroperoxide. This molecule undergoes thermal breakdown to give an aryloxy and hydroxyl radical:-



Cumyloxy radicals react readily with vinyl groups on a methyl-vinyl polymer to give cross-links; even so it was not found possible to produce a vulcanisate with cumene hydroperoxide. After suitable press cures the polymer was always found to be completely soluble, and viscosity measurements indicated a significant drop in molecular weight (see Table 2).

Table 2

Effect of heating methyl-vinyl silicone with cumene hydroperoxide

Concentration of hydroperoxide	Heat treatment	% soluble	M.Wt. in toluene at 25°C
0	None	100	549 500
2.75 parts	2 hr at 180°C	100	467 700

These results suggest that there is an appreciable amount of main chain scission occurring during the heat treatment, and this is presumably due to the production of water in the system.

3.3 Post cure

The final stage in processing silicone rubbers for low compression set resistance is to subject them to an open high temperature post cure in air; this often lasts for 24 hours at 250°C.

It is instructive to see how the ideas developed in the previous section fit the observed effects of post cure on compression set.

Table 3

Effect of post cure on compression set resistance in silica filled
silicone rubbers

Polymer	Curative	Filler concentration	Post cure treatment	% compression set in 24 hr at 160°C
Methyl-vinyl	1.5 parts DCEP	40 pt AEROSIL	None	69
Methyl-vinyl	1.5 parts DCEP	40 pt AEROSIL	24 hr at 250°C	29
Methyl-vinyl	2 parts VX	40 pt AEROSIL	None	33
Methyl-vinyl	2 parts VX	40 pt AEROSIL	24 hr at 250°C	38
Dimethyl	8 parts dicumyl peroxide	40 pt AEROSIL	None	79
Dimethyl	8 parts dicumyl peroxide	40 pt AEROSIL	24 hr at 250°C	38

The results in Table 3 show that high temperature post cure has virtually no effect on the compression set resistance of a VX vulcanisate. In the DCEP system it produces a large improvement. During post cure in air hydroperoxide groups on the polymer will be broken down and any water formed will be removed from the system. The compression set resistance of a DCEP vulcanisate should then become roughly the same as that of a VX vulcanisate. This is confirmed by the experimental results. High temperature post cure also produces a big improvement in compression set resistance in polydimethyl silicone vulcanisates, the values becoming comparable with those for fully post cured methyl-vinyl vulcanisates (see Table 3).

It has been proposed that high temperature post cure is effective in reducing compression set because it removes harmful by-products of vulcanisation from the system, and in particular in the DCEP system it gets rid of 1.4 dichlorobenzoic acid^{2,4}. Long term compression set tests on fully post cured DCEP vulcanisates are shown in Fig.3 along with those on a VX vulcanisate and on irradiation cured silicone at 200°C. The actual values for compression set are of no significance in this case because the DCEP vulcanisate is at a

much higher cross-link density than the others; what is significant is the different shape of the DCBP curve relative to the others. In compression set tests at 200°C oxidative cross-linking will be proceeding at a significant rate and its effect will be superimposed upon that of hydrolytic scission. The shape of the DCBP curve is suggestive of a catalysed oxidative reaction whereas that of the VX and irradiation vulcanisates is not. It is known that trace acidic impurities catalyse the oxidation of hydrocarbons and it would therefore appear that a post cure of 24 hours at 250°C is inadequate for the removal of 1,4 dichlorobenzoic acid from a 0.25 inch thick specimen of silicone rubber.

High temperature post cure has a marked structural effect on silicone vulcanisates, quite apart from the proposed decomposition of hydroperoxide groups and removal of volatile residues. Heating a methyl-vinyl vulcanisate in air at 250°C introduces additional cross-links at a substantial rate (see Fig.4), and the results show that in a gum vulcanisate the value of C_1 increases by a factor of about 10 during the post cure normally given to a low compression set silicone rubber. This in itself is likely to have a beneficial effect on compression set resistance.

4 CONCLUSIONS

The compression set resistance of press cured silicone rubbers is very dependent upon the type of peroxide used in vulcanisation. These differences are attributable to differences in reactivity of peroxides towards methyl group on the polymers. In vinyl containing polymers only the most "vinyl specific" reagents should be used if maximum compression set resistance is to be achieved on press curing. Use of non specific reagents such as DCBP and benzoyl peroxide involves the polymers in side reactions which detract from their compression set resistance. In these cases it is proposed that hydroperoxide groups are produced on the polymer as a result of abstraction of primary hydrogen atoms by aryloxy radicals. Thermal decomposition of these hydroperoxides during a compression test leads to the formation of water which in turn results in an increased rate of hydrolytic scission.

The effects of high temperature post cure are to destroy the hydroperoxide groups and remove the water from the system, and also to produce a substantial increase in cross-link density. The indications are that a full high temperature post cure fails to remove all the residual dichlorobenzoic acid in a DCBP vulcanisate.

This work shows that if "vinyl specific" reagents, such as VX, are used a high temperature post cure is not required to produce optimum resistance to

compression set. It is clearly a retrograde step to introduce vinyl groups into the polymer and then to persist in the use of non-specific reagents.

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○ → DCBP
● → VX

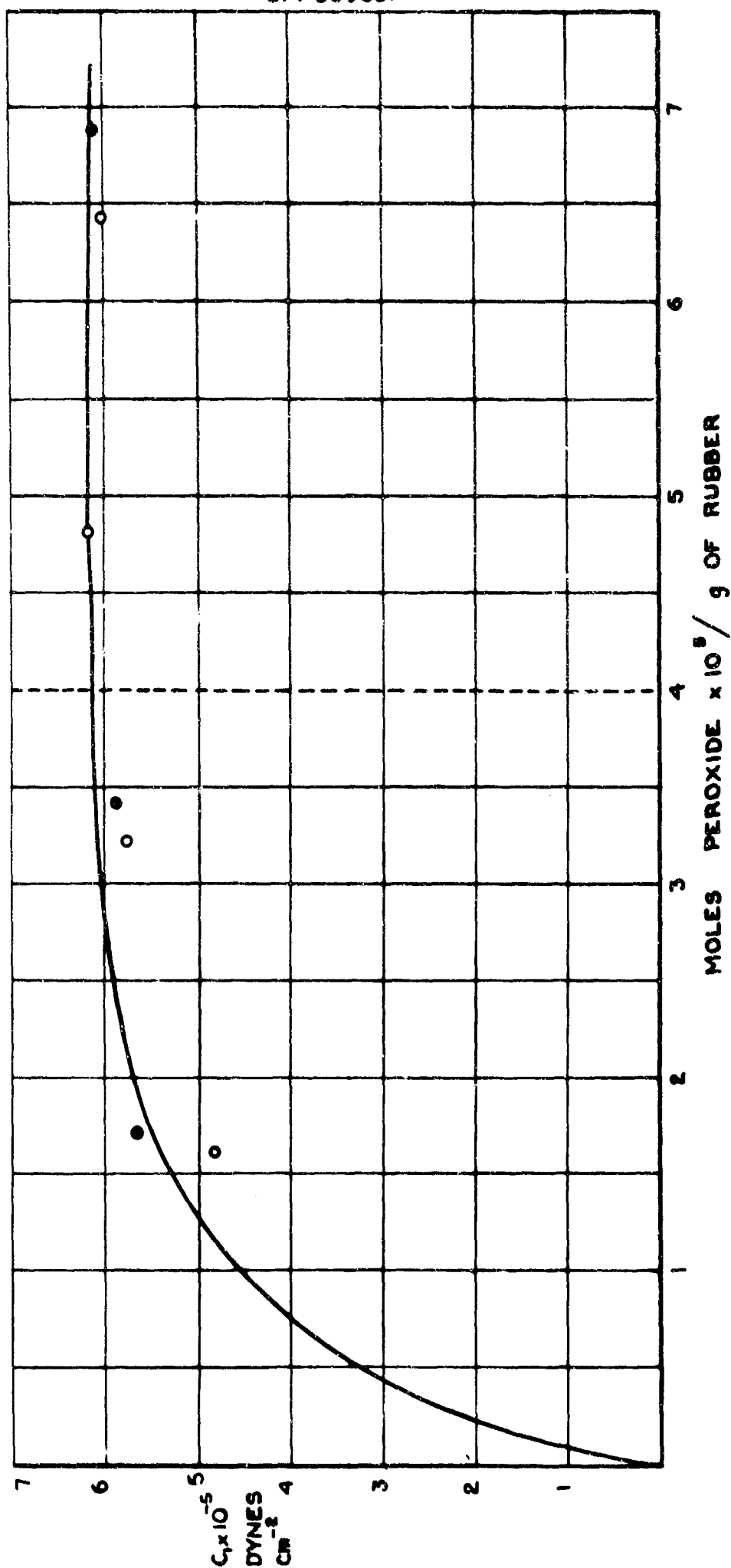


Fig. 1

FIG.1 CROSS-LINKING OF A VINYL SILICONE WITH ORGANIC PEROXIDES

Fig. 2

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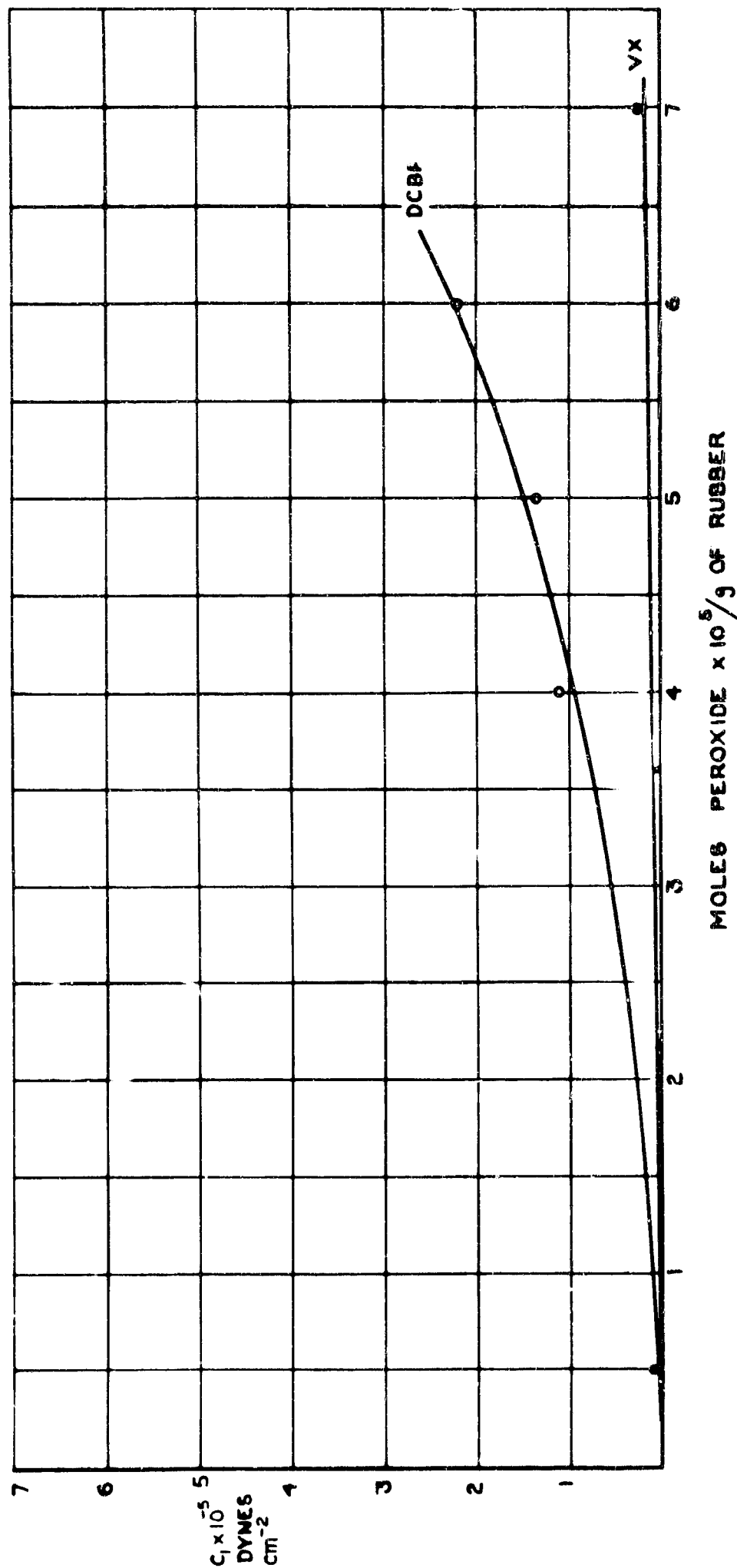


FIG. 2 CROSS-LINKING OF NON-VINYL SILICONE WITH ORGANIC PEROXIDES

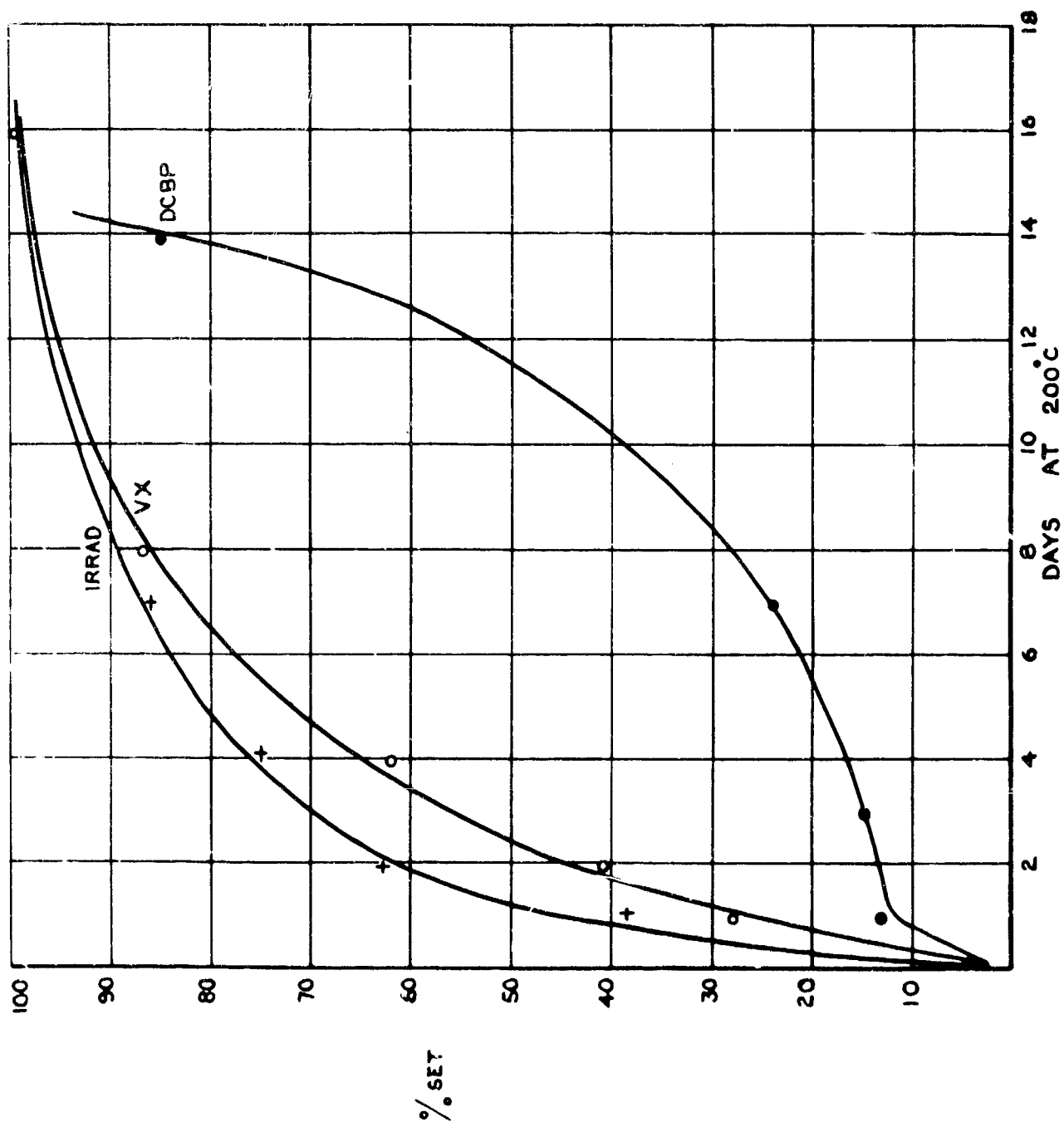


FIG.3 COMPRESSION SET IN SILICONE RUBBERS AT 200°C

Fig. 4

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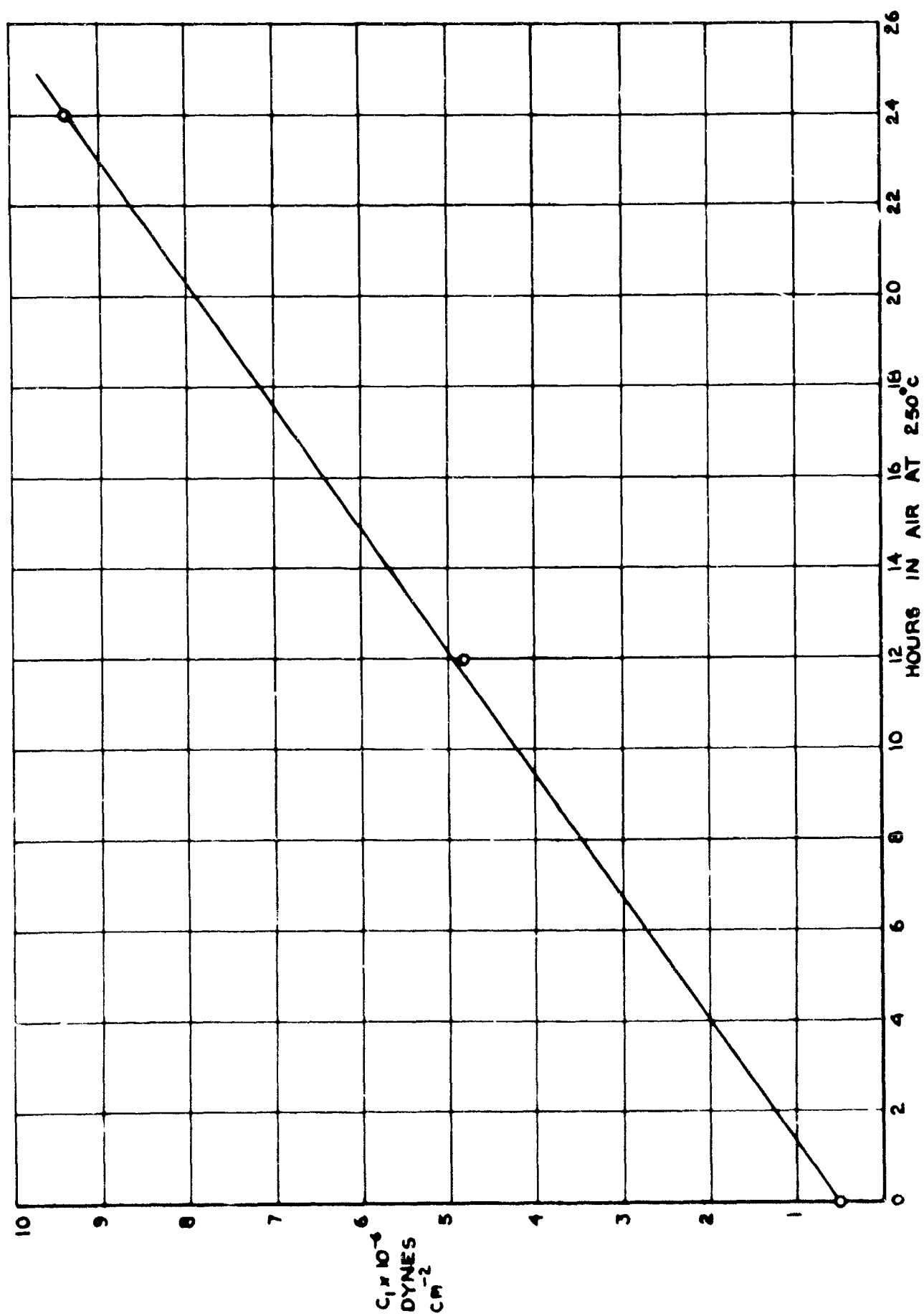


FIG 4 EFFECT OF POST-CURE ON C_1 IN Me-Vi SILICONE