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DIRECTORATE OF MATERIALS RESEARCH AND DEVELOPMENT

VULCANIZATION OF FLUORINE-CONTAINING POLYMERS

A. NODER-BLANCO and W. FLAVELL
(Yarsley Research Laboratories, Limited)

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FOREWORD

This report was prepared by Yarsley Research Laboratories Ltd. for the Directorate of Materials and Structures Research and Development Ministry of Technology, under Contract No. KS/1/0493/CB 43A2 and is based upon work carried out for the same authority under Contract No. KS/1/0124/CB 43A2 over the period March 1962 to March 1965.

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ADMINISTRATION OF WORK

The work was planned, progressed and administered under the direction of A.D.Mat.(N.M.), Ministry of Aviation.

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AUTHOR AND CONTRIBUTORS

The work described in this report was carried out by Dr. A. Nodar-Blanco, with experimental assistance by Messrs. J. Bayne and P. de la Morena, and Miss A. Willows. Most of the analyses and infra-red spectra were determined by Yarsley Testing Laboratories under the supervision of Mr. I. Muten. Physical tests on vulcanized rubbers were carried out by Yarsley Testing Laboratories Ltd. under the supervision of Messrs. D. J. Trafford and J. A. Mead. Compounding of vulcanizates was carried out by Messrs. M.H. Elson, D. Munday and G. L. Redfearn.

The work was under the general direction of Mr. W. Flavell, Manager, Chemical Research Department, Yarsley Research Laboratories Ltd.

PATENT APPLICATIONS

The following patent applications have been filed.

1. British Application No. 23507/65 (2nd June 1965).
2. United States Application No. 517,989 (3rd January 1966).

SUMMARY

An investigation has been WAS carried out into novel systems for the vulcanization of Viton A, in the hope that vulcanizates displaying improved properties at high temperature (especially with regard to compression set) would result.

The following systems have been studied:

1. p-xylylene dihalides in conjunction with sodium alkoxides.
2. 4, 4'-dichloromethyl diphenyl oxide in conjunction with sodium alkoxides.
3. Quaternary ammonium compounds.
4. Dihydric phenols in conjunction with sodium alkoxides.
5. 4,4'dihydroxymethyl diphenyl oxide in conjunction with sodium alkoxides.
6. 4,4'-diazidodiphenyl.
7. 4,4'-diphenyl bis (diazonium fluoroborate).
8. Pyromellitic dianhydride (dipotassium salt).
9. Dihydrophenazine.

Systems 1 and 3 above have been investigated in greatest detail. It has been found that quaternary ammonium salts, both bifunctional and monofunctional, are effective vulcanizing agents, the former being the more effective. The preferred vulcanizing system is comprised of a mixture of equal parts of calcium oxide and 1,4-phenylene dimethylene bis (triethyl ammonium chloride). This system gives vulcanizates with compression set at high temperatures superior to those given by dicinnamylidene hexamehtylene diamine. Other mechanical properties and resistance to ageing at 250°C in air are similar for vulcanizates prepared with 1,4-phenylene dimethylene bis(triethyl ammonium chloride) and with dicinnamylidene hexamethylene diamine.

(This report contains no classified information of overseas origin)

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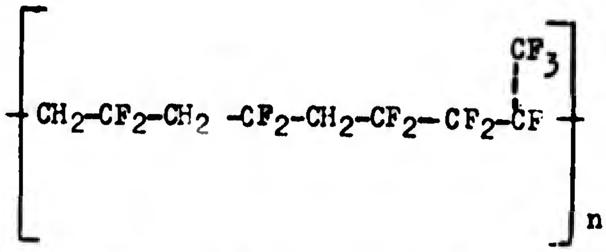
1. INTRODUCTION

Fluorinated elastomers such as the "Vitons" and "Fluorel", copolymers of vinylidene fluoride and hexafluoropropene, possess excellent thermal stability in the raw gum state, combined with good resistance to many oils and chemicals. The structure of these elastomers can be represented as:-



$$\left[-CH_2-CF_2-CH_2-CF_2-CH_2-CF_2-CF_2-\overset{CF_3}{\overset{|}{C}}F-\right]_n$$

As the polymer chain contains no significant amount of unsaturation, the techniques which are used for the vulcanization of conventional elastomers cannot be applied in the case of Viton. Three general methods have been reported for the vulcanization of elastomers of this type, namely:-

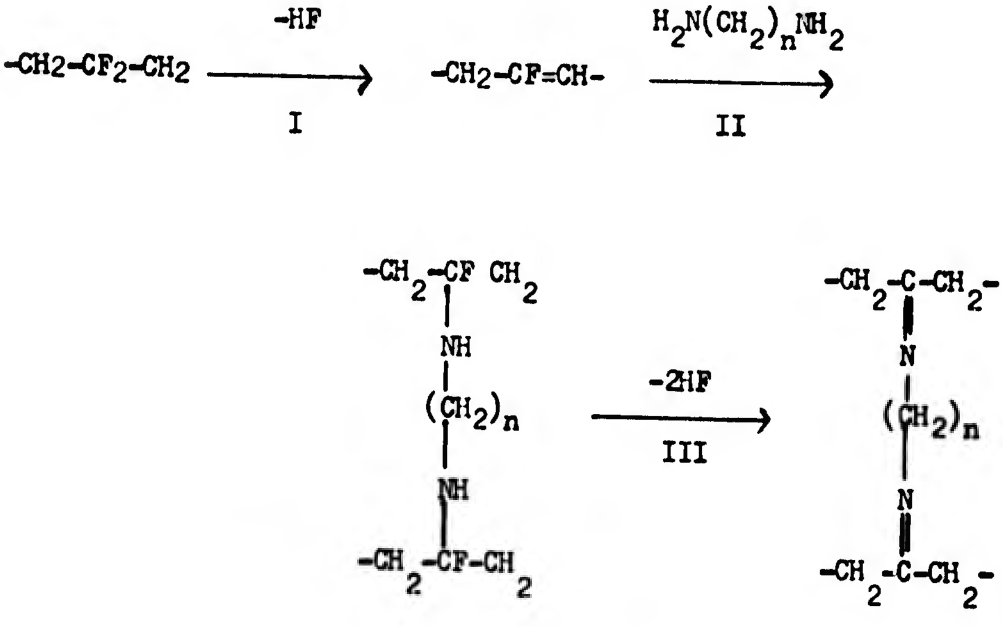
(a) the action of peroxides at high temperature

(b) the use of high energy radiation

(c) reaction with polyamines, or simple derivatives thereof.

The last-named is the most widely used commercially.

It has been fairly well established that cross-linking of Viton with amines takes place through a preliminary elimination of hydrogen fluoride to produce a double bond. This reacts with more amine to produce a saturated, unstable structure, which tends to lose hydrogen fluoride to form double bonds in the cross-link. The cross-linking reaction has been postulated[1] as taking place in three stages:-



Concurrently with imine formation, carbon to carbon double bonds are formed, and it has been suggested[2] that the gain in mechanical properties observed when Viton compounds are heated in a ventilated oven at 200-205°C is due to the interaction of neighbouring chains through these unsaturated centres, to form additional cross-links of much higher thermal stability.

Amine derivatives which are, or have been, used commercially for the vulcanization of Viton include hexamthylene diamine dicarbamate, ethylene diamine dicarbamate and dicinnamylidene hexamethylene diamine. In all cases a metal oxide (CaO, MgO or PbO) is added to the compound to assist the cure and to take up hydrogen fluoride which is eliminated. The dicarbamates present some difficulties in that they are inclined to scorch, and also tend to cause porosity through evolution of carbon dioxide. The curing agent which is currently preferred is dicinnamylidene hexamethylene diamine.

The present techniques used for the vulcanization of Viton have deficiencies, in that they introduce centres of lower thermal stability, either in the cross-links themselves or at the junctions of the cross-links with the main chains. This is reflected in lower stability of vulcanized Viton as compared with the raw gum, and some loss in mechanical properties (tensile strength and modulus, compression set, etc.) on prolonged ageing at elevated temperatures.

The objective of the work described in this report was to develop new systems for the vulcanization of Viton which would produce vulcanizates with improved thermal stability. The guiding principle behind most of the work was to devise systems which would cross-link Viton without going through a stage which involved elimination of HF and formation of unsaturated centres.

2. PROGRAMME

The programme as originally planned envisaged that novel cross-linking systems would be devised on the basis of experiments with model compounds, representing parts of the "Viton" molecule, and that such novel systems would later be applied to the rubber itself. In practice, the model compound approach proved to be unrewarding and therefore this aspect of the programme was abandoned, and effort was concentrated upon a study of the vulcanization of "Viton" itself using novel cross-linking agents.

In this part of the work, swelling of the vulcanizates by solvent and solubility were used as the first screening criteria, and promising formulations were then evaluated with respect to thermal stability. Selected formulations were then tested with respect to mechanical properties of vulcanizates such as compression set at elevated temperatures, tensile strength and modulus, and elongation at break.

3. WORK CARRIED OUT AND RESULTS OBTAINED

3.1. General background

The novel cross-linking systems evaluated in this work can be divided into three groups, based on the type of bond expected to be formed between the Viton polymer and the cross-linking agent.

Type of Bond	Cross-linking Agents
Carbon-carbon	p-xylylene dihalides 4,4'-dichloromethyl diphenyl oxide quaternary ammonium compounds.
Carbon-oxygen	dihydric phenols 4,4'-dihydroxymethyl diphenyl oxide
Carbon-nitrogen	4,4'-diazidodiphenyl 4,4'-diphenyl bis(diazoniumfluoroborate) pyromellitic diimide dihydrophenazine

3.2. Cross-linking systems forming carbon-carbon bonds

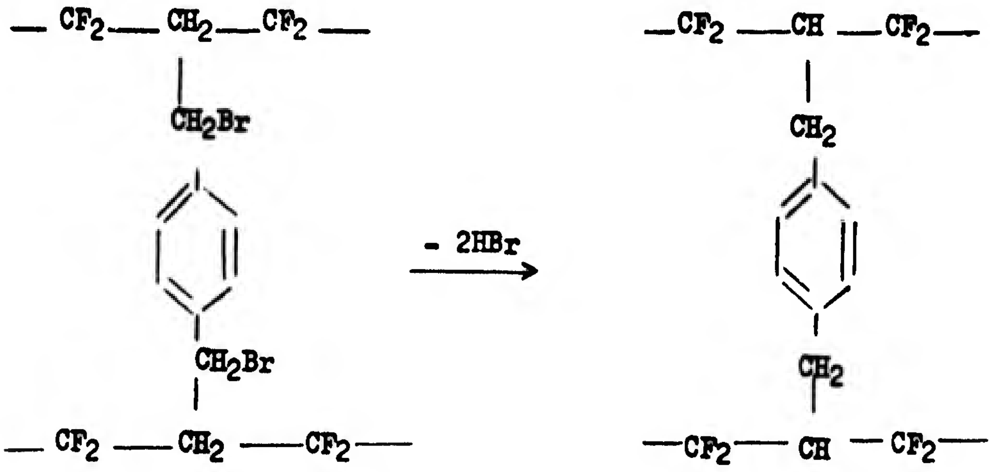
3.2.1. p-xylylene dihalides

3.2.1.1. Introduction

The possibility that p-xylylene dihalides might be useful as cross-linking agents for Viton was suggested by the observation of Bergman and Szinai(3) that benzyl bromide reacts with ethyl fluoroacetate:-

$$PhCH_2Br + FCH_2.CO_2Et \rightarrow PhCH_2CHFCO_2Et$$

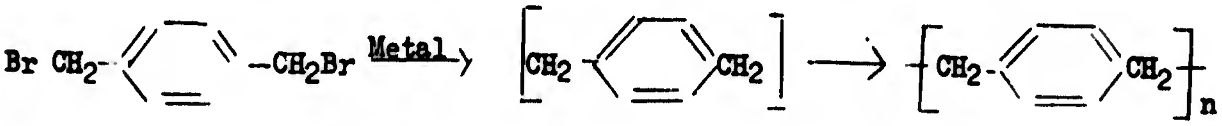
This suggested the possibility that the methylene groups of the Viton backbone might be sufficiently activated by the presence of the adjacent strongly electronegative CF_2 groups to make them reactive towards bifunctional compounds analogous to benzyl bromide. The type of reaction envisaged was as follows.



Some initial experiments were done on the reactions between p-xylylene dibromide with simple model compounds representing the Viton chain, but these were abandoned in favour of an investigation on the rubber itself. Studies were carried out on the reactions between Viton A and p-xylylene dihalides in solution, excluding metal oxides and fillers in order to avoid complication of the experimental conditions.

Reaction of "Viton A" with p-xylylene dibromide in 1,2-dimethoxyethane failed to gel on refluxing at the boiling point of the solvent, the p-xylylene dibromide being quantitatively recovered. Viton A elastomer treated with p-xylylene dibromide and KF in 1,2-dimethoxyethane at 80°C did not result in gelation. After reaction, the polymer was precipitated with water and found to be still readily soluble in acetone. 68% of the p-xylylene dibromide was recovered unchanged, the rest of the p-xylylene dibromide being probably retained by the precipitated polymer, its presence being shown as sparkling crystals on the surface of the dried polymer.

Attempts were then made to cross-link "Viton A" with p-xylylene dibromide in the presence of metals. It is known that p-xylylene dibromide itself can be polymerised in the presence of metals, and 81% yield of poly p-xylylene has been reported by K. Sisido et al(4). The polymerization appears to take place through the formation of p-xylylene biradicals as follows:



It was speculated that if such biradicals were formed in the presence of "Viton A", interaction between them and the methylene groups in the Viton chain could be expected, with the consequent formation of cross-links.

Two experiments were carried out in solution using dimethyl formamide and tetrahydrofuran as solvents and iron powder as catalyst, but in neither case was appreciable cross-linking density attained as judged by solubility tests in acetone. The insoluble product which was isolated in both experiments did not melt up to 350°C, was insoluble in most common solvents, and although it was not fully studied it was believed to be poly p-xylylene.

3.2.1.2. Vulcanization experiments

In spite of the unpromising results of the solution experiments with Viton and p-xylylene dihalides, some trials were conducted in which the rubber was compounded with p-xylylene dibromide in the presence of sodium ethoxide, giving vulcanisates with swelling ratios similar to that obtained with dicinnamylidene hexamethylene diamine as vulcanizing agent. It was found that solubility and swelling ratio decreased as the sodium ethoxide concentration increased, but more than 10% (based on the weight of rubber) of sodium ethoxide gave compounds which were "scorchy" and difficult to process.

The percent retention of vulcanizing agent in the systems "Viton A"-p-xylylene dibromide-sodium ethoxide and "Viton A"-p-xylylene dichloride-sodium ethoxide was determined by heating the compounded, uncured mixtures at 200°C for given periods of time until no more solid material sublimed, the results being presented in Tables 1 and 2. 82.7% of p-xylylene dibromide was retained when no sodium ethoxide was included in the compounded mixture, and the retention rose to 93.9% when the concentration of sodium ethoxide was 8%. However, it should be pointed out that these data do not necessarily prove the unrecovered p-xylylene dihalide to be part of the polymer network.

A comparative study of the thermal stability at 300°C of Viton A vulcanisates prepared with p-xylylene dibromide-sodium ethoxide showed that, in the main, the thermal stability observed in air was maintained in oxygen (Fig.1). The thermal stability of Viton A vulcanisates prepared with p-xylylene dichloride-sodium ethoxide was also studied, the results being represented in Fig.2 The weight loss of these vulcanisates at 325° was higher than that of uncompounded Viton A itself and comparable with that of Viton A vulcanisates prepared with dicinnamylidene hexamethylene diamine, but at 300° they were slightly more stable than the raw polymer.

Viton A vulcanizates prepared with p-xylylene dihalides in conjunction with sodium ethoxide dissolved in acetone to the extent of 8 to 20%, which solubility was considered to be high in view of the low swelling values obtained with this solvent.

It had been observed that the mixture of p-xylylene dihalides and sodium ethoxide was not easy to disperse in the "Viton", and an attempt was therefore made to find out whether the high solubility in acetone was related to inefficient dispersion of the cross-linking agent, due to an undue shortening in the milling time, which is limited by the heat built up during the compounding. The results of this experiment are summarised in Table 3. Table 4 shows swelling, solubility and compression set data for some formulations prepared with p-xylylene dihalide-sodium ethoxide.

Sulphur has been extensively used in the vulcanization of unsaturated elastomers, and inasmuch as it appeared that the cross-linking system formed by p-xylylene dihalides and sodium ethoxide produces double bonds in Viton to a certain extent, it appeared worthwhile to investigate its action on the

Viton A vulcanizates prepared with p-xylylene dibromide and sodium ethoxide. It was found that the addition of 1% sulphur (based on polymer) appeared to diminish scorching and to increase the rate of cure during the press cure, giving no significant sacrifices in compression set (See Table 4).

3.2.2. 4,4'-dichloromethyl diphenyl oxide

A sample of 4,4'-dichloromethyl diphenyl oxide was obtained from Dow Chemical Co. under the label "Chloromethylated diphenyl oxide CMDPO-25". This material was shown to be a complex mixture from which the desired compound was obtained by repeated recrystallisations from petroleum ether (b.p. 40-60°) until a white crystalline material with a constant melting point was obtained.

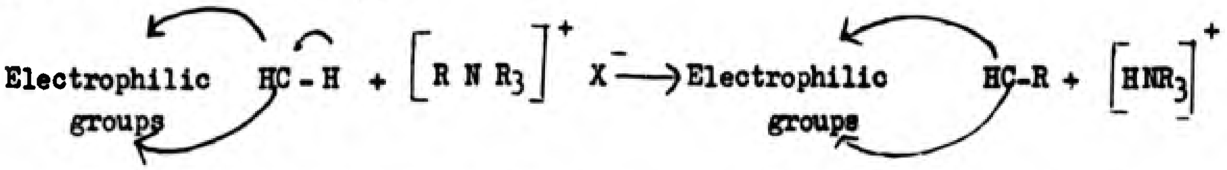
"Viton A" mixed with a filler and a metal oxide acid acceptor was vulcanized with 4,4'-dichloromethyl diphenyl oxide in the presence of sodium ethoxide or sodium methoxide, and in all cases vulcanizates were obtained with rather high solubility (13.3 to 43.7%) in acetone, the results being summarised in Table 5.

Compression set measurements were carried out on the most promising formulation (as judged by the thermal stability in air and oxygen, and by the swelling and solubility tests in acetone), the results being also summarised in Table 5.

3.2.3. Quaternary ammonium compounds

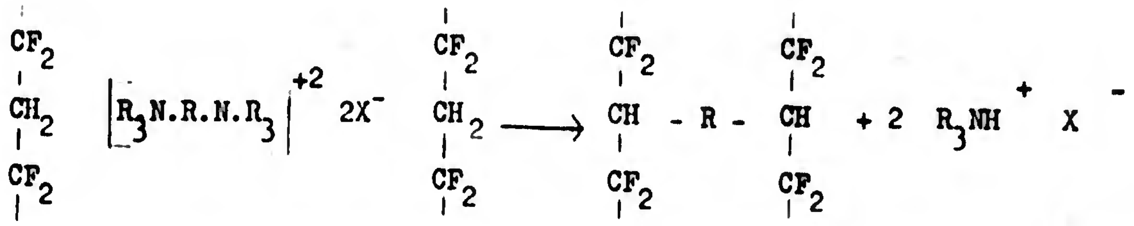
3.2.3.1. Introduction

Successful alkylation reactions of active methylene groups with quaternary ammonium derivatives have been reported (5), and it was originally suggested that the alkylation reactions proceed by the same elimination-addition mechanism as the alkylation with Mannich bases. On the other hand, it has been found (6) that alkylation reactions take place even with quaternary ammonium derivatives in which there is no possibility of decomposition to an olefinic substance. It therefore appears that elimination-addition is not the only path by which alkylation reactions with quaternary ammonium compounds may proceed, the alternative being direct substitution by an ionic path.



$$\text{Electrophilic groups} \; HC-H + \left[R\,N\,R_3\right]^+ X^- \longrightarrow \text{Electrophilic groups} \; HC-R + \left[HNR_3\right]^+ X^-$$

These ideas suggested the possibility of bifunctional quaternary ammonium derivatives acting as cross-linking agents for Viton in which the methylene groups are in such a position between two electronegative groups, that some degree of activation of the methylene hydrogens might be expected. The envisaged reaction is as follows:



$$\begin{array}{c}|\\CF_2\\|\\CH_2\\|\\CF_2\\|\end{array}\ \left[R_3N.R.N.R_3\right]^{+2}\ 2X^-\ \begin{array}{c}|\\CF_2\\|\\CH_2\\|\\CF_2\\|\end{array} \longrightarrow \begin{array}{c}|\\CF_2\\|\\CH\\|\\CF_2\\|\end{array} - R - \begin{array}{c}|\\CF_2\\|\\CH\\|\\CF_2\\|\end{array} + 2\ R_3NH^+\ X^-$$

It was originally though that the amine derived from the decomposition of the salt might be an effective catalyst, but this was found to be not the case with the quaternary ammonium derivatives which were tested, and the assistance of a basic catalyst to initiate the cross-linking reaction was found necessary. Monofunctional quaternary ammonium salts were also tested in this application and, somewhat surprisingly, were found to be effective cross-linking agents.

Six quaternary ammonium derivatives have been tested as cross-linking agents, comprising both mono- and difunctional compounds:

$$\left[(CH_3)_3\ N.CH_2.C_6H_4.\ CH_2.N\ (CH_3)_3\right]^{+2},\ 2Cl^-$$

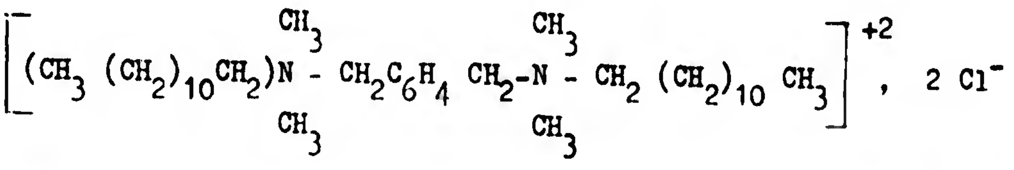
1,4-phenylene dimethylene bis (trimethylammonium chloride). (1,4-PDTMAC)

$$\left[(CH_3.CH_2)_3\ N.CH_2.C_6H_4-CH_2.N\ (CH_2.CH_3)\right]^{+2},\ 2Cl^-$$

1,4-phenylene dimethylene bis (triethylammonium chloride), 1,4-PDTEAC)

$$\left[(CH_3.(CH_2)_2\ CH_2)_3\ N-CH_2C_6H_4-CH_2-N(CH_2(CH_2)_2CH_3)_3\right]^{+2},\ 2Cl^-$$

1,4-phenylenedimethylene bis (tributylammonium chloride) (1,4-PDTBAC)



$$\left[(CH_3\ (CH_2)_{10}CH_2)\overset{CH_3}{\underset{CH_3}{N}} - CH_2C_6H_4\ CH_2-\overset{CH_3}{\underset{CH_3}{N}} - CH_2\ (CH_2)_{10}\ CH_3\right]^{+2},\ 2\ Cl^-$$

1,4-phenylene dimethylene bis (dimethyl lauryl ammonium chloride) (1,4-PDMLAC)

$$\left[(CH_3)_3\ N\ CH_2-C_6\ H_5\right]^{+},\ Cl^-$$

benzyl trimethyl ammonium chloride (BTMAC)

$$\left[ICH_3.CH_2)_3\ N-CH_2-C_6\ H_5\right]^{+},\ Cl^-\ \ (BTEAC)$$

benzyl triethyl ammonium chloride

All of the above when compounded with "Viton A", gave vulcanizates with comparable level of cure as judged by solubility and swelling experiments. The degree of swelling expressed as the volume fraction of rubber in the equilibrium swollen vulcanizate, and the solubility in acetone of "Viton A" vulcanizates prepared with quaternary ammonium compounds are recorded in Table 6.

Some of the quaternary ammonium derivatives were found to crystallise with several molecules of water and this led to trouble with blistering during the post-cure of thick slabs. The addition of calcium oxide in concentration equal to that of the cross-linking agent was found to alleviate this trouble to a considerable extent, but not completely to remove it. Some blistering was also obtained when using 1:4-PDTBAC, which does not contain water of crystallisation, but it is possible that in this case (and also in the case of other quaternary ammonium compounds which contain water) the blistering stems from water contained in the other components of the vulcanizate, e.g., the carbon black, or from water liberated by the cross-linking reaction.

Differential thermal analyses were carried out on 1,4-PDTEAC alone and in admixture with calcium oxide. The quaternary salts alone gave two distinct endothermic peaks, Fig.3, the first at about 167°, which is probably due to loss of water, and the second over the range 205-285°, which is probably due to melting of the salt. At higher temperatures exothermic decomposition occurs. In the presence of calcium oxide, Fig.3, the two peaks are almost fused into a single broad band and the point of maximum intensity of the second peak is displaced about 40°C towards lower temperature. The detailed interpretation of the role played by the calcium oxide in the vulcanization of "Viton A" with quaternary ammonium compounds is not clear, but there is no doubt from the experimental findings that the presence of calcium oxide is beneficial.

3.2.3.2. Curing cycle

In common with other curing systems for Viton, the quaternary ammonium salts require a two-stage cure: a press cure followed by an oven cure. The necessity for the oven cure is shown by the data presented in Figs.4 and 5. In general a press cure of 45 mins. at 160-170° was employed followed by cure in a ventilated oven rising from about 125°C to 205°C, followed by a hold at 205°C for periods up to 24 hours. The effect of varying the duration of the final hold at 205°C on the mechanical properties of Viton A vulcanizates cured with bifunctional and monofunctional quaternary ammonium compounds is shown in Tables 7 and 8 respectively.

Vulcanizates prepared with difunctional compounds show an increase in modulus during the first 7-8 hours of oven cure, after which time the modulus remains practically constant up to 24 hours cure. Elongation at break decreases to a substantially constant value over the same period of time.

These results suggest that the oven cure is almost completed during the first 7-8 hours. On the other hand, tensile strength reaches a maximum after 3 hours of the oven cure and then falls steadily.

The effect of the step-oven cure on the physical properties of the formulations prepared with monofunctional quaternary ammonium compounds is summarised in Table 9, in comparison with an oven cure in which the specimens were placed directly into an oven at 205°C.

Both treatments gave comparable figures although slightly higher results were obtained for the step-oven cured formulations which, moreover, were completely free from voids and imperfections.

3.2.3.3. Physical properties of vulcanizates

Formulations containing varying concentrations of the cross-linking agent, ranging from 1 to 4% (based on polymer), have been evaluated, and the results of the measurements of tensile strength, modulus and elongation at break are summarised in Tables 10 and 11.

It was found that, in general, on increasing the concentration of the cross-linking agent, the modulus increased proportionally while tensile strength and elongation at break decreased.

The compression set properties of "Viton A" vulcanizates prepared with quaternary ammonium compounds are listed in Table 12, as compared with those of a vulcanizate prepared with dicinnamylidene hexamethylene diamine.

The effect of a post-stoving for 24 hours at 250°C upon the mechanical properties of these vulcanizates is shown in Table 13.

Stress relaxation measurements carried out by the Royal Aircraft Establishment, on the vulcanizates prepared with the bifunctional quaternary ammonium compound 1,4-PDTEAC, showed these to be similar in behaviour to Viton cured with dicinnamylidene hexamethylene diamine. A post cure of 24 hours at 250°C and solvent extraction both improved thermal stability.

3.2.3.4. Resistance to ageing

Long term heat-ageing studies of some vulcanizates prepared with quaternary ammonium compounds were carried out, using volume swelling and solubility measurements as criteria, or by measuring the variation in tensile strength and modulus at 100% extension at different intervals over the ageing period. In the first case, ageing tests were run for 25 days at 250°C in a ventilated oven and the solubility and volume swelling results obtained are summarised in Table 14 and Fig.6 respectively.

The change in hardness on ageing at 250°C was very similar when using either dicinnamylidene hexamethylene diamine or the quaternary ammonium derivatives as cross-linking agents. The results are summarised in Table 15.

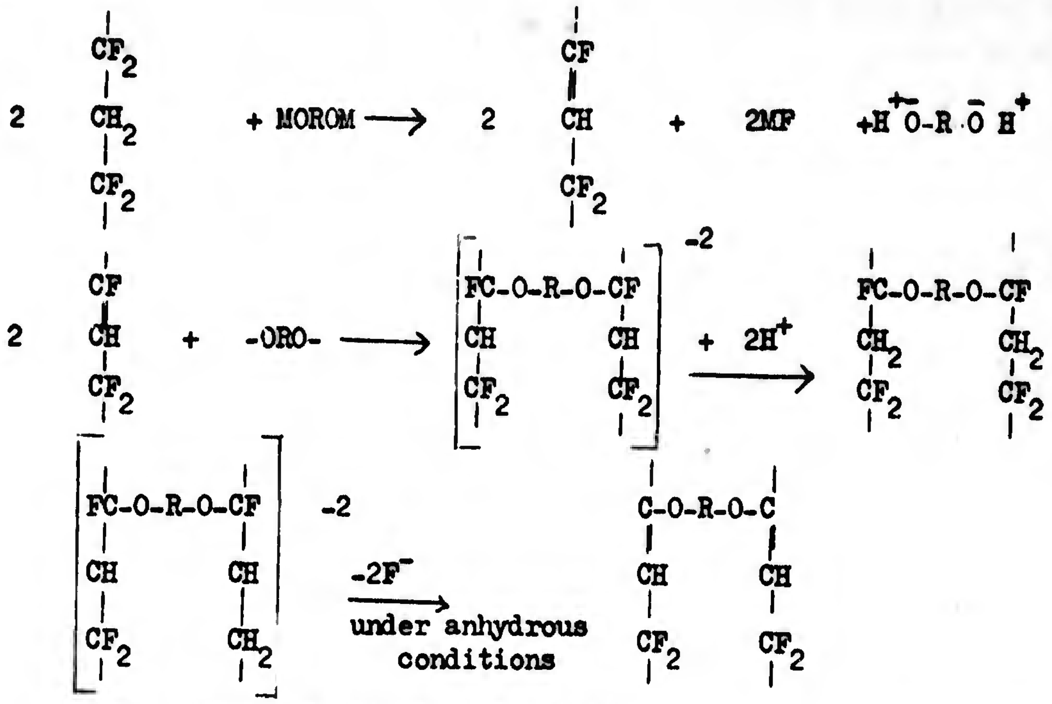
The resistance to ageing at 250°C of some vulcanizates was also studied by measuring the variation in tensile strength and modulus, tests being carried out at room temperature. The results are represented in Table 16, and Figures 7 and 8. Tensile strength increased during the first 15 hours and then decreased continuously for the rest of the ageing period. With respect to modulus, a sharp increase occurred during the first 15 hours followed by a fall with a minimum value after about 25 hours, and then increased continuously during the ageing period. Dicinnamylidene hexamethylene diamine and quaternary ammonium halide vulcanizates behaved similarly in this respect. The change in modulus between 15 and 40 hours during ageing might be interpreted as due to a rearrangement of the first network to a more stable second network. The resistance to compression set on ageing for long periods of time under compression was studied on vulcanizates prepared with 2% of 1,4-PDTEAC and the results are shown in Table 17 and Fig.9. Values are quoted at 160 and 250°C for vulcanizates which had been conditioned for 24 hours at 250°C in a relaxed state.

The long-term compression set results of Viton A vulcanizates prepared with 2% of 1,4-PDTEAC which had been oven-cured for only four hours at 200°, are also listed in Table 17 and represented in Fig.10, as compared with a similar vulcanizate which had been oven cured for 20 hours at the same temperature. Both vulcanizates had been preconditioned at 250°C for 24 hours before the long-term test was carried out. The 24 hour compression set at 160° of a 4 hour oven cured vulcanizate was in general higher than that obtained on a similar vulcanizate which had been oven-cured for 24 hours.

3.3. Cross-linking systems forming carbon-oxygen bonds

3.3.1. Hydroquinone-sodium ethoxide and 4,4'-dihydroxymethyl diphenyloxide-sodium ethoxide

Wall and his co-workers[7] have reported that tetrafluoroethyl phenyl ether, $C_6H_5.O.CF_2.CF_2H$, prepared by the reaction of sodium phenolate with tetrafluoroethylene, is very resistant to dehydrofluorination even by such reagents as molten NaOH at 250°C or KOH in boiling collidine. This indicated that the structures obtained by the addition of phenols to double bonds in the chain of "Viton A" might also withstand dehydrofluorination, and it was therefore considered that the reaction of metallic salts of dihydric phenols with "Viton A" should be investigated. The envisaged reactions are represented as follows:



R = phenylene radical; M = metal

The mechanism of this reaction is similar to that reported by Tarrant (8) for his preparation of various substituted fluoroethylenes by Grignard reagents.

Viton A vulcanizates prepared with hydroquinone or 4,4'-dihydroxymethyl diphenyl oxide conjunctly with sodium ethoxide showed high solubility in acetone, the latter producing vulcanizates with superior thermal stability (see Fig.11). Compounds containing carbon black were more thermally stable than those without carbon black.

Thermal stability measurements on the acetone-soluble matter extracted from "Viton A" compound prepared with 4,4'-dihydroxymethyl diphenyl oxide and sodium ethoxide are shown in Fig.11.

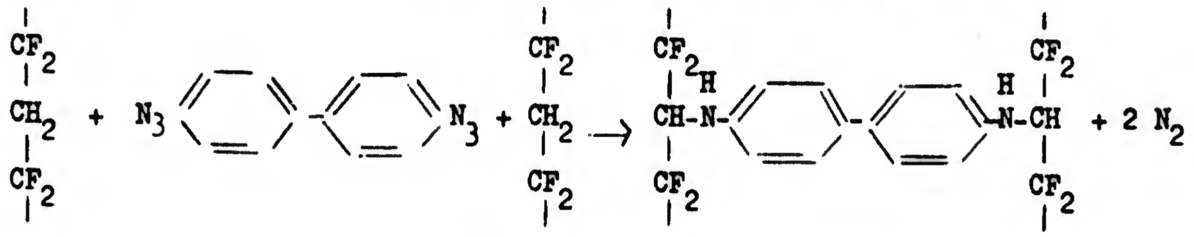
Compression set, swelling value and solubility of some formulations are given in Table 18.

3.4. Cross-linking systems forming carbon-nitrogen bonds

3.4.1. 4,4'-diazidophenyl and 4,4'-diphenyl bis(diazonium fluoroborate)

The reactions envisaged in the cross-linking of Viton with azides or with diazonium salts would in all cases involve the evolution of nitrogen and could proceed by ionic or free radical mechanisms or both, as various investigations of the decomposition of these types of compounds have shown.

Phenylazide PhN_3, is known to act, particularly in the presence of catalysts such as $AlCl_3$, as a source of Ph-N< radicals. This radical readily extracts hydrogen atoms from a variety of substances. Although phenyl azide itself is a rather unstable liquid and explodes on heating, 4,4'-diazidodiphenyl is much more stable thermally and can be readily prepared. The envisaged reaction of diazides with Viton is represented as follows:

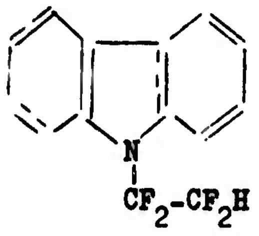


4,4'-diazidodiphenyl has been used alone or in the presence of benzoyl peroxide or $AlCl_3$ in an attempt to produce Viton A vulcanizates, but in all cases very porous vulcanizates have been obtained with high solubility in acetone, (see Table 19). The system 4,4'-diazidodiphenyl-$AlCl_3$ gave vulcanizates with poor thermal stability, but the weight loss of Viton A vulcanizates prepared with 4,4'-diazidoiphenyl alone was comparable with that found for Viton A compounds prepared with dicinnamylidene hexamethylene diamine (Fig.12). Decomposition products condensed on the cold parts of the apparatus as a brown resinous material, and the internal surface of the glass was severely etched.

Similar results have been achieved with Viton A vulcanizates prepared with 4,4'-diphenylbisdiazonium fluoroborate alone or in the presence of benzoyl peroxide, although their thermal stability was somewhat lower than that shown by the Viton A azide system (Fig.12).

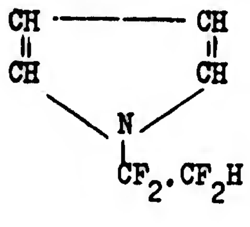
3.4.2. Pyromellitic diimide dipotassium salt and dihydrophenazine

In work carried out by Yarslev Research Laboratories under Contract No. KS/1/0108/CB 43A2 (9) the preparation of N-(1,1,2,2,-tetrafluoro ethyl) carbazole (I) was described.



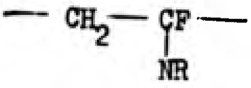
I

This compound proved to be resistant both to hydrolysis and to dehydrofluorination. The same compound had previously been reported by England et al (10) but no comment had been made on its stability. These authors also reported the preparation of N-(1,1,2,2,-tetrafluoroethyl) pyrrole (II) by the addition of pyrrole to tetrafluoroethylene.



II

This compound was shown to be stable to refluxing 20% KOH. Addition of, for example, carbazole to a double bond in the chain of Viton should give a structure of the type III.

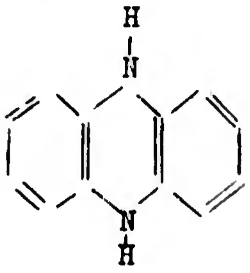


$$—CH_2—\underset{\displaystyle NR}{\underset{|}{CF}}—$$

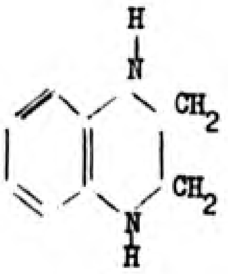
III (R = carbazole group)

By analogy with our earlier work and that of England et al, such a structure could be expected to be stable. It was therefore suggested that the reactions of suitable bifunctional nitrogenous compounds analogous to carbazole and/or pyrrole with "Viton A" should be investigated.

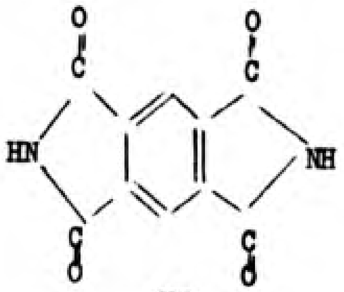
Examples of bifunctional nitrogenous compounds of possible use in this application are:- dihydrophenazine (IV), tetrahydroquinoxaline V, pyromellitic diimide VI, cyclopentanetetracarboxylic diimide (VII) and di-pyrrole VIII.



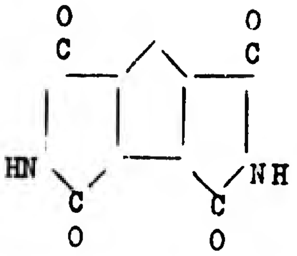
IV



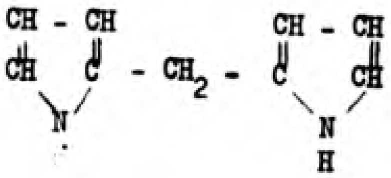
V



VI



VII



VIII

Of these, only IV and VI were briefly studied.

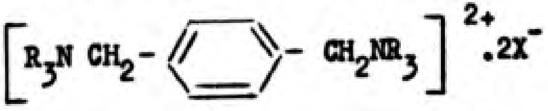
Both compounds produced Viton A vulcanizates with a low degree of cure as judged by their solubility in acetone, Table 20.

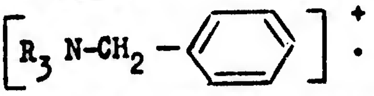
It has been found that the thermal stability of a Viton A compound prepared with 5% of the dipotassium salt of pyromellitic diimide is comparable with that found for a "Viton A" compound cured with dicinnamylidene hexamethylene diamine.

This approach has not been fully investigated because priority was given to other systems which appeared to be more promising in the preliminary tests.

4. CONCLUSIONS

The results reported show that quaternary ammonium compounds represent a useful new class of vulcanizing agents for Viton, and the properties of vulcanizates prepared with such compounds are, in some cases, superior to those obtained by the use of a conventional vulcanizing agent such as dicinnamylidene hexamethylene diamine.

Both bifunctional quaternary ammonium salts of general formula 

and monofunctional salts of general formula 

appear to be effective vulcanizing agents. While a mechanism has been proposed for the cross-linking by the difunctional compounds, it is not clear how vulcanisation takes place when using the monofunctional compounds.

The preferred quaternary ammonium salt is 1,4-phenylene dimethylene bis (triethyl ammonium chloride) and, by using this compound, vulcanizates have been prepared which show improved compression set characteristics as compared with dicinnamylidene hexamethylene diamine as vulcanizing agent. The other mechanical properties which have been measured (tensile strength and modulus, and elongation at break) are not inferior to those given by dicinnamylidene hexamethylene diamine. On long term ageing in air at 250°C, the vulcanizates based on the quaternary ammonium salt and on the blocked diamine behave similarly.

When using dicinnamylidene hexamethylene diamine as cross-linking agent, it is necessary to employ an oven cure of some 24 hours at 200-205°C in order to develop the optimum properties in the vulcanizate. There is some evidence that a high degree of cure is achieved in the case of vulcanizates based on quaternary ammonium compounds when using a shorter oven cure at 205°C, e.g. 4-8 hours. This offers the possibility of significant saving in processing costs.

The vulcanizates based on 1,4-phenylene dimethylene bis (triethyl ammonium chloride) are easy to process and show no excessive tendency to scorch. It has been found advantageous, particularly in the moulding of thick sections, to premix the quaternary ammonium salt with an equal weight of calcium oxide. This eliminates any tendency to form voids in the mouldings.

5. EXPERIMENTAL

5.1. PREPARATION AND PURIFICATION OF NOVEL CROSS-LINKING AGENTS

5.1.1. Xylylene dihalides

The xylylene dihalides which have been used throughout this work are commercially available materials and they were used without further purification.

5.1.2. Purification of 4,4'-dichloromethyl diphenyl oxide

A portion (10g.) of the commercially available crude material, consisting of a heterogeneous mixture of solid and liquid components, was filtered by suction in order to separate the yellow liquid from the white solid (6.2g., m.p. 57-62°C), which was then boiled for 10 minutes with pet. ether (b.p. 40-60°C). The clear solution was filtered while hot from an oily material which solidified after cooling, and this was extracted three times more with more pet. ether. A white crystalline solid (4.8g., m.p. 60-64°C) precipitated from the united pet. ether fractions after cooling to room temperature, the solid being collected in a sintered glass funnel and dried in a desiccator over silica gel-paraffin wax. This solid was recrystallised twice to a constant melting point 64-65°C. Yield 4.2g. Reported melting point 50-65°C (11), depending on the concentration of 4,4'-dichloromethyl diphenyl oxide in the mixture of isomers.

5.1.3. Purification of 4,4'-dihydroxymethyl diphenyl oxide

The commercially available buff coloured, waxy solid (10g.) was refluxed with benzene for 15 minutes, and the colourless benzene solution decanted while hot from a yellow oil which remained insoluble in the bottom of the flask. A white crystalline material precipitated at once from the solution as it was slowly cooled to room temperature. The solid was filtered and dried in a desiccator. 8g. of material, m.p. 110-120°, were recovered. This material was recrystallised three times to a constant melting point 135-136°, the overall yield being 5.4g.

In another experiment, water was used as solvent and the material (10g.) had to be recrystallised four times to attain a constant melting point 136°C. Yield 5.8g.

5.1.4. Preparation of the quaternary ammonium salts

Several quaternary ammonium salts of p-xylylene dihalides have been prepared. The following is a typical preparation.

Preparation of 1,4-phenylene dimethylene bis (dimethyl phenyl ammonium bromide).

A mixture of p-xylylene dibromide (1.32g.; 0.005 mole) and dimethylaniline (2.42g.; 0.02 mole) in ethyl acetate was refluxed for one hour. The resulting precipitate was separated and washed three times with anhydrous ether. The solid crystalline material weighed 1.8g. (71% of the theoretical) after being dried overnight in a desiccator under vacuum, m.p. 145-146°C.

Purification of the sample for analysis:

0.4g. of the crude material was dissolved in boiling absolute alcohol (10 ml.) and the clear solution allowed to cool to room temperature overnight. A needle-like precipitate was filtered off, washed with a few drops of absolute alcohol and dried in a desiccator under vacuum overnight. The solid weighed 0.233g., m.p. 154-155°C. A second recrystallisation was carried out with 0.20g. of product and 0.186g. (93%) of white crystalline product was recovered. m.p. 154-155°C.

0.184g. of the product with constant melting point was kept in a drying pistol for two hours at 56°C under 0.05 mm. Over 6 hours the sample lost 11.7% of its original weight, which corresponds to the loss of 4 molecules of water from hexahydrate. The same amount of water was rapidly absorbed on exposure to the atmosphere, to give the hexahydrate.

The elemental analysis of the dried sample showed a bromine content corresponding to the dihydrate.

	% Br
Calculated for $C_{24}H_{30}N_2Br_2.2H_2O$	29.5
Found	29.6

The following quaternary ammonium derivatives of p-xylylene dihalides with various other tertiary amines were obtained in a similar manner.

1,4-phenylene dimethylene bis (trimethyl ammonium bromide)

	White solid, m.p. over 320°C	% Br
Anal.	Calculated for $C_{14}H_{26}N_2Br_2$	41.8
	Found	41.6

1,4-phenylene dimethylene bis (tributylammonium chloride)

	White solid, m.p. 196-198°C	% Cl
Anal.	Calculated for $C_{32}H_{62}N_2Cl_2$	13.0
	Found	13.10

1,4-phenylene dimethylene bis (2,2-diethoxy)ethyl dimethyl ammonium bromide

	White solid, m.p. 197°C	% Br
Anal.	Calculated for $C_{24}H_{46}N_2O_4Br_2$	27.2
	Found	27.3

Preparation of 1,4-phenylenedimethylene bis(triethyl ammonium chloride)

p-Xylylene dichloride (3.49g.) and triethylamine (4.45g., 10% excess over the theoretical) were dissolved in acetonitrile and allowed to react for 48 hours at room temperature. A fine crystalline precipitate was obtained, which was filtered off, washed with acetone and finally dried in a desiccator under vacuum. The bulk product weighed 7.01g. (92.9% of the theoretical), m.p. 230-232°C. A small portion was dissolved in a mixture of acetone and ethanol and reprecipitated by adding dry ether, this process being repeated until a constant melting point 272-275° was obtained.

		% Cl
Anal.	Calculated for $C_{30}H_{38}N_2Cl_2 4H_2O$	15.8
	Found	15.5

Preparation of 1,4-phenylene dimethylene bis (trimethyl ammonium chloride)

p-Xylylene dichloride (3.5g.) and 5 ml. of a 40% alcoholic solution of trimethylamine were dissolved in acetonitrile and the mixture kept for 48 hours at room temperature. A large excess of dry ether was then added to the solution and the crystalline precipitate was filtered, washed with acetone and dried.

Yield 4.23g. (90% of the theoretical), m.p. over 300°C.

Preparation of 1,4-phenylenedimethylene bis(dimethyl lauryl ammonium chloride)

p-Xylylene dichloride (3.5g.) and dimethyl lauryl amine (6.39g.) were dissolved in acetonitrile and allowed to react overnight at room temperature. A white, crystalline precipitate was obtained which was filtered off, washed with acetone and finally dried in a desiccator under vacuum.

Yield 7.7g., m.p. 230°C.

Preparation of trimethyl benzyl ammonium chloride

Benzyl chloride (6.25g.) was weighed into a 50 ml. conical flask and dissolved in 10 ml. of acetonitrile. A 40% ethanolic solution of triethylamine 8.88g.) was added dropwise while the reaction flask was kept at room temperature by cooling in an ice-bath. The reaction was very exothermic. The mixture was allowed to stand at room temperature for 4 hours, but no precipitate appeared at this stage; some dry ether was added in order to induce crystallisation, and a white crystalline material began to precipitate at once. The mixture was kept overnight at room temperature and the solid material filtered and washed with a small portion of acetonitrile, and then diethyl ether, being finally dried in a desiccator under vacuum.

Yield 5.75g., m.p. 240-242°C.

Preparation of triethyl benzyl ammonium chloride

Benzyl chloride (6.3g.) and triethylamine (5.27g.) were dissolved in acetonitrile (10 ml.) and the mixture allowed to react at room temperature for 72 hours. An abundant, white, crystalline material precipitated and was filtered and washed with small portions of acetonitrile and then dry ether.

Yield 8g., m.p. 195°C.

5.1.5. Preparation of 4,4'-diazidodiphenyl

Benzidine (2.42g.) was dissolved in conc. hydrochloric acid (6.5 ml.) and 65 ml. of water. The solution was cooled to 0°C and sodium nitrite (1.8g.) was slowly added. The diazonium salt solution was mixed with a solution of p-toluenesulphonamide (4.6g.) and sodium hydroxide (4.8g.) in 50 ml. of water at -5°C. The mixture was allowed to stand for 12 hours at room temperature and after this period of time the orange precipitated product was filtered, washed several times with water, and recrystallised from ethyl alcohol.

Yield 2g., m.p. 126-127°C. Literature m.p. 127° (12).

5.1.6. Preparation of 4,4'-diphenyl bisdiazonium fluoroborate

40% Fluoroboric acid (19 ml.) was placed into a 100 ml. 3-necked round-bottomed flask fitted with a stirrer and condenser. Water (19 ml.) was added to dilute the acid, and then benzidine (3.7g.) carefully added to this solution which was previously cooled in an ice-bath. Ice-cooled sodium nitrite (1.4g.) solution was slowly added to the stirred mixture, the temperature not being allowed to exceed 10°C.

On continued stirring the precipitate gradually thickened especially near the end of the reaction. The mixture was cooled in an ice-bath and filtered. The precipitate was washed with cold 5% fluoroboric acid until a clear yellow filtrate was obtained, then cold methanol and finally ether. The powdery, creamish-yellow solid, after being dried in air for 3 hours, weighed 6.5g. Decomposition temp. 137°C, which agrees well with the value reported in the literature. (13).

5.1.7. Preparation of the diimide of pyromellitic acid

In a Pyrex 100 ml. round-bottomed flask were placed a mixture of pyromellitic dianhydride (2.18g., 0.01 mole) and 28% aqueous ammonia (2.7ml.; 0.04 mole). The flask was fitted with an air condenser and was then slowly heated in an oil bath until the temperature was about 200°C in the bath. It was necessary, during the heating period, to shake the flask occasionally. The reaction was completed after 5 hours heating. After this period of time, the reaction flask was allowed to cool to room temperature, and the reaction mixture was washed several times with water to extract some unreacted ammonium salt. The residue was dried and recrystallised from dimethyl formamide.

Yield, 1.8g. m.p. 441°C with decomposition. Quoted melting point 440°C with decomposition (14).

5.1.8. Preparation of the dipotassium salt of pyromellitimide

Pyromellitimide (2.16g.; 0.01 mole) was dissolved in a solution of potassium hydroxide (1.12g.; 0.02 mole) in 10 ml. of water. The aqueous solution of the dipotassium pyromellitimide was poured into 30 ml. of absolute alcohol. A crystalline precipitate appeared at once, which was filtered and dried overnight in a desiccator over $CaCl_2$. Yield 2.2g.

5.2. Cross-Linking Experiments in solution

5.2.1. Attempted cross-linking of "Viton A" with p-xylylene dibromide in the presence of metals

a) Solvent, DMF "Viton A" (5g.) was dissolved in 100 ml. of dimethyl formamide (DMF) and p-xylylene dibromide (0.4g.) was added with constant stirring and finally iron metal (200 mesh)(0.125g.) was introduced into the mixture. The reaction mixture was stirred for one hour at room temperature and benzoyl peroxide 0.1g. was added while stirring. Temperature was increased to 100°C and reaction was allowed to proceed for four hours. At this stage, a second portion of benzoyl peroxide (0.1g.) was added and the temperature was increased to 130°C, this temperature being held for 16 hours. The reaction mixture was centrifuged and the solid washed with acetone, water and finally dilute hydrochloric acid. The residue was a yellowish organic material which did not melt below 350°C, and was insoluble in most common organic solvents. This material was thought to be poly p-xylylene. In the aqueous extracts were qualitatively identified Br^-, F^-, Fe^{+++}, and amine. The fraction soluble in DMF was precipitated with water and the insoluble material was uncross-linked "Viton A" as judged by its solubility in acetone.

In another experiment, cross-linked "Viton A" deposited on the walls of the flask when DMF was partially distilled off, but this cross-linking was due to the free amine present in the DMF itself, as proved by a blank experiment with DMF and Viton A alone.

b) Solvent THF "Viton A" (5g.) was dissolved in THF (50 ml.), and p-xylylene dibromide (0.4g.) and 200 mesh Zn metal (0.125g.) were added. The mixture was stirred while benzoyl peroxide (0.1g.) was added, and then allowed to react for 8 hours under reflux. The reaction mixture was treated as in a, the same products, except amine, being found. The THF solution of the soluble portion was poured into water and "Viton A" was recovered and found to be completely soluble in acetone, indicating that no cross-linking had taken place.

5.2.2. Reaction of "Viton A" and p-xylylen dibromide in 1,2-dimethoxyethane

"Viton A" (2.35g.) was dissolved in 30 ml. of 1,2-dimethoxyethane, and 2.3g. of p-xylylene dibromide added. The mixture was placed in a 100 ml. flask and refluxed for 20 hours with constant stirring. The course of the reaction was followed by passing any gas from the reaction through a dilute solution of NaOH containing a drop of phenolphthalein. No acidic gases able to decolorise the phenolphthalein were evolved. After 20 hours the reaction mixture was allowed to cool to room temperature and 2.3g. (100%) of p-xylylene dibromide were recovered.

5.2.3. Reaction of "Viton A" and p-xylylene dibromide in presence of potassium fluoride

In a 250 ml. flask were placed 2.35g. of "Viton A" together with 30 ml. of 1,2-dimethoxyethane, 2.3g. of p-xylylene dibromide and 0.2g. of potassium fluoride. The mixture was heated under reflux for 8 hours. Little, if any, evidence of reaction was observed, so the mixture was boiled for four days under an ultraviolet lamp (Hanovia 200 watts). Again, the reaction was followed by absorbing the cooled gases in a sodium hydroxide solution containing a drop of phenolphthalein, but no change in the red colour of the phenophthalein was observed. 1.57g. of material m.p. 145° were recovered. "Viton A" dissolved in the 1,2-dimethoxyethane was precipitated by pouring the solution into water. The precipitated material was completely soluble in M.E.K.

5.2.4. Reaction of "Viton A" with p-xylylene dibromide at 200° in a sealed tube

"Viton A" (0.57g.) was dissolved in 20 ml. of 1,2-dimethoxyethane placed in a thick-walled tube and 1g. of p-xylylene dibromode added. The tube was sealed and kept at 200°C for 48 hours. After this time, the solution had turned slightly red, but it was completely transparent. The tube was opened, and the contents poured into water. 1.12g. of solids were recovered. The recovered Viton was found to be completely soluble in M.E.K. The water in which the Viton was precipitated gave a positive test for bromide, no fluoride being found.

5.3. PREPARATION OF VULCANISATES

5.3.1. Materials

5.3.1.1. Fillers

The addition of reinforcing filler to Viton is necessary to increase modulus, reduce elongation and increase the hardness of the vulcanisates. MT carbon black has been found to be a satisfactory filler and was used in all vulcanizates.

5.3.1.2. Acid acceptors

It is common practice to add metallic oxides or salts to act as acid acceptors and neutralise acidic materials which may be evolved at the high temperatures of cure or in use. Such ingredients are essential to develop a high state of cure and maximum heat resistance in the vulcanisate. The type and grade of acid acceptor can exert a marked influence on the properties of the end product. In the work described in this report, a special grade of magnesium oxide, "Maglite Y", was used, and appears to give a good balance of properties.

5.3.1.3. Calcium oxide

When using quaternary ammonium salts as vulcanising agents, the salt was premixed with an equal weight of calcium oxide. A grade sold as "Calcium Oxide VG" was found to be suitable for this purpose.

5.3.2. Milling procedure

Typical "Viton A" formulations employing the novel cross-linking systems were prepared by conventional mill mixing techniques using either a 4" x 2" laboratory mill or a 12" x 6" mill. After banding the rubber on the mill, the metal oxide was added, followed by the filler and finally the vulcanizing agent. In those cases where the cross-linking agent was a mixture of two components, usually both components were mixed before being added to the stock; such was the case of vulcanizates prepared with quaternary ammonium compounds and calcium oxide, hydroquinone and sodium ethoxide, and 4,4'-dihydroxymethyl diphenyl oxide and sodium ethoxide. In some cases the two components were added separately, the less active being added first. Thus, the preparation of vulcanizates containing p-xylylene dihalides and sodium ethoxide was carried out by adding to the stock first the p-xylylene dihalide, followed by the sodium ethoxide.

In general, Viton A vulcanizates prepared with the novel cross-linking agents were press-cured for 30 to 60 minutes at 140-170°C followed by a step-cure in a ventilated oven rising at 25°C/hour from 125°C plus 17-24 hours at 205°C.

5.4. TEST PROCEDURES

5.4.1. Swelling and solubility studies

Samples of about 0.1g. were cut from sheets 0.020" thick and accurately weighed, then placed in about 70 ml. of solvent (acetone or MEK) and allowed to swell for seventy-two hours at 23-25°C. The swollen samples were surface dried and re-weighed in tared stoppered bottles. The samples were finally dried in a vacuum oven at 50°C to constant weight. The swelling ratio was calculated from the formula:-

$$\text{Swelling ratio, } Q = \frac{\text{Weight of swollen vulcanizate}}{\text{Weight of dried sample}}$$

The initial and final weights give the soluble fraction, and using 0.78 and 1.78 as the densities at 25°C of acetone and Viton A respectively, the volume fraction of rubber V_R can also be calculated. The weight of the extracted vulcanizate was corrected for the weight of insoluble compounding material present, prior to computing the volume fraction in the swollen sample.

5.4.2. Thermal stability

Samples with swelling ratio below 10 and solubility less than 25% were chosen for the thermal stability studies. The weight loss on heating in air or oxygen for 6 hours at different temperatures was determined on single specimens of about 10mg. in a quartz spring thermobalance. In an alternative procedure, several samples of about 0.2g. were heated in an oven, samples being withdrawn at intervals. The period of heating and the temperature were usually arbitrarily selected, but in some cases samples had been previously studied to find out the range of temperatures which should be investigated. All samples had been heated in vacuo at 140°C to constant weight before carrying out the tests.

The experiments in oxygen were carried out using oxygen pressure of 300 mm.

5.4.3. Determination of the percent retention of vulcanising agent in the system "Viton A"-p-xylylene dichloride-sodium ethoxide

Uncured samples of Viton A vulcanizates prepared with p-xylylene dichloride-sodium ethoxide were cut into very small pieces after milling and placed into a tube fitted with a cold finger and a side arm through which the system was kept under slightly diminished pressure while heating at 200°C.

The sublimed material was collected every two hours by immersing the end of the cold finger in ether contained in a small flask which had been previously weighed. Each experiment took about 18 hours to complete. The other solution was carefully evaporated and the residue dried in a desiccator over $CaCl_2$ and P_2O_5.

The melting point of the recovered material and mixed melting point with authentic p-xylylene dichloride were identical with that of pure p-xylylene dichloride. The experimental results found for the samples are shown in Table 2.

5.4.4. Compression set measurements

Compression set measurements were carried out according to B.S.903, A6, 1963 at 160° and 250°. Discs 0.25" thick and 0.55" in diameter were compressed by 25 percent of their original thickness and aged under these conditions at the given temperature during the experimental period. On being released from compression, the samples were allowed to recover for ten minutes at the experimental temperature plus ten minutes in water at room temperature, and their thickness measured with a B.S.907 domed surface thickness gauge.

5.4.5. Tensile strength, elongation at break and modulus

Tensile strength, modulus and elongation at break were measured on samples 0.05" thick cut with a B.S.903 type E dumb-bell cutter and tested at a cross-head speed of 20 in./min. at 22°C.

/REFERENCES
TABLES
FIGURES

6. REFERENCES

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TABLE 1

Retention of p-xylylene dibromide in the system Viton A/p-xylylene dibromide/NaOEt

Basic formulation:		
	Viton A	5g.
	MT carbon black	1g.
	Magnesium oxide	0.75g.
	XDB	0.19g.
	NaOEt	as table

Compound Reference	% NaOEt (based on Viton)	X.D.B. recovered (g.)	X.D.B. retained (% of amount added)
X.D.B.1	Nil	0.03296	82.7
X.D.B.2	2	0.01992	90.1
X.D.B.3	4	0.01253	93.4
X.D.B.4	8	0.01175	93.9

TABLE 2

Retention of p-xylylene dichloride in the system Viton A/p-xylylene dichloride/NaOEt

Basic formulation:		
	Viton A	5g.
	MT carbon black	1g.
	Magnesium oxide	0.75g.
	X.D.C.	0.15g.
	NaOEt	as table

Compound Reference	% NaOEt (based on Viton)	X.D.C. recovered (g)	X.D.C. retained (% of amount added)
X.D.C.1	4	0.062	59.7
X.D.C.2	7	0.040	73.9
X.D.C.3	10	0.029	80.6

TABLE 3

Effect of milling time upon acetone solubility of Viton A/p-xylylene dichloride/NaOEt vulcanizates

Formulation:		
	Viton A	100g.
	MT carbon black	20g.
	Magnesium oxide	15g.
	X.D.C.	3g.
	NaOEt	10g.

Compound Reference	Milling Time (minutes)	Solubility (%)
X.D.C.3 (15)	15	8.8
X.D.C.3 (30)	30	9
X.D.C.3 (45)	45	8.7
X.D.C.3 (60)	60	9

TABLE 4

Swelling, solubility and compression set data on vulcanizates of Viton/p-xylylene dihalides/NaOEt

Formulae	Compound reference				
	X.D.B.1	X.D.B.S	X.D.C.1	X.D.C.2	X.D.C.3
Viton A	100	100	100	100	100
MT carbon black	20	20	20	20	20
MgO	15	15	15	15	15
X.D.B.	3.8	3.8	-	-	-
NaOEt	10	10	4	7	10
Sulphur	-	1	-	-	-
X.D.C.	-	-	3	3	3
Cure	Press cure:- 30 mins. at 150°C Oven cure:- Rise from 125° to 200°C 17 hrs. at 200°C				
Swelling ratio	1.05	-	1.48	1.37	1.35
Solubility (%)	8.6	-	24.8	10.8	9.3
Compression set at 160°C (%)	51	30	-	-	31
Compression set at 250°C (%)	100	82	-	-	100

Notes: X.D.B. = p-xylylene dibromide

X.D.C. = p-xylylene dichloride

TABLE 5

Swelling and solubility data on vulcanizates of Viton A/4, 4'-dichloromethyl diphenyl oxide/sodium alkoxide

Formulae	Compound reference											
	DDO 1	DDO 2	DDO 3	DDO 4	DDO 5	DDO 6	DDO 7	DDO 8	DDO 9	DDO 10	DDO 11	DDO 12
Viton A	100	100	100	100	100	100	100	100	100	100	100	100
MT Carbon black	20	20	20	20	20	20	20	20	20	20	20	20
MgO	15	15	15	15	15	15	15	15	15	15	15	15
DDO	5	10	5	10	5	10	5	10	5	10	5	10
NaOEt	3	3	6	6	10	10	-	-	-	-	-	-
NaOMe	-	-	-	-	-	-	2	2	5	5	7	7
Cure	Press cure:- 30 mins at 150°C Oven cure:- 3 hours at 150°C 24 hours at 205°C											
Swelling ratio	2.99	1.8	-	2.04	1.00	1.24	2.58	2.29	1.65	1.38	1.24	2.69
Solubility (%) in acetone	34.6	32.8	21.2	25.6	13.3	17.4	41.5	42.2	23.0	36.8	19.0	33.9
Compression set	-	-	-	-	24	-	-	-	-	-	-	-
Compression set at 250°C (%)	-	-	-	-	81	-	-	-	-	-	-	-

DDO - 4,4'-dichloromethyl diphenyl oxide

TABLE 6

Swelling and solubility in acetone at 25°C of Viton A vulcanized with quaternary ammonium salts

Composition: Viton A, 100
MT carbon black, 20
MgO, 15
Curing agent, see Table

When quaternary ammonium derivatives were used as curatives, CaO was added in the same proportion as the curative

Press cure:- 45 mins. at 165°C
Oven cure:- Rising from 125°C
to 205°C
24 hours at 205°C

Curing agent	Concentration %	Solubility %	Swelling ratio
Dicinnamylidene hexamethylene diamine	1	5.1	2.6
	2	4.2	2.4
	3	2.3	2.1
"	4	1	1.5
"	5	0.4	1.2
1,4-PDTEAC	1	5.2	2.79
"	2	3	2.50
"	3	1.5	2.11
"	4	0.5	1.31
"	5	0.2	1.12
1,4-PDTBAC	1	2.76	3.01
"	2.5	0.77	2.81
"	4	0.45	2.12
"	5	0	1.81
1,4-PDDMLAC	1	11.42	3.21
"	2	4.27	2.63
"	3	2.51	2.41
"	4	1.54	2.15
"	5	1.63	1.91

Cont'd.

TABLE 6 (Contd.)

Curing agent	Concentration %	Solubility %	Swelling ratio
1,4-PDTMAC			
"	2	6.1	2.61
"	3	2.2	2.22
"	4	2	1.51
"	5	1	1.20
TEBAC	1	5.4 (without CaO)	2.67
	1	3.7 (with CaO)	2.37
"	2	3.2	2.03
"	3	2.6	1.95
"	4	1.9	1.88
"	5	1	1.78
TMBAC	1	4.8	2.48
"	2	2.9	2.31
"	3	2.6	1.88
"	4	1.5	2.04
"	5	1	2.10

TABLE 7

Effect of duration of oven cure on mechanical properties of Viton A vulcanized with 1,4-phenylene dimethylene bis (triethyl ammonium chloride)

Formula:-		
	Viton A	100
	MT carbonblack	20
	MgO	15
	PDTEAC) premix	1
	CaO) premix	1

Press cure:- 45 mins. at 165°C.

Oven cure:- Rise from 125°C to 205°C at 25°C per hr.

Hold at 205°C as shown in table.

Duration of oven cure (hrs.)	0	3	7	16	24
Tensile strength (p.s.i.)	2210	2920	2740	2510	2375
Ditto. (N/M^2) ($X10^5$)	152	210	188.5	173	163
100% modulus (p.s.i.)	300	400	420	490	460
Ditto. (N/M^2) ($X10^5$)	20.7	27.6	28.9	33.8	31.7
Elongation at break (%)	540	400	330	260	330

TABLE 8

Effect of duration of oven cure on mechanical proerties of Viton A vulcanized with benzyl triethyl ammonium chloride

Formula:-		
	Viton A	100
	MT carbon black	20
	MgO	15
	BTEAC } Premix	2
	CaO } Premix	2

Press cure:- 45 mins. at 165°C.

Oven cure:- Rise from 125°C to 205°C at 25°C per hr.,
Hold at 205°C as shown in table.

Duration of oven cure (hrs.)	0	2	4	6	16
Tensile strength (p.s.i.)	1970	2190	2150	2215	2270
Ditto (N/M^2) ($X10^5$)	136	151	148	152	156
100% Modulus (p.s.i.)	675	1235	1300	1230	1490
Ditto (N/M^2) ($X10^5$)	46.5	85	89.5	85	103
Elongation at break (%)	230	160	150	150	130

TABLE 9

Effect of type of oven cure on mechanical properties of vulcanizates of Viton A with mono-functional quaternary ammonium salts

Formulae	Compound Reference			
	BEAC 4		BMAC 4	
Viton A	100		100	
MT carbon black	20		20	
MgO	15		15	
BEAC } premixed	2		-	
CaO	2		-	
BMAC } premixed	-		2	
CaO	-		2	
Cure cycle	A	B	A	B
Ultimate tensile strength (p.s.i.)	2460	2230	2550	2150
Ditto (N/M^2) ($X10^5$)	169.3	153.7	175.7	148.1
100% Modulus (p.s.i.)	2180	2160	1360	1250
Ditto (N/M^2) ($X10^5$)	150.2	148.8	93.6	86.1

BEAC - benzyl triethyl ammonium chloride

BMAC = benzyl trimethyl ammonium chloride

Cure cycle A:- Press cure 45 mins. at 160°C, then cure in a ventilated oven rising at 25°C per hour from 125°C to 205°C, plus 20 hours at 205°C.

Cure cycle B:- Press cure 45 mins. at 160°C, then cure 20 hours in a ventilated oven at 205°C.

TABLE 10

Effect of concentration of monofunctional quaternary ammonium salts on mechanical properties of Viton A vulcanizates

Formulae	Compound Reference							
	BEAC 2	BEAC 3	BEAC 4	BEAC 5	BMAC 2	BMAC 3	BMAC 4	BMAC 5
Viton A	100	100	100	100	100	100	100	100
MT carbon black	20	20	20	20	20	20	20	20
MgO	15	15	15	15	15	15	15	15
BEAC premixed	1	1.5	2	2.5	-	-	-	-
CaO	1	1.5	2	2.5	-	-	-	-
BMAC premixed	-	-	-	-	1	1.5	2	2.5
CaO	-	-	-	-	1	1.5	2	2.5
Cure	45 mins. press cure at 165°C, followed by oven cure rising at 25°C per hour from 125°C to 205°C, plus 24 hours at 205°C							
Ultimate tensile strength (psi)	1730	1750	2450	2000	2175	2490	2620	2000
Ditto (N/m^2) ($X10^5$)	119.1	120.5	168.9	137.7	149.9	171.5	180.4	137.7
100% modulus (psi)	845	1430	2170	-	740	850	1350	2000
Ditto (N/m^2) ($X10^5$)	58.2	98.5	149.5	-	51.0	58.6	93.0	137.7
Elongation at break (%)	173	116	108	83	206	180	180	100

BEAC = benzyl triethyl ammonium chloride

BMAC = benzyl trimethyl ammonium chloride

TABLE 11

Effect of concentration of vulcanizing agent upon the mechanical properties of Viton A vulcanized with 1,4-phenylene dimethylene bis (triethylammonium chloride)

Formulae	Compound Reference				
	D3	PDEAC 2	PDEAC 4	PDEAC 6	PDEAC 8
Viton A	100	100	100	100	100
MT Carbon black	20	20	20	20	20
MgO	15	15	15	15	15
D	3	-	-	-	-
PDTEAC } premixed	-	1	2	3	4
CaO	-	1	2	3	4
Cure	Press cure 45 mins. at 165°C, followed by oven cure rising at 25°C per hour, from 125° to 205°C, plus 24 hours at 205°C				
Ultimate tensile strength (psi)	2320	2375	2300	1880	1870
Ditto $(N/m^2)(X10^5)$	159.9	163.7	159.0	129.5	128.8
100% modulus (psi)	800	460	1090	1660	-
Ditto $(N/m^2)(X10^5)$	55.1	31.7	75.1	114.2	-
Elongation at break (%)	190	335	180	130	110
Hardness	75	62	65	70	-
Weight loss during cure (%)	1.9	1.1	-	-	-
Shrinkage during press cure (%)	2.5	2.2	-	-	-
Shrinkage during oven cure (%)	1.7	1.3	-	-	-
Compression set (%) 24 hours at 160°C	20.3	-	9	-	-
24 hours at 250°C	97	-	45	-	-

D = dicinnamylidene hexamethylene diamine

TABLE 12

Compression set data on Viton A vulcanized with quaternary ammonium salts

Formulae	Compound Reference					
	D3	PDEAC 4	PDBAC 4	PDLAC 6	BMAC 6	BEAC 6
Viton A	100	100	100	100	100	100
MT Carbon black	20	20	20	20	20	20
MgO	15	15	15	15	15	15
D	3	-	-	-	-	-
PDTEAC	-	2	-	-	-	-
PDTBAC	-	-	2	-	-	-
PDMLAC	-	-	-	3	-	-
BTMAC	-	-	-	-	3	-
BTEAC	-	-	-	-	-	3
Press cure 45 mins. at 165°C, followed by oven cure rising from 125°C to 205°C at 25°C per hour, plus 24 hours at 205°C						
Compression set at 160°C (%)	20	9.6	14.1	18.3	18	23
Compression set at 250°C (%)	100	45	37	93.2	100	100

N.B. The quaternary ammonium salts were premixed with a equal amount of calcium oxide. The quantities shown in the table represent the weight of quaternary ammonium salt alone.

D = dicinnamylidene hexamethylene diamine

PDTEAC = 1,4-phenylene dimethylene bis (triethyl ammonium chloride)

PDTPAC = 1,4-phenylene dimethylene bis (tributyl ammonium chloride)

PDMLAC = 1,4-phenylene dimethylene bis (dimethyl lauryl ammonium chloride)

BTMAC = benzyl trimethyl ammonium chloride

BTEAC = benzyl triethyl ammonium chloride

TABLE 13

Effect of post-stoving on mechanical properties of Viton A vulcanized with 1,4-phenylene/dimethylene bis(triethyl ammonium chloride). (Compare Table 11)

Formulae		Compound Reference	
	D3	PDEAC2	PDEAC4
Viton A	100	100	100
MT carbon black	20	20	20
MgO	15	15	15
D	3	-	-
PDTEAC) premixed	-	1	2
CaO)	-	1	2
Cure	Press cure 45 mins. at 165°C. Oven cure rising at 25°C per hr. from 125°C to 205°C. 24 hours at 205°C. 24 hours at 250°C.		
Ultimate tensile strength (p.s.i.)	2360	2300	-
Ditto (N/M^2) ($X10^5$)	162.5	158.4	
100% Modulus (p.s.i.)	1290	560	-
Ditto (N/M^2) ($X10^5$)	89.0	38.6	
Elongation at break (%)	150	280	-
Compression set			
24 hrs. at 160°C	7.5	-	3.6
72 hrs. at 160°C	20	-	14
500 hrs. at 160°C	50	-	42

D = dicinnamylidene hexamethylene diamine

PDTEAC = 1,4-phenylene dimethylene bis(triethyl ammonium chloride)

TABLE 14

Effect of ageing at 250°C on the solubility in acetone of Viton A vulcanizates

Formula:		
	Viton A	100
	MT carbonblack	20
	MgO	15
	Vulcanizing agent:-	See table

Cure: Press cure 45 mins. at 165°C.
Oven cure rising from 125°C to 205°C at 25°C per hour. 24 hrs. at 205°C.

Days heating at 250°C	% Soluble in acetone at 23-25°C		
	Vulcanizing agent		
	D (3%)	PDTEAC (3%)	PDTEAC (4%)
1	6.7	6.7	3.6
2	7.2	7.6	5
3	7.6	7.8	6.3
4	7.8	8	6.8
5	8	8.2	7.2
10	8.2	8.2	7.3
15	9	8	7.5
18	9.5	7	7
20	10	7	7
23	10.5	6.5	6.2
25	10.8	6	6.2

D = dicinnamylidene hexamethylene diamine
PDTEAC = 1,4-phenylene dimethylene bis(triethyl ammonium chloride)
The quaternary ammonium salt was premixed with an equal weight of calcium oxide.

TABLE 15

Variation in hardness during ageing at 250°C of vulcanizates prepared with 1,4-PDTEAC at different concentrations

Formula	Viton A	100
	MT Carbon black	20
	MgO	15
	Vulcanizing agent:- see table	
Cure	Press cure 45 mins. at 165°C	
	Oven cure rising at 25°C per hour from 125°C to 205°C	
	Oven cure 20 hours at 205°C	

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Number of hours aged	D	Concentrations of PDTEAC		
	3%	2%	3%	4%
20 at 205°C (nil ageing)	75	65	67	63
24 at 250°C	76	62	65	62
48 Ditto	74	61	65	63
72 "	73	59	67	60
96 "	72	62	67	67
120 "	74	65	69	63
168 "	79	62	69	66
192 "	78	65	74	68
216 "	77	66	80	65
240 "	78	66	78	65
264 "	81	65	78	69
336 "	86	75	76	80
360 "	89	83	81	83
384 "	93	80	90	87
408 "	91	82	95	88
432 "	90	86	92	86
528 "	93	86	96	92
552 "	91	84	99	90
576 "	92	82	95	91
600 "	95	91	99	96

D = dicinnamylidene hexamethylene diamine
PDTEAC = 1,4-phenylene dimethylene bis (triethyl ammonium chloride)

The quaternary ammonium salt was premixed with an equal weight of calcium oxide.

TABLE 16

Effect of ageing at 250°C in air on the mechanical properties of Viton A vulcanizates

Formulae	Compound Reference	
	D 3	PDEAC 2
Viton A	100	100
MT carbon black	20	20
MgO	15	15
D	3	-
PDTEAC)	-	1
CaO)premix	-	1
Cure	Press cure:- 45 mins. at 165°C Oven cure :- Rise to 205°C at 25° per hr. 24 hrs. at 205°C	

Hours ageing at 250°C	Tensile strength				100% Modulus				Elongation at break (%)	
	D3		PDEAC2		D3		PDEAC2		D3	PDEAC2
	psi	N/m^2 (X 10^5)	psi	N/m^2 (X 10^5)	psi	N/m^2 (X 10^5)	psi	N/m^2 (X 10^5)		
0	2320	160	2430	168	850	59	420	29	200	330
15	2610	180	2500	173	1440	99	650	45	180	230
24	2510	173	2500	173	1290	89	560	39	150	280
210	1950	135	1940	134	1910	132	1190	82	110	150

D = dicinnamylidene hexamethylene diamine

PDTEAC = 1,4-phenylene dimethylene bis (triethyl ammonium chloride)

TABLE 17

Long-term compression set data on Viton A vulcanized with 1,4-phenylene dimethylene bis(triethyl ammonium chloride)

Formula	Viton A		100
	MT Carbon black		20
	MgO		15
	PDTEAC)	premixed	2
	CaO)		2

Cure

A. Press cure 45 mins. at 165°C
Oven cure rising at 25°C per hr. from 125°C to 205°C
Oven cure 20 hours at 205°C, followed by 24 hrs. at 250°C.

B. Press cure 45 mins. at 165°C
Oven cure rising at 25°C per hr. from 125°C to 205°C
Oven cure 4 hrs. at 205°C, followed by 24 hrs. at 250°C.

C. Press cure 45 mins. at 165°C
Oven cure rising at 25°C per hr. from 125°C to 205°C
Oven cure 4 hrs. at 205°C.

Days under compression at indicated temperature	Compression set (%) 160°C			250°C		
	A	B	C	A	B	C
1	3.2	9.7	42	67	57	100
2	7.9	14.7	-	-	62	-
3	14.2	16.2	-	92.6	83	-
5	20.2	-	-	-	-	-
8	30.2	29.8	-	-	-	-
15	38.7	-	-	-	-	-
20	41.9	49.7	-	-	-	-

TABLE 18

Swelling, Solubility and compression set data on Viton A vulcanized with hydroquinone/NaOEt or 4,4'-dihydroxymethyl diphenyl oxide/NaOEt.

Formulae	Compound Reference					
	H1	H2	H3	DHO1	DHO2	DHO3
Viton A	100	100	100	100	100	100
MT carbon-black	20	20	20	20	20	20
MgO	15	15	15	15	15	15
Hydroquinone	1.25	7.55	11	-	-	-
4,4'-dihydroxymethyl diphenyl oxide	-	-	-	4	7	10
NaOEt	2	2	6.8	1.92	3.72	4.72
Cure	Press cure:- 30 mins. at 150°C. Oven cure:- Step-cure to 200°C, then 17 hrs. at 200°C					
Swelling ratio	1.4	3.01	-	2.5	1.9	2.3
Solubility in acetone at 25°C(%)	15.6	21.4	-	36.9	24.6	23.8
Compression set (%)						
At 160°C	39	39	30	-	30	-
At 250°C	96	96	80	-	96	-
Weight loss over 6 hrs. in air at 330°C(%)	15.2	-	-	-	-	12.4

TABLE 19

Swelling and solubility data on Viton A vulcanised with 4,4'-diazide diphenyl or 4,4'-diphenyl bis (diazonium fluoroborate)

Formulae	Compound reference										
	Az1	AZ2	AZ3	AZ4	AZ5	AZ6	AZ7	DDFI	DDF2	DDF3	DDF4
Viton A	100	100	100	100	100	100	100	100	100	100	100
MT carbon black	20	20	20	20	20	20	20	20	20	20	20
MgO	15	15	15	15	15	15	15	15	15	15	15
AZ	10	20	2	5	5	10	20	-	-	-	-
Benzoyl peroxide	-	-	2	2	5	-	-	-	2	2	5
$AlCl_3$	-	-	-	-	-	5	6.18	-	-	-	-
DDF	-	-	-	-	-	-	-	2.6	2	5	10
Cure	Press cure:- 45 mins. at 112°C Oven cure:- Rise from 145°C to 200°C 17 hrs. at 200°C							Press cure:- 30 mins. at 145°C Oven cure:- Rise from 145°C to 200°C 17 hrs. at 200°C			
Swelling ratio	5.8	2.8	4.7	3.6	8.2	2.3	4.95	17	2.2	3.7	3.7
Solubility in acetone at 25°C (%)	25.4	21.1	34.1	28.0	38.9	10.5	19.6	51.0	20.0	17.9	21.6

AZ = 4,4'-diazidodiphenyl

DDF = 4,4'-diphenyl bis (diazonium fluoroborate)

TABLE 20

Swelling and solubility data on Viton A vulcanised with pyromellitic diimide dipotassium salt or with dihydrophenazine

Formulae	Compound reference		
	PD1	DHP1	DHP2
Viton A	100	100	100
MT carbon black	20	20	20
MgO	15	15	15
PD	5	-	-
DHP	-	12	12
NaOEt	-	9.4	-
AZDN	-	-	5
Cure	Press cure:- 30 mins. at 150°C. Oven cure:- Rise from 125°C to 200°C. 17 hrs. at 200°C.		
Swelling ratio	1.6	1.5	4.1
Solubility in acetone at 25°C. (%)	15.2	11.1	37.5

PD = dipotassium salt of pyromellitic diimide
DHP = dihydrophenazine
AZDN = azo bis (isobutyronitrile).

TABLE 21

Experimental Viton A vulcanizates - Summary of formulations

Compound Reference	XDB 1	XDB 2	XDB 3	XDB 4	XDC 1	XDC 2	XDC 3	XDBS	DDO 1	DDO 2	DDO 3	DDO 4	DDO 5	DDO 6
Viton A	100	100	100	100	100	100	100	100	100	100	100	100	100	100
MT Carbon black	20	20	20	20	20	20	20	20	20	20	20	20	20	20
MgO	15	15	15	15	15	15	15	15	15	15	15	15	15	15
p-xylylene dibromide	3.8	3.8	3.8	3.8	-	-	-	3.8	-	-	-	-	-	-
sodium ethoxide	-	2	4	8	4	7	10	10	3	3	6	6	10	10
p-xylylene dichloride	-	-	-	-	3	3	3	-	-	-	-	-	-	-
sulphur	-	-	-	-	-	-	-	1	-	-	-	-	-	-
4,4'-dichloro methyl diphenyl oxide	-	-	-	-	-	-	-	-	5	10	5	10	5	10

(Continued)

TABLE 21 (Contd.)

Compound Reference	DDO 7	DDO 8	DDO 9	DDO 10	DDO 11	DDO 12	BEAC 2	BEAC 3	BEAC 4	BEAC 5	BEAC 6	BMAC 2	BMAC 3	BMAC 4	BMAC 5
Viton A	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
MT Carbon black	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
MgO	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Sodium Methoxide	2	2	5	5	7	7	-	-	-	-	-	-	-	-	-
4,4'-dichloromethyl diphenyl oxide	5	10	5	10	5	10	-	-	-	-	-	-	-	-	-
BTEAC	-	-	-	-	-	-	1	1.5	2	2.5	3	-	-	-	-
BTMAC	-	-	-	-	-	-	-	-	-	-	-	1	1.5	2	2.5
CaO	-	-	-	-	-	-	1	1.5	2	2.5	3	1	1.5	2	2.5

(Continued)

TABLE 21 (Contd.)

Compound Reference	PDEAC 2	PDEAC 4	PDEAC 6	PDEAC 8	PDBAC 4	PDLAC 6	H1	H2	H3	DHO1	DHO2	DHO3
Viton A	100	100	100	100	100	100	100	100	100	100	100	100
Mt Carbon black	20	20	20	20	20	20	20	20	20	20	20	20
MgO	15	15	15	15	15	15	15	15	15	15	15	15
PDTEAC	1	2	3	4	-	-	-	-	-	-	-	-
PDTBAC	-	-	-	-	2	-	-	-	-	-	-	-
PDMLAC	-	-	-	-	-	3	-	-	-	-	-	-
CaO	1	2	3	4	2	3	-	-	-	-	-	-
Hydroquinone	-	-	-	-	-	-	1.25	7.55	11	-	-	-
4,4'-dihydroxymethyl diphenyl oxide	-	-	-	-	-	-	-	-	-	4	7	10
Sodium ethoxide	-	-	-	-	-	-	2	2	6.8	1.92	3.72	4.72

(Continued)

TABLE 21 (Contd.)

Compound Reference	AZ 1	AZ 2	AZ 3	AZ 4	AZ 5	AZ 6	AZ 7	DDF 1	DDF 2	DDF 3	DDF 4	PD1	DHP1	DHP2	D3
Viton A	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
MT Carbon black	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
MgO	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
AZ	10	20	2	5	5	10	20	-	-	-	-	-	-	-	-
DDF	-	-	-	-	-	-	-	2.6	2	5	10	-	-	-	-
PD	-	-	-	-	-	-	-	-	-	-	-	5	-	-	-
DHP	-	-	-	-	-	-	-	-	-	-	-	-	12	12	-
AZDN	-	-	-	-	-	-	-	-	-	-	-	-	-	5	-
Sodium ethoxide	-	-	-	-	-	-	-	-	-	-	-	-	9.4	-	-
Benzoyl peroxide	-	-	2	2	5	-	-	-	2	2	5	-	-	-	-
D	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3
Aluminium chloride	-	-	-	-	-	5	6.18	-	-	-	-	-	-	-	-

NOTES ON TABLE 21

BTEAC = benzyl triethyl ammonium chloride

BTMAC = benzyl trimethyl ammonium chloride

PDTEAC = 1,4-phenylene dimethylene bis (triethyl ammonium chloride)

PDTBAC = 1,4-phenylene dimethylene bis (tributyl ammonium chloride)

PDMLAC = 1,4-phenylene dimethylene bis (dimethyl lauryl ammonium chloride)

AZ = 4,4'-diazido diphenyl

DDF = 4,4'-diphenyl bis (diazonium fluoroborate)

PD = dipotassium salt of pyromellitic diimide

DHP = dihydrophenazine

AZDN = azo bis (isobutyronitrile)

D = dicinnamylidene hexamethylene diamine

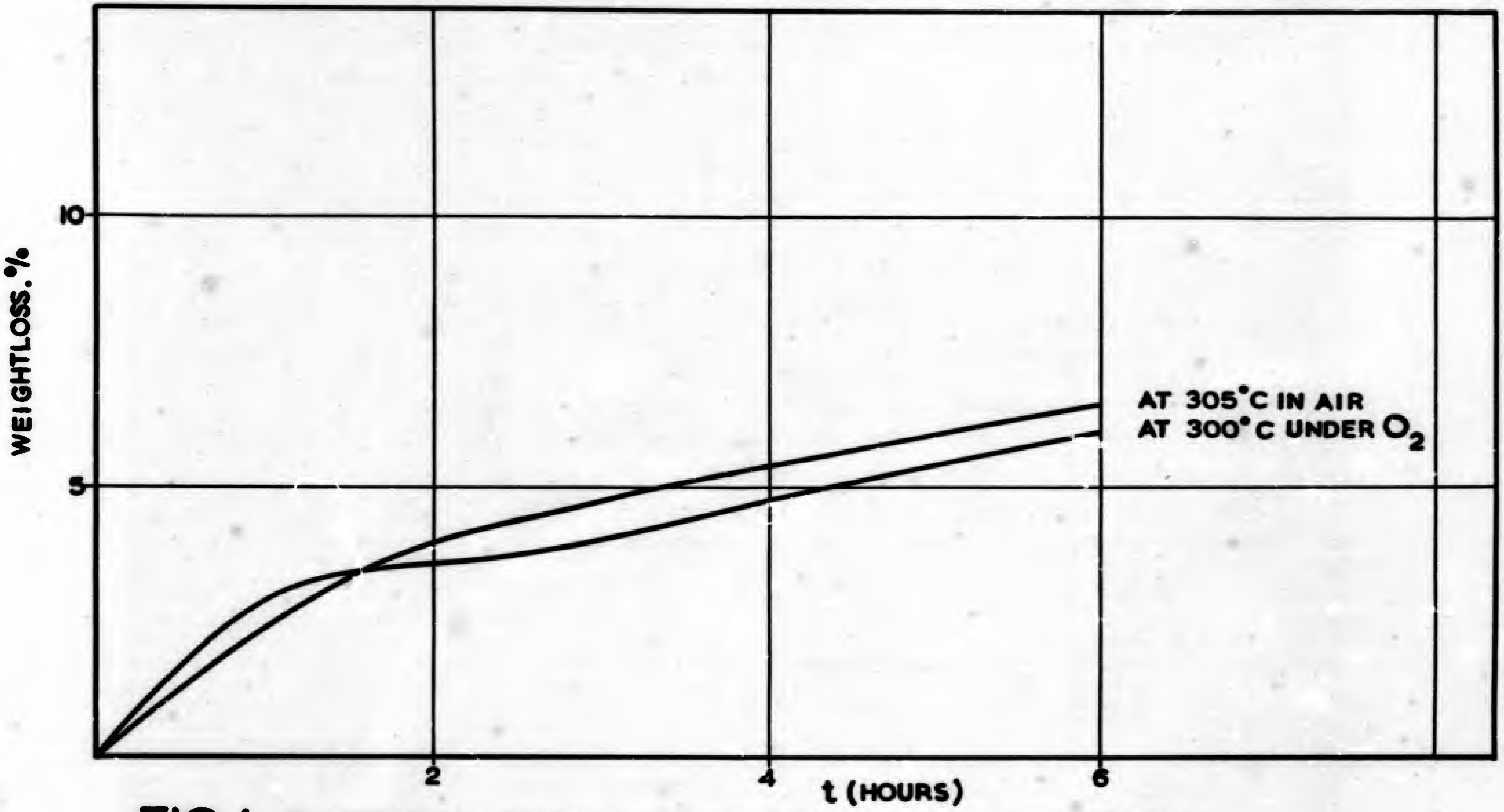

FIG. 1. THERMAL STABILITY OF VULCANIZATE XDBI.
SECTION 3.2.1.2.

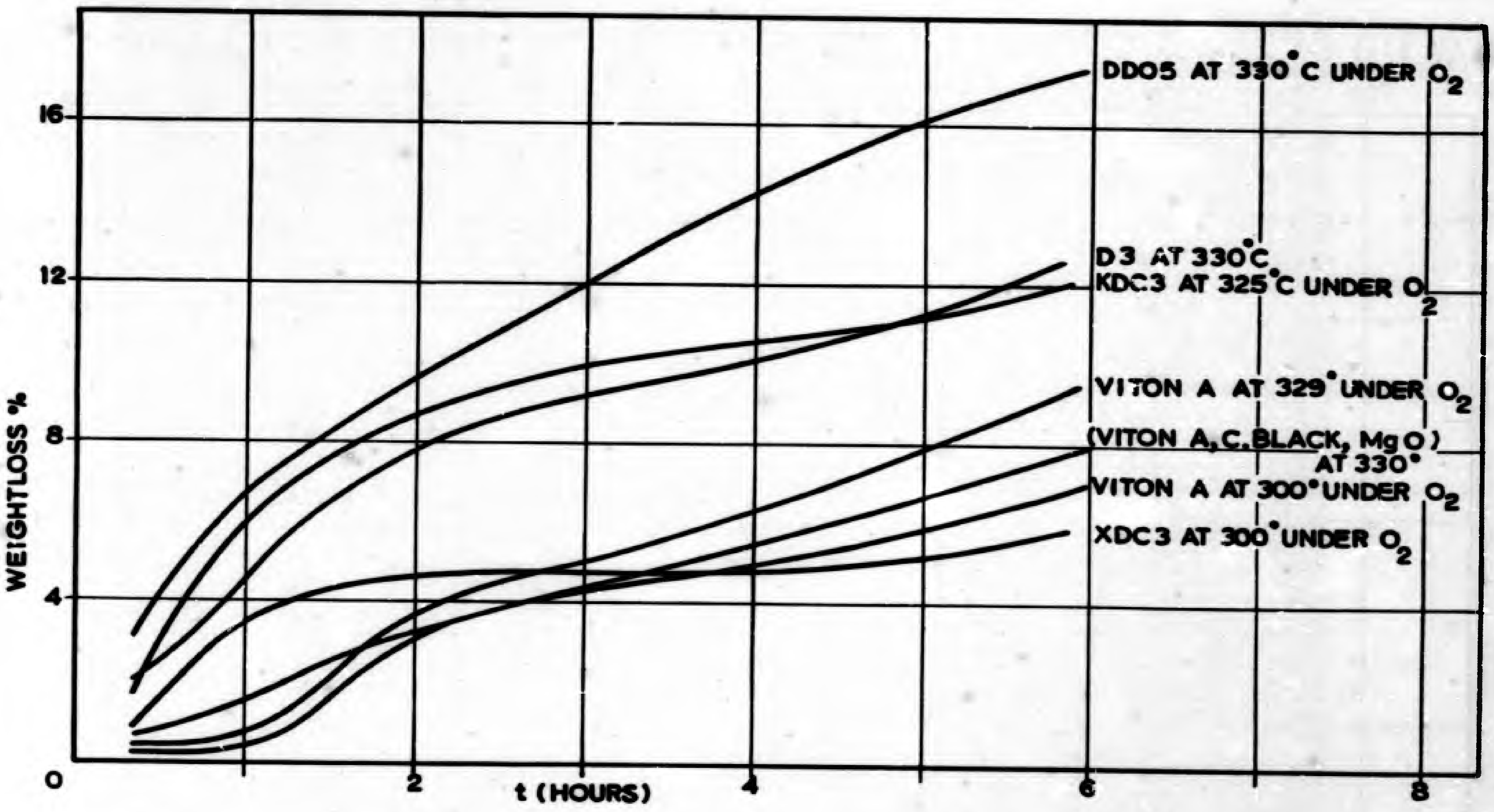

FIG. 2. THERMAL STABILITY STUDIES ON VITON A VULCANIZATES

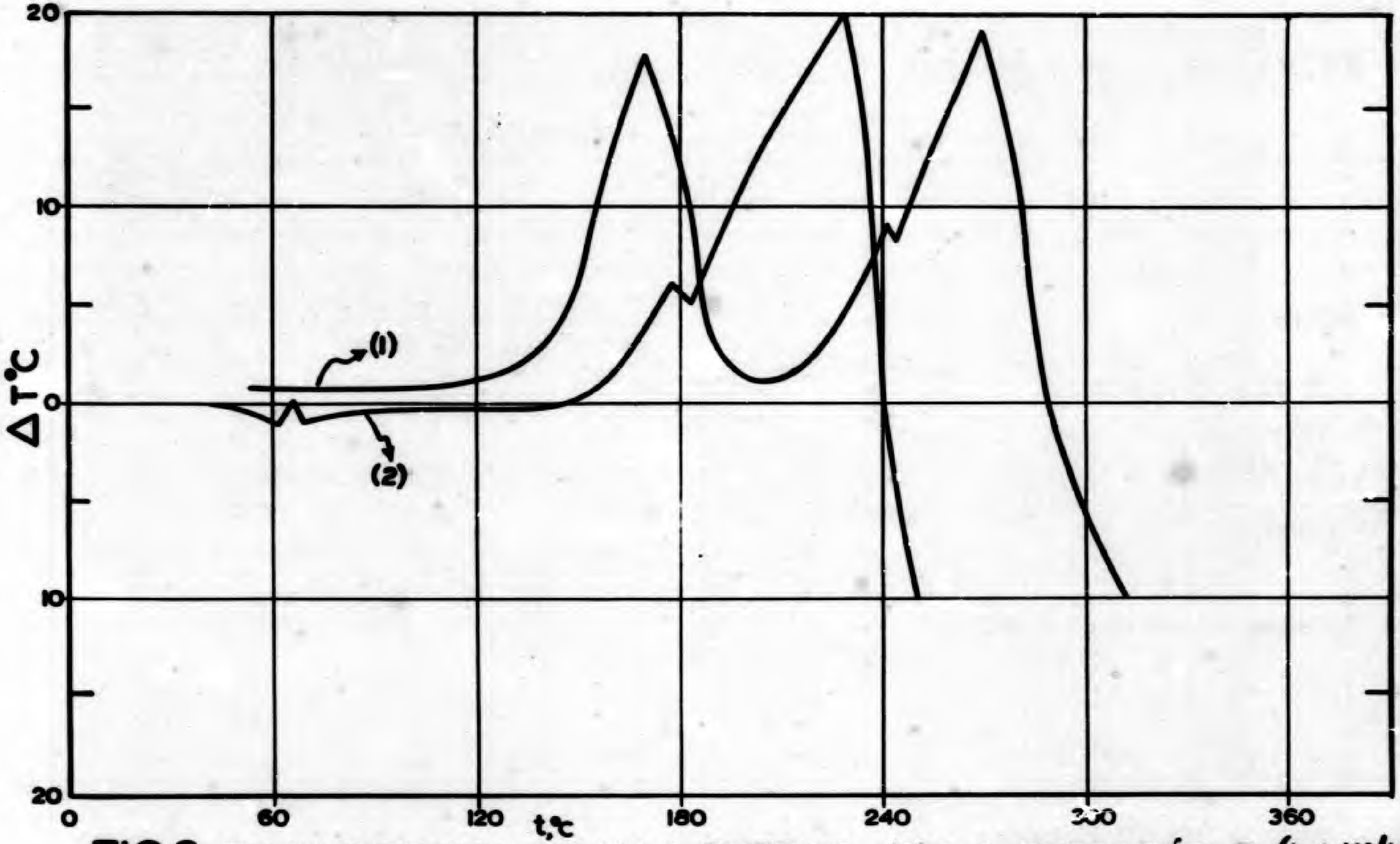

FIG.3. THERMOGRAMS OF:(1) 1.4-PDTEAC, (2) 1, 4-PDTEAC/CaO (1:1 W/W)
SECTION 3.2.3.1.

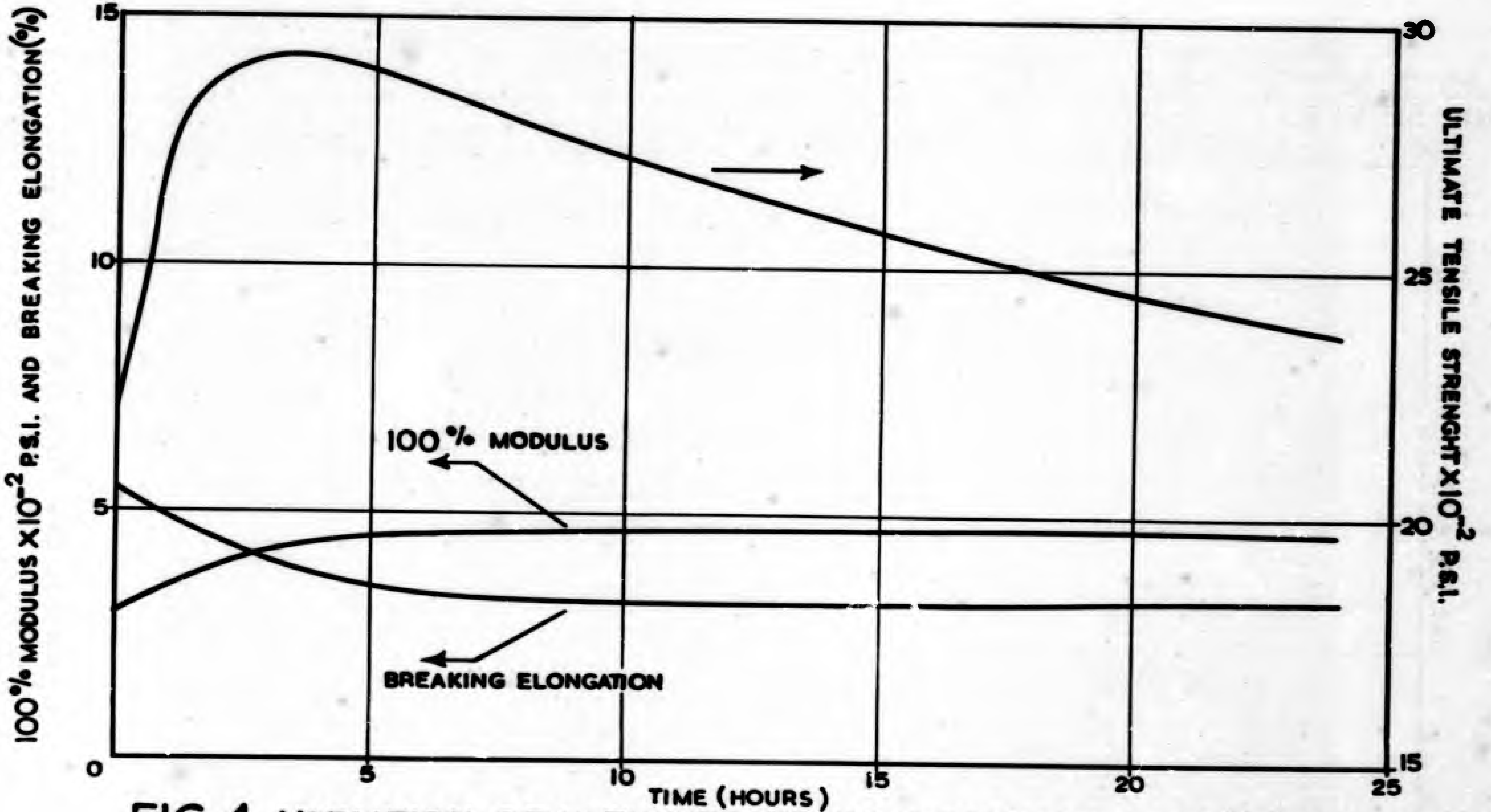

FIG. 4. VARIATION OF ULTIMATE TENSILE STRENGTH, 100% MODULUS AND BREAKING ELONGATION DURING THE OVEN CURE AT 205° OF A 1,4-PDTEAC VULCANISATE.

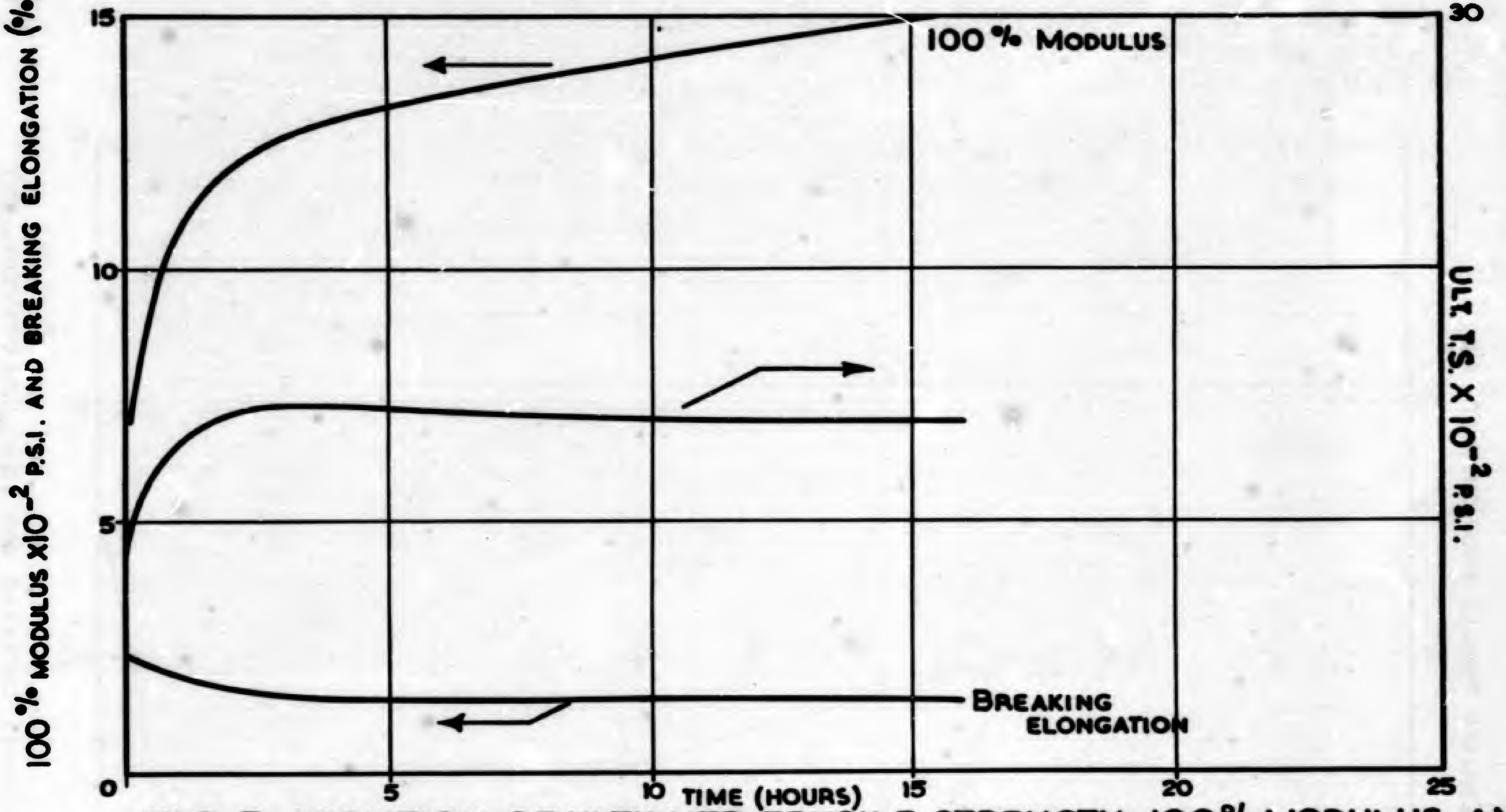

FIG. 5. VARIATION OF ULTIMATE TENSILE STRENGTH, 100% MODULUS AND BREAKING ELONGATION DURING THE OVEN CURE AT 205°C OF A VULCANISATE CONTAINING 2% OF BENZYL TRIETHYL AMMONIUM CHLORIDE.

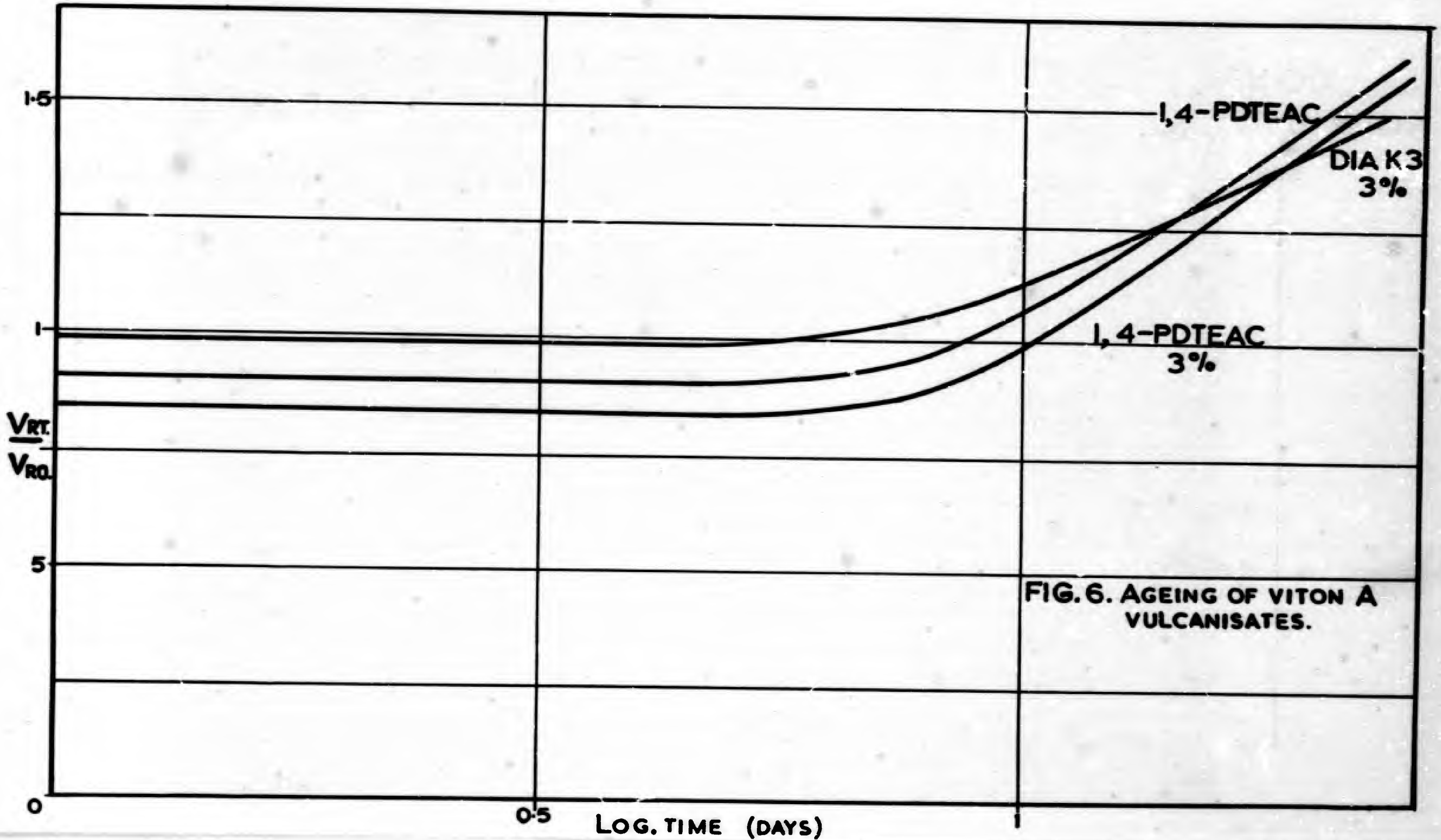

FIG. 6. AGEING OF VITON A VULCANISATES.

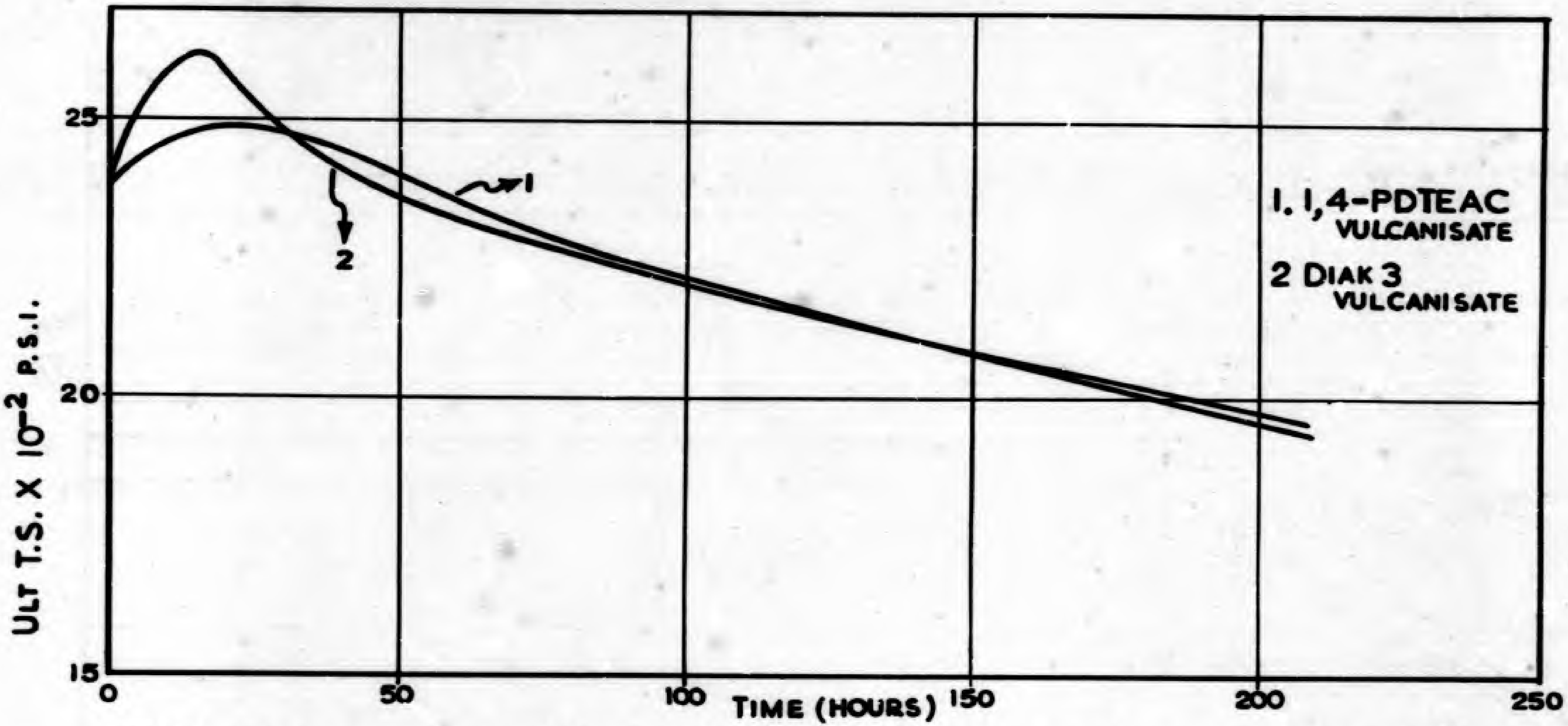

FIG. 7. AGEING OF VITON A VULCANISATES IN AIR AT 250° VARIATION OF THE MAX. TENSILE STRENGTH OVER THE·AGEING PERIOD.

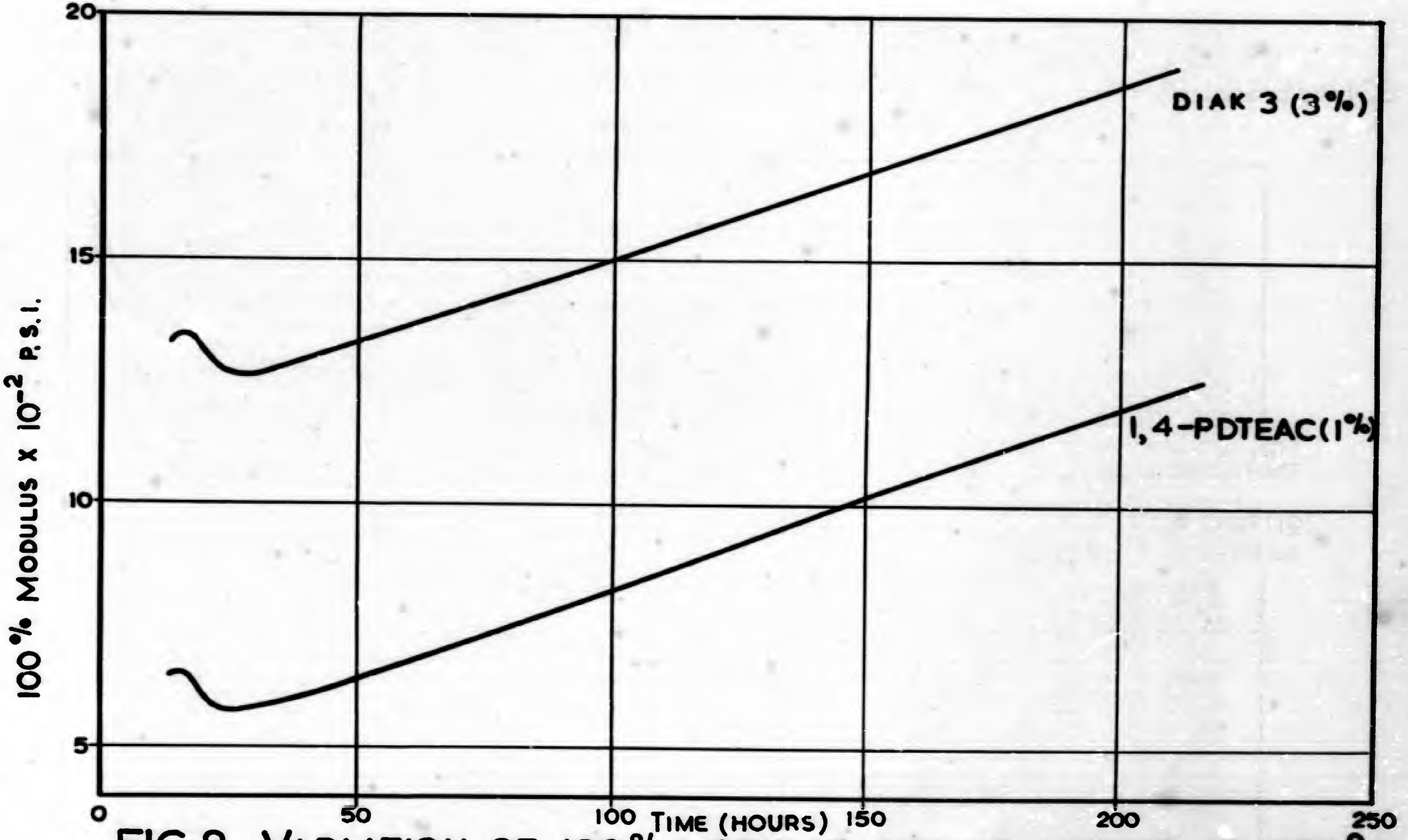

FIG. 8. VARIATION OF 100% MODULUS DURING AGEING AT 250°C

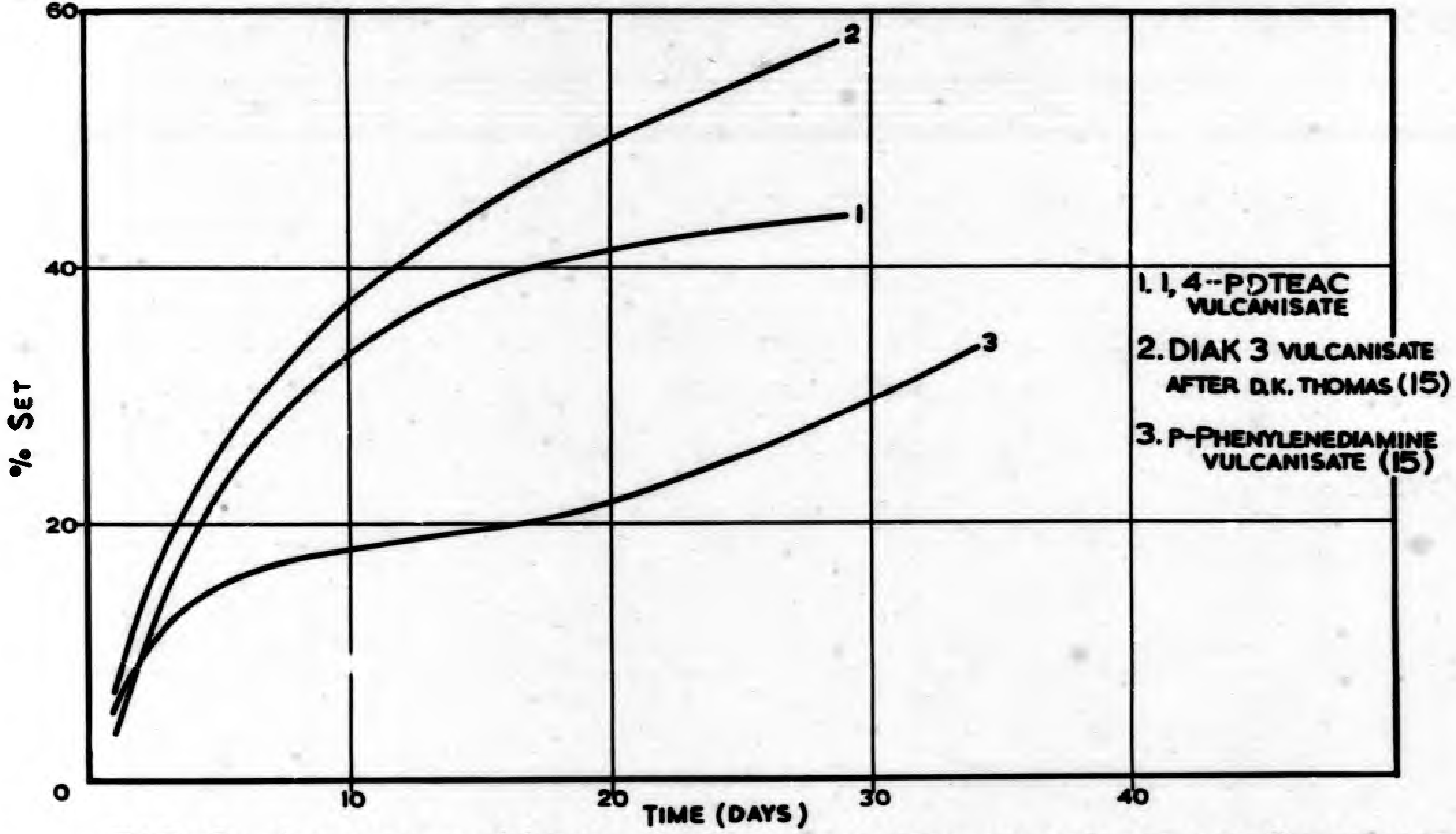

FIG. 9. AGEING OF VITON A VULCANISATES IN AIR AT 250 °C. RESISTANCE TO COMPRESSION SET OF 1, 4-PDMTEAC VULCANISATES AS COMPARED WITH DIAK 3 VULCANISATE.

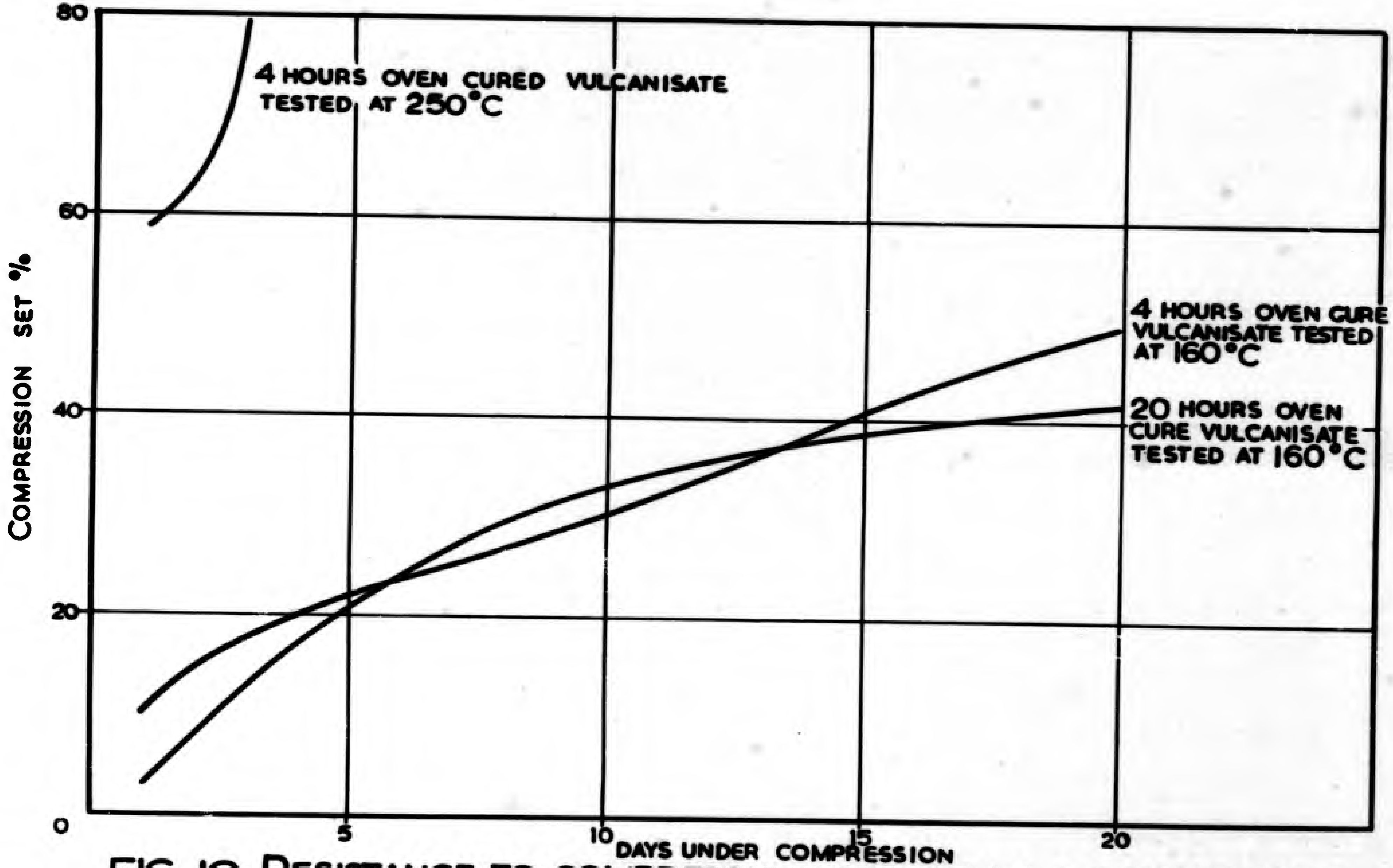

FIG. 10. RESISTANCE TO COMPRESSION SET OF A 1,4-PDTEAC VULCANISATE WHICH HAS BEEN OVEN CURED FOR 4 HOURS AT 200°C AS COMPARED WITH A SIMILAR COMPOUND OVEN CURED 20 HOURS.

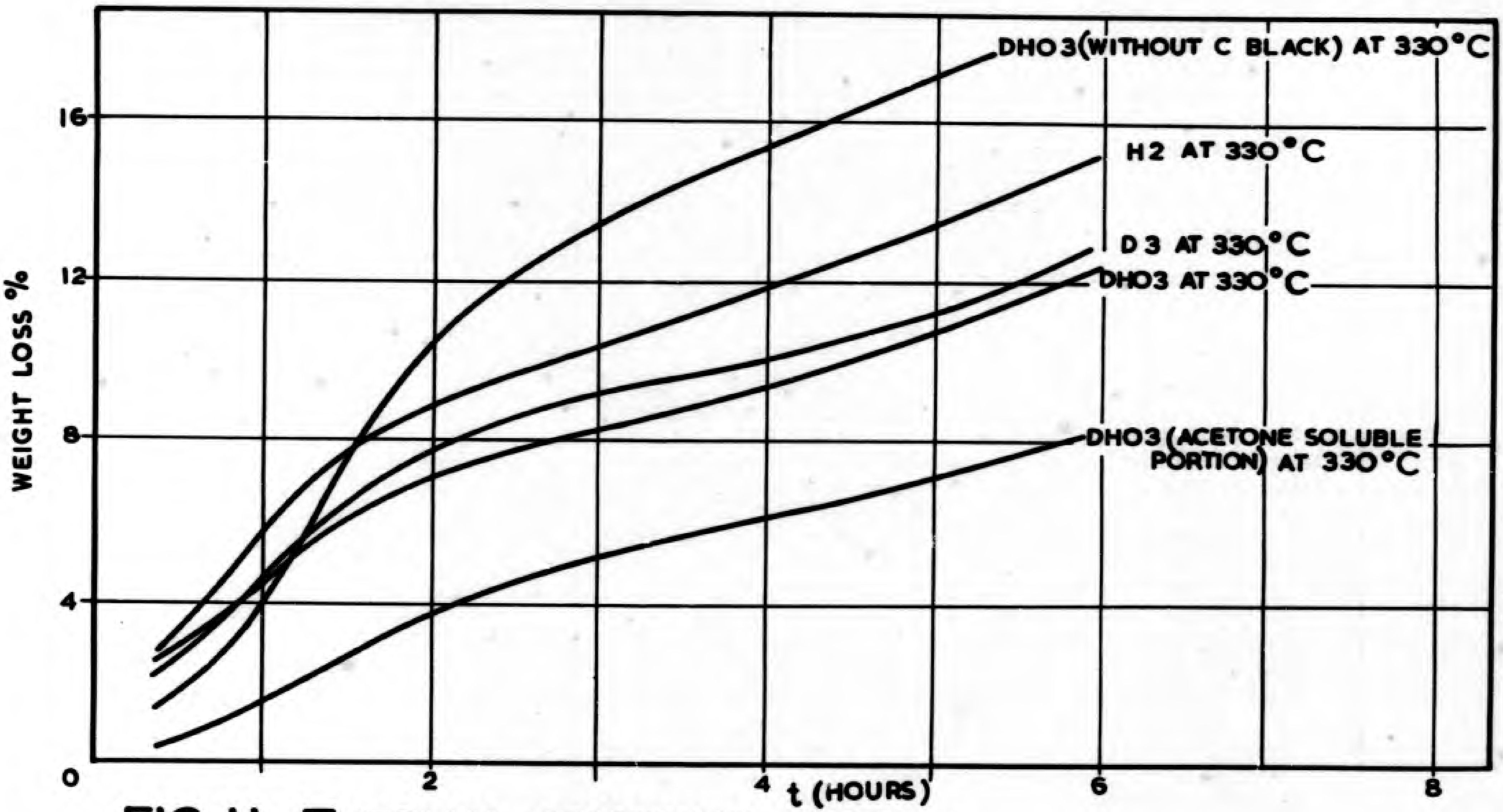

FIG. 11. THERMAL STABILITY STUDIES

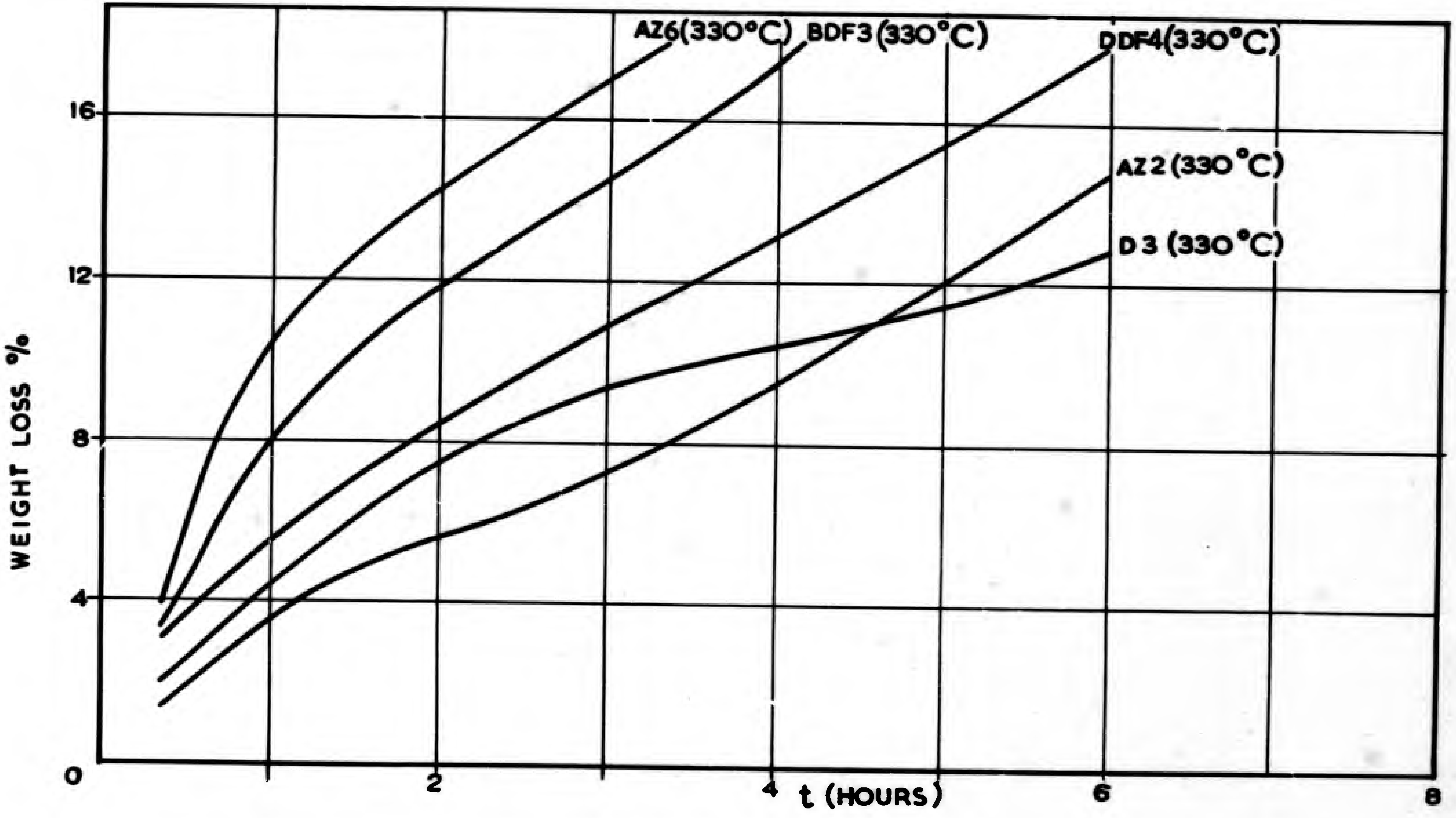

FIG. 12. THERMAL STABILITY STUDIES
SEC. 3.3.6.