

The Mechanism of Post Cure of Viton A* Fluorocarbon Elastomer†

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INTRODUCTION

The Viton fluorocarbon elastomers are copolymers of hexafluoropropylene and vinylidene fluoride designed for use where resistance to high temperatures and solvents is important. Viton A contains an alternation of methylene and difluoromethylene groups,



(I)

and in a basic environment it is very prone to lose hydrogen fluoride. Previous work¹ has shown that such a dehydrohalogenation is a preliminary to crosslinking during cure and that diamine curing agents form crosslinks by reacting at the unsaturated cure sites formed on the polymer chains by the loss of hydrogen fluoride. This article presents some new information on the more detailed chemistry of the amine reaction with the polymer chains.

The following general compounding and curing procedure is used in the processing of Viton stocks. First the polymer is compounded on conventional rubber processing equipment with fillers, acid acceptors, and curing agents; the stock is then press cured in a mold at temperatures between 100 and 150°C. for times varying from 5 to 60 min. The press-cured, partially vulcanized stock is then oven-cured at 200°C. for up to 24 hr. It is important to realize that the rate of cure during the press cycle is very rapid, so that only a few minutes at 150°C. are required in order to achieve the maximum properties obtainable from a press cure. When the partially cured sample is removed from the press, however, and heated in an oven, the

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degree of cure as measured by the modulus at 200% elongation approximately doubles. This post-curing process is illustrated in Figure 1. It is slow, taking 10-20 hr. at 200°C. or several months at room temperature. It does not occur at all except in an open system, in which the elastomer sample is exposed to the open air.

The work to be described consists chiefly of attempts to explain this behavior.

PROCEDURE AND RESULTS

Density of Crosslinking

As a preliminary to this study, a method was developed for determining crosslinking densities in the vulcanized polymer, in order to insure that extraneous factors, such as the mechanical stiffness of the polymer, did not confuse the arguments involved. The crosslinking density could be measured directly by the method of Cluff et al.,² which involves compression modulus measurements on swollen pellets. According to the theory of rubber elasticity the equation which relates the number of moles of effective network chains to the force required to deform the network is

$$F/A_0 = RT\nu_e V^{1/3}(\alpha - \alpha^{-2}) \quad (1)$$

where F is the total force, i.e., weight, on the sample, A is the cross-sectional area of the unswollen sample, ν_e is the number of moles of effective network chains per cm.³ of polymer, V is the volume fraction of rubber in the swollen sample, α is the deformation ratio of the swollen sample, R is the gas constant, and T the absolute temperature. In our case, corrections to eq. (1) were necessary because of the substantial amount of acid acceptors included in Viton fluorocarbon elastomer formulations. If we treat the additives as diluents which do not contribute to the elasticity of the sample, eq. (1) becomes

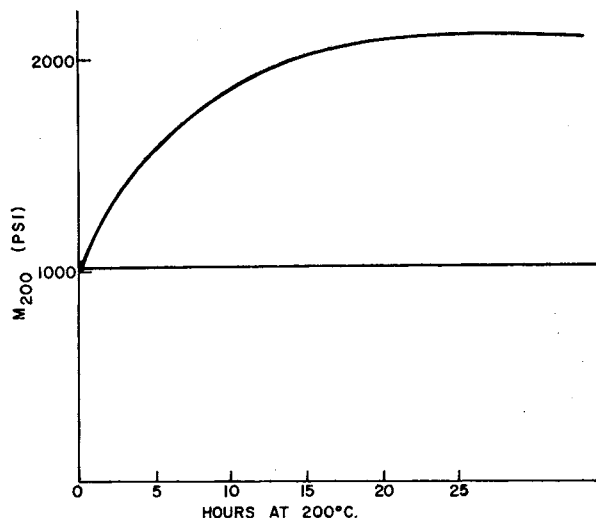


Fig. 1. Comparison of press cure (top curve) and oven cure (bottom curve) of Viton A containing 20 phr MT black, 15 phr MgO, and 1.5 phr HMDA-C. The oven-cured sample was first press-cured for 10 min. at 150°C.

$$\frac{F}{A_0} = RT \nu_e \left(\frac{V_r}{V_r + V_s} \right)^{-1/2} \left(\frac{V_r}{V_r + V_a} \right)^{2/3} (\alpha - \alpha^{-2}) \quad (2)$$

where V_r , V_s and V_a are the volumes of rubber, solvent and additives, respectively, in the sample. For small deformations (as in the present case), we have

$$(\alpha - \alpha^{-2}) \cong 3\Delta L_s / L_{0,s} \quad (3)$$

where $L_{0,s}$ is the undeformed swollen sample height and ΔL_s is the change in height, and eq. (2) becomes:

$$\frac{F}{A_0} = \frac{3RT}{L_0} \nu_e \left[\frac{V_r}{V_r + V_a} \left(1 - \frac{V_a}{V_r + V_a + V_s} \right) \right]^{1/3} \times \Delta L_s \quad (4)$$

$$\cong (3RT/L_0) \nu_e \phi_r^{1/3} \Delta L_s \quad (5)$$

where L_0 is the dry undeformed sample height and $\phi = V_r / (V_r + V_a)$. It was found that eq. (5) was sufficiently accurate for the present work. Plots of F versus ΔL_s gave straight lines, the slopes of which yielded the effective network chain concentration and hence the crosslinking density. In the above derivations it is assumed that the volumes are additive, with no increase or decrease in volume occurring upon mixing of the components.

It was also necessary to apply a correction for loose chain ends according to the equation

$$C = (\nu_e/2\rho) + (1/\bar{M}_n) \quad (6)$$

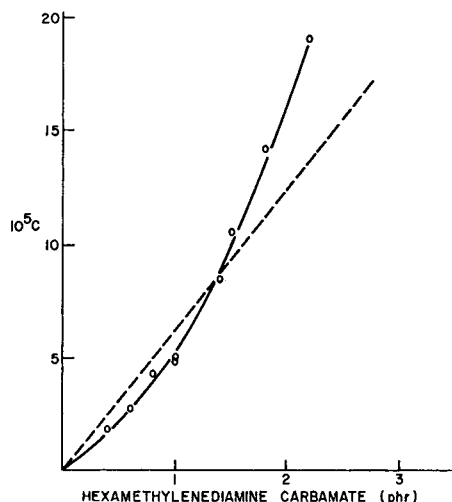


Fig. 2. Effect of HMDA-C concentration on the crosslinking density of Viton A: (—) crosslinking density corrected for loose chain ends; (- -) curve calculated assuming one mole of crosslinks per mole of diamine curing agent.

where C , the crosslinking density, is expressed in terms of moles of tetrafunctional crosslinks per gram of polymer, ρ is the density of the polymer, and $1/\bar{M}_n$ gives the number of moles of loose chain ends which do not contribute to the elasticity of the vulcanizate. The number-average molecular weight of Viton A fluorocarbon elastomer, determined by osmometry, was 70,000.

A series of Viton pellets was prepared containing varying amounts of hexamethylenediamine carbamate curing agent. The crosslinking densities were measured by the method outlined above. Figure 2 is a plot of corrected crosslinking densities against curing agent level. Fair agreement is seen between the experimental curve and the theoretical line representing direct equivalence between crosslinking density and curing agent concentrations, especially at lower levels of curing agent. Some reasons for the deviations in the experimental curve will be discussed later.

An independent method of measurement of crosslinking densities having been developed, our attention turned to the three outstanding aspects of the curing process which were least understood. They were: (1) the role of the acid acceptor in the curing process; (2) the necessity for a prolonged, high-temperature oven cure; (3) the detailed nature of the crosslink.

1. Role of the Acid Acceptor

There is no doubt that free HF in the polymer is deleterious to heat aging properties and that ma

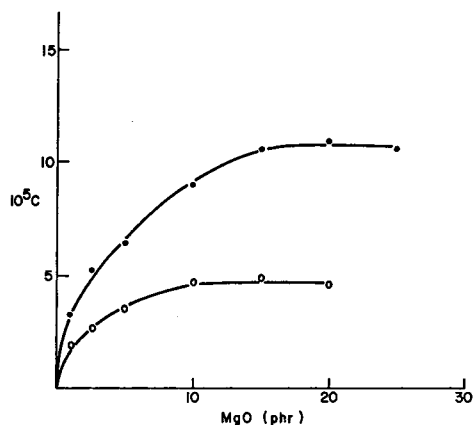


Fig. 3. Effect of MgO on the crosslinking density of Viton A with (O) 1.0 phr and (●) 1.5 phr hexamethylenediamine carbamate.

materials which will absorb HF improve the heat aging of the vulcanizate. The major role of acid acceptors, however, is not to improve the heat aging. They are an essential part of the curing formulation of the elastomer. None of the known curing formulations will operate in the absence of magnesium oxide or some other similar basic substance. Even radiation, which will gel un compounded Viton, does not develop optimum properties in the polymer unless magnesium oxide is included in the formulation. There is infrared evidence¹ that the magnesium oxide contributes to the elimination of HF from the polymer during irradiation, and probably also during chemical cures.

The method of measuring crosslinking density was used to determine the exact dependence of crosslink formation on the acid acceptor level. Figure 3 shows that increasing the concentration of magnesium oxide increases the measured crosslinking density up to a certain limiting value; beyond this value further increase in magnesium

oxide content has no effect. The limiting value, as might be expected, is dependent on the amount of diamine curing agent present.

These results serve to show that the magnesium oxide plays an integral role in the curing process; taken in conjunction with infrared evidence they indicate that the oxide almost certainly acts as a catalyst for hydrogen fluoride elimination during the crosslinking reactions.

2. The Necessity for Post-Curing

At first the possibility was considered that post-curing was accelerated in the presence of air and that lack of oxygen prevented the full development of properties in a closed mold. This hypothesis was tested by post-curing press-cured Viton strips enclosed separately in glass vessels containing oxygen, nitrogen, and air. The surprising result emerged that, while the rate of development of cure was inhibited by nitrogen to about the same degree in this environment as in a closed mold, oxygen had a degrading effect on the polymer, causing an apparent decrease in the state of cure. Air, as might be expected, was intermediate between oxygen and nitrogen in its effect. When the post-curing was carried out in a vessel attached to a vacuum pump, the full state of cure was developed after some 10 hr. at 200°C., even in the absence of air. These results are given graphically in Figure 4.

The data summarized in Figure 4 seemed to suggest that the full development of cure in a closed system was prevented by an inhibition of the crosslinking reaction by some by-product of the cure. The nature of this inhibiting substance was accordingly investigated.

Post-cures of Viton A were conducted in closed vessels containing a number of absorbents (see Fig. 10). In Table I is a list of some of the absorbents

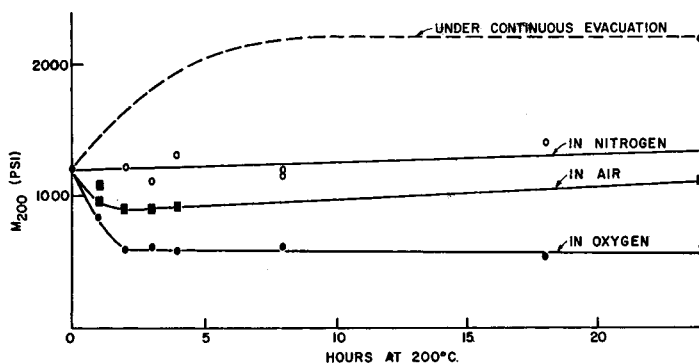


Fig. 4. Effect of gaseous environments on 200°C. post-cures of Viton A with 18 phr MT black, 15 phr MgO, and 1.5 phr HMDA-C, initially press-cured for 10 min. at 150°C.

TABLE I
Effect of Environment on the Post-Curing of Viton A^a

Condition of post-curing	M_{200} after 18 hr. at 200°C.
None (press cure, 10 min. at 150°C.)	1050
Sealed tube	1400
Sealed tube with NaF	1410
Sealed tube with $MgClO_4$	1650
Sealed tube with CaO	1850
Sealed tube with P_2O_5	2070
Sealed tube with cold trap ($-80^\circ C.$)	>2100
N_2 flow	>2100
Steam flow	1610
Open oven	1930

^a 18 phr MT Black, 15 phr MgO, 1.5 phr HMDA-C.

It was concluded from the results of these experiments that the post-cure of Viton fluorocarbon elastomer was inhibited by water evolved from the polymer during vulcanization. Final confirmation was obtained by using a suitable dehydrating agent as a compounding ingredient. A press-curing study with Viton A compounded with calcium oxide in addition to the normal curing ingredients gave a complete cure in a closed system. This is demonstrated in Figure 5, a plot of vulcanizate properties as percentages of the ultimate obtainable from a normal oven post-cure. That these percentages tended towards 100 showed that the maximum properties were obtainable in a closed system where provision was made to remove water through reaction with calcium oxide. Cure in this system was impracticably slow, however, taking 15 hr. to develop ultimate properties. Thus, while it is necessary to remove water during the post-curing reaction, the presence of water is not the only reason for the slow rate of cure in a closed system. We tested, together with the stress at 200% elongation developed after 20 hr. It is clear that the development of cure was closely associated with the ability of the absorbent to react with water at the temperature of the test. Following this lead, we conducted the post-cure in a closed evacuated tube connected to a small receiver cooled to $-80^\circ C.$ with Dry Ice. The post-cure proceeded normally and a small volume of a clear liquid collected in the receiver. The liquid was shown to be almost pure water by its refractive index and near-infrared spectrum. Post-cures conducted in a continuous nitrogen sweep gave high-modulus vulcanizates, but post-cures in a continuous steam flow did not develop the full state of cure. These results are also summarized in Table I.

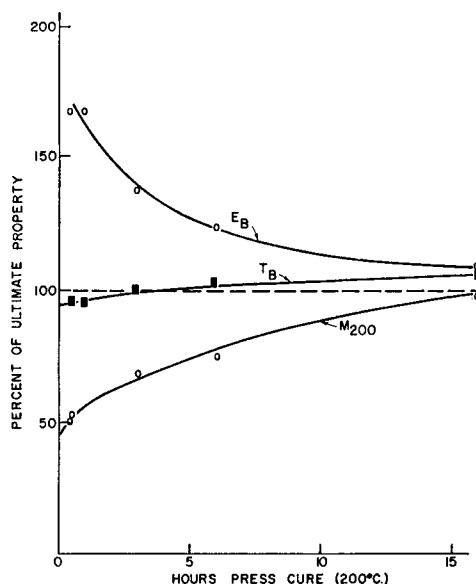


Fig. 5. Press cures of Viton A containing CaO (15 phr) in addition to 18 phr MT black, 15 phr MgO, and 1 phr HMDA-C. The ultimate property is taken as the mean property (I_B , E_B , M_{200} , etc.) after normal oven cure.

must assume that the post-curing reaction is intrinsically slow.

Several practical corollaries arise from the finding that water can inhibit the post-cure of Viton A fluorocarbon elastomer. For example, Viton has a tendency to sponge during oven cure if an insufficient number of crosslinks has been incorporated into the vulcanizate during the press-curing cycle. This sponging is due to the evolution of water vapor. It can be a serious problem in some cases where scorching difficulties dictate the use of a slow-curing formulation or in the case of peroxide cures, which are very prone to sponge during oven cure. Where sponging is a problem it can be overcome by incorporating a water absorber such as calcium oxide into the curing formulation.

The importance of the post-curing environment makes it plain that care should be taken to provide adequate ventilation in ovens used for post-curing Viton and other fluoroelastomers. In particular, open steam cures of Viton articles must be expected to be slow and probably will not go to completion but should be followed by a post-curing cycle in dry heat.

3. The Nature of the Crosslink

The fact that water was evolved during post-cures of Viton suggested a method of examining the crosslinking reaction in more detail. It has been

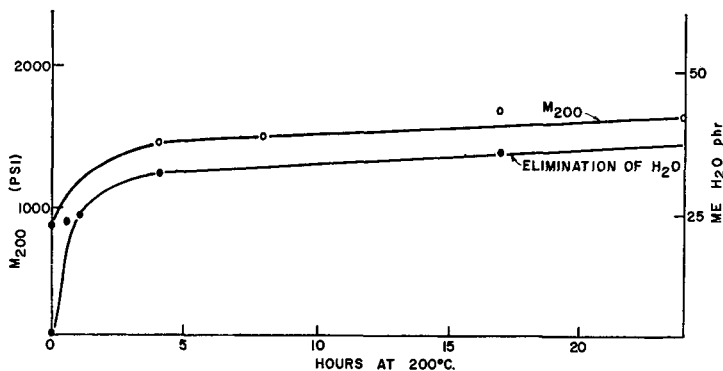


Fig. 6. Development of M_{200} and elimination of water from Viton A during cure at 200°C.

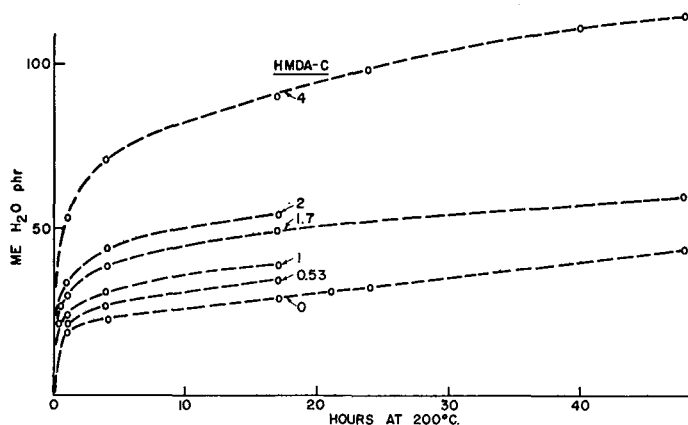
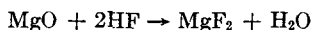


Fig. 7. Effect of concentration of curing agent HMDA-C on rate of elimination of H_2O from Viton A.

shown that magnesium oxide is necessary to the cure and that HF elimination is an integral reaction of the vulcanizing process. It is very reasonable to put these two facts together and assume that the water is derived from neutralization of magnesium oxide with HF according to the simple equation



If this were true, clearly then the measurement of the amount of water evolved from a stock during post-curing would be a direct measurement of the degree of elimination of HF from the polymer; indirectly this would provide a method of following the development of cure.

Following this reasoning, we devised methods of measuring the amount of water evolved during post-curing of a series of Viton fluorocarbon elastomer stocks containing various amounts of diamine curing agents. The results showed three important features. In the first place, the rate of evolution of water was quite similar to the rate of development of cure of the polymer. This is demonstrated

in Figure 6 where both rate of evolution of water and M_{200} of the sample are plotted against time. Secondly, as shown in Figure 7, the amount of water evolved in a given time was related to the

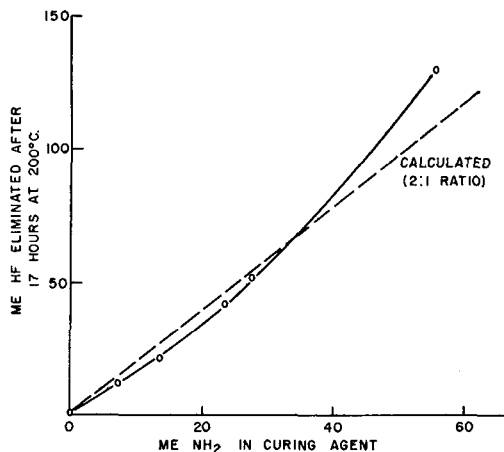


Fig. 8. Relationship between HF eliminated and amine curing agent level in Viton A post-cures.

amount of curing agent present. And finally, it is clear from the lowest curve of Figure 7 that considerable quantities of water were evolved even in the absence of curing agent.

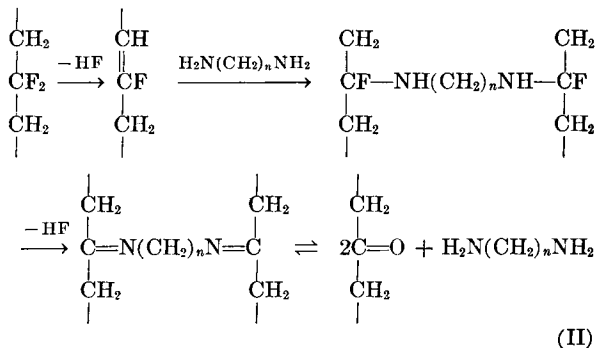
The source of the water evolved from uncured stocks could not be definitely decided. The water could have been derived from adventitious contamination due to the difficulty of drying completely such materials as carbon black. However, it could equally well have arisen from an elimination of hydrogen fluoride from the polymer chain which was not catalyzed by the action of curing agents. In any case, in order to determine the effect of curing agent on the amount of water evolved during post-curing, corrections for the uncatalyzed water evolution were necessary. This correction was applied by subtracting the lowest curve of Figure 7 from the other curves. The relationship obtained in this manner between curing agent level and HF evolved, assuming the stoichiometry of eq. (1), is compared in Figure 8 with the straight line calculated from a ratio of four moles of HF per mole of curing agent. A fair concordance with the calculated curve is observed, although the same kind of deviation from linearity occurred as was seen in the crosslinking density measurement discussed earlier.

We had available at this point two independent estimates of the crosslinking density of cured Viton fluorocarbon elastomer. These were (a) the direct measurements outlined previously, and (b) estimates based on the amount of water evolved during post-curing, assuming a ratio of four moles

of HF derived from each mole of crosslinks. A direct comparison of the two methods was therefore made.

Crosslinking densities were calculated from the data of Figure 8 assuming that four moles of HF were eliminated from the polymer per mole of crosslinks. Figure 9 is a plot of these values against crosslinking densities of Figure 1 calculated from physical measurements.

Very good agreement is seen in Figure 9 between the experimental curve and the straight line representing a direct equivalence between the two methods up to and beyond the levels of curing agent commonly used (1.5 parts hexamethylenediamine carbamate). A higher levels substantial deviation occurred, owing probably to inaccuracies caused by the hard, unyielding nature of the over-cured vulcanizates at these higher states of cure.



The foregoing data indicate that four moles of hydrogen fluoride are eliminated per mole of tetrafunctional crosslinks formed. The diimine structure (II) is one which satisfies this stoichiometry. We would like to propose that the crosslinking reaction taking place when Viton A is vulcanized with a diamine consists of the following three stages: first, a reaction at the chain to form double bonds; second, a reaction of the diamine with these double bonds to form crosslinks; and third, an elimination of HF from the double bonds to form (II). Now, if (II) is in fact present in vulcanized Viton A, it should be readily hydrolyzable. Hydrolysis was demonstrated in the following manner: a vulcanized sample of Viton A was swollen in aqueous tetrahydrofuran, the swollen sample heated at 200° for 24 hr., and the filtered extract was titrated with acid. Seventy per cent of the amine originally present in the vulcanizate was found in the aqueous washings. This hydrolysis must, of course, be an equilibrium process, and the possibility exists that the importance of water in the post-curing of Viton rests in the proper establishment of this equilibrium

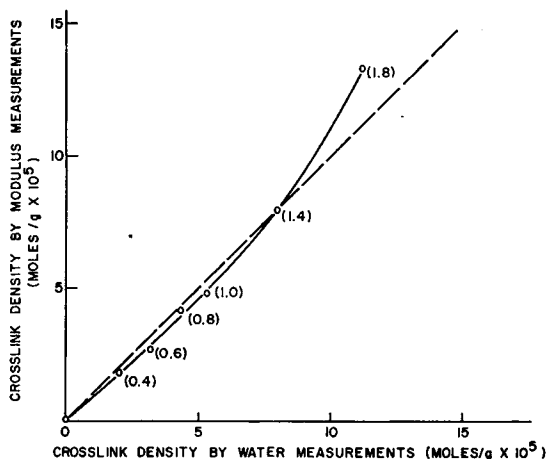


Fig. 9. Comparison of densities of crosslinking determined from HF elimination and from swollen compression modulus: (O) experimental points, (---) points calculated assuming the methods to be equivalent. The numbers in parentheses represent curing agent concentrations (phr).

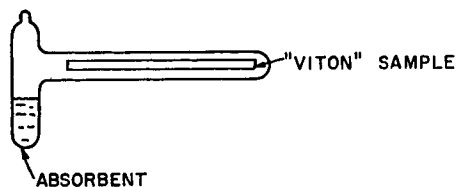


Fig. 10. Apparatus for heating Viton samples with absorbents.

It may be that water present must be removed in order to drive the equilibrium completely in the direction of imine formation and the establishment of a permanent crosslink.

EXPERIMENTAL DETAILS

Stress-strain measurements and weight loss determinations were made on 1/4-in. strips cut from $3 \times 6 \times 0.08$ -in. slabs. All stocks were made up from carefully dried Viton. Carbon black and magnesium oxide were heated for at least 2 weeks at 200°C . prior to use. The standard compound contained 18 phr MT black and 15 phr MgO. Stress-strain measurements were made on an Instron test machine at a head speed of 10 in./min. Stocks for post-curing experiments were press-cured for 10 min. at 150°C . and kept in sealed jars for the shortest possible time before use.

Post-Cures in Sealed Vessels

For the purpose of studying the effect of a gaseous environment on development of a post-cure, a Viton sample was placed in a Pyrex tube which was then connected through a constriction to a vacuum system. After evacuation at 10^{-5} mm. for 24 hr., the gas to be tested was admitted at some-

what less than 1 atmosphere into the tube which was then sealed off at the constriction. The tubes were wrapped in wire gauze because of the danger of explosion and heated in an oven at 200°C . for the required time.

For the purpose of examining the effect of absorbents, Viton samples were placed in tubes shaped as shown in Figure 10, and the absorbents were placed in the side tube as indicated. The tubes were sealed without being evacuated and the whole tube, including the absorbent, was heated in an oven at 200°C .

Post Cures in Gas Flow

The apparatus sketched in Figure 11 was used to study the effect of gas flow on post-curing. Viton samples were held in a tube placed in a silicone oil bath held at $200^\circ \pm 2^\circ\text{C}$. by a "Magnaset" thermostat while nitrogen was passed through the tube. The nitrogen, metered at 20 cc./min., was dried by passage through a Dehydrite tower. Analysis of the effluent gas was accomplished by weighing the other three absorption tubes before and after an experiment. In the experiment with steam, the absorption tubes were removed and process steam was passed over the heated sample. For experiments under continuous evacuation, the gas inlet tube was sealed off and an oil pump that developed a 0.1 mm. vacuum was connected to the exit tube.

Determination of Crosslinking Density

The polymer was compounded with 15 parts magnesium oxide and the requisite amount of hexamethylenediamine carbamate. Yezley pellets 0.5 in. high by 0.75 in. in diameter were molded,

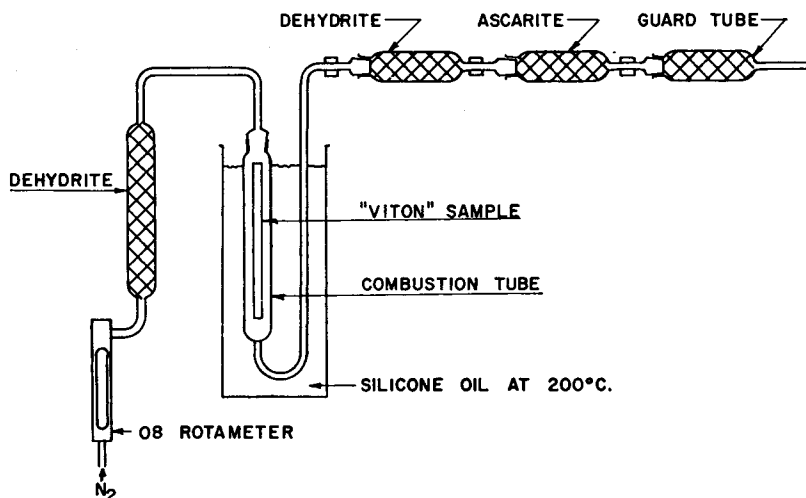


Fig. 11. Measurement of water evolved during post-curing.

press-cured for 1 hr. at 150°C., and oven-cured for 24 hr. at 200°C. The pellets were weighed and their dimensions determined. It was found that the pellets tended to break apart when swollen in pure methyl ethyl ketone, and so it was necessary to conduct preliminary swellings in various benzene/MEK mixtures. The pellets were then allowed to stand in pure MEK for 7 days, after which the solvent was changed and the pellets were left to stand in the fresh MEK for another 7 days. They were then blotted dry, weighed, and immersed in MEK in an apparatus for measurement of compression modulus similar to that described in Reference 2. The procedure of Reference 2 was followed and the results treated as described above.

Hydrolysis of Cured Viton

Several strips of compounded and cured Viton (19.7 g.) containing 20.8 meq. amine curing agent were placed in a stainless steel bomb with 100 ml. tetrahydrofuran containing 10 ml. water. After 48 hr. of heating at 200°C., the disintegrated polymer suspension was poured into water and the polymer filtered off and washed with water. The combined filtrate and washings were titrated against perchloric acid and found to contain 13.5 meq. of amine, representing a total recovery of 65%.

References

1. Smith, J. F., *Proc. Internat. Rubber Conf.*, 1959, p. 575.
2. Cluff, E. F., E. K. Gladding, and R. Pariser, *J. Polymer Sci.*, **45**, 341 (1960).

Synopsis

The necessity for oven post-curing Viton A vulcanizates is explained in the following way: The formation of crosslinks is accompanied by the elimination of HF from the polymer. In the subsequent reaction of HF with the magnesium oxide present as acid acceptor water is formed which acts to inhibit the full development of cure unless it is removed from the vicinity of the polymer by post-curing in

an open system. Measurement of the rate of elimination of water from the polymer serves as a method of following the development of crosslinking during cure. Approximately two moles of water, derived from four moles of hydrogen fluoride, are associated with the use of one mole of diamine curing agent. This ratio is confirmed by independent estimates of the relationship of crosslinking density to curing agent level based on measurements of swollen compression moduli.

Résumé

On explique la nécessité d'un recuit du Viton A vulcanisé de la manière suivante. La formation de ponts s'accompagne de l'élimination de HF aux dépens du polymère. L'acide fluorhydrique réagit avec l'oxyde de magnésium présent qui agit en tant que base. Il y a formation d'eau qui empêche l'achèvement complet du traitement, ce qui nécessite son élimination du polymère par un recuit dans un système ouvert. La mesure de la vitesse d'élimination de l'eau du polymère est utilisée pour suivre le développement du pontage durant le traitement. Lorsqu'on utilise un mole de diamine comme agent de pontage, on retrouve deux moles d'eau provenant de 4 moles d'acide fluorhydrique. Le rapport est confirmé par des estimations indépendantes de la relation liant la densité de pontage et l'agent de traitement par des mesures du module de compression à l'état gonflé.

Zusammenfassung

Die Notwendigkeit einer Ofen-Nachvulkanisation von Viton A Vulkanisaten wird folgendermassen erklärt: Die Bildung der Vernetzungen wird von einer HF-Abspaltung aus dem Polymeren begleitet. Durch die Reaktion von HF mit dem als Säureacceptor vorhandenen Magnesiumoxyd bildet sich dann Wasser, das die vollständige Vulkanisation solange verhindert, bis es aus dem Polymeren durch eine Nachbehandlung in einem offenen System entfernt wird. Die Messung der Abspaltungsgeschwindigkeit des Wassers aus den Polymeren ist zur Verfolgung der Vernetzungsbildung während der Vulkanisation geeignet. Ungefähr 2 Mol Wasser, die aus 4 Mol Fluorwasserstoff entstehen, sind mit dem Umsatz von 1 Mol Diamin-Vulkanisierungsmittel verbunden. Dieses Verhältnis wurde unabhängig durch Bestimmung der Beziehung zwischen Vernetzungsgrad und Gehalt an Vulkanisationsmittel mittels Messung des Kompressionsmoduls im gequollenen Zustand bestätigt.

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