PERMEABILITY OF ELASTIC POLYMERS TO HYDROGEN

By Theron P. Sager

ABSTRACT

The permeabilities to hydrogen of natural rubber, Perbunan, Neoprene G, Vistanex, Thiokol Dx, and Pliofilm diminished in the order of mention. The increase in rate of permeation with increasing temperature was exponential in all cases. Values for the activation energies of permeability for hydrogen were found to be 6,800 cal/mole for natural rubber and 8,400 to 9,500 cal/mole for the synthetic materials. The greater magnitude of the energy requirements of the latter indicates that their lower permeability may be attributed to differences in their molecular structure.

CONTENTS

I. INTRODUCTION

Natural rubber has been the material generally employed as the gas-retaining membrane in various inflated structures. This is because of its unique combination of high tensile strength and almost completely reversible extensibility. Its inherent limitations are low gas impedance and the lack of resistance to deterioration. There are relatively few materials which can be used for this purpose. A majority of the film-forming substances—cellulose derivatives, drying oils, resins—which are employed in varied applications in our economy, fail in one respect or another to meet the peculiar requirements. Within recent years however a number of synthetic materials have become available which are characterized by high elasticity and are also less permeable than rubber to gases. The values reported here result from a continuation of the study of the permeability of these materials for the Bureau of Aeronautics of the United States Navy Department.

II. MATERIALS AND METHOD

The materials which were examined included natural rubber; Perbunan, a co-polymer of butadiene and acrylonitrile; Neoprene G, one of the types of polymerized chloroprene; Thiokol Dx, a product resulting from the condensation of halogenated olefins and sodium polysulphide; Vistanex, a polymer composed of isobutene units; and Pliofilm, composed of rubber hydrochloride. Pliofilm is not a rubber-like material, although it is somewhat extensible and exhibits elasticity at elevated temperatures. This material was examined in the form

in which it was received. Films, ranging in thickness from 0.025 to 0.06 cm, were prepared from the other materials. Those materials which attain their most desirable physical properties as the result of vulcanization were compounded with only the essential ingredients and heat-cured. The compounding formulas are shown in table 1. Because Vistanex is not a vulcanizable material, no compounding ingredients were added to it.

TABLE 1.—*Compounding formulas*

[Each column represents a separate compound]

Material	Parts by weight			
Smoked sheet rubber	100			
Perbunan		100		
Neoprene *G*			100	
Thiokol *Dx*				100
Sulfur	4	1		
Zinc oxide	5	5	5	10
Magnesium oxide			4	
Mercaptobenzothiazol (Captax)	1			
Benzothiazyl disulfide (Altax)		1		0.25
Diphenylguanidine				.1
Phenyl-*δ*-naphthylamine (Neozone *D*)	1		2	

The method of determining permeability and the conditions of test were those which have been previously described.[1] It was assumed in all cases that the rate of permeation in mass per unit time is proportional to the partial pressure of the gas and inversely proportional to the thickness of film. Permeability is expressed herein as milliliters of hydrogen which penetrates a film 1 cm thick over an area of 1cm^2 in 1 minute. It was assumed that only a negligible partial pressure of hydrogen exists on the low pressure side; then the permeability in volume of hydrogen (at the initial pressure) is independent of that pressure. The effect of temperature was found to be characteristic of each material and was included in the study.

III. EXPERIMENTAL RESULTS

In table 2 are shown the permeabilities obtained at 25° C, the temperature at which determinations on balloon fabrics are customarily made. Table 3 contains the rates of permeation at various temperatures, ranging generally from below 10° C to slightly above 40° C. The exponential character of the temperature-permeability relationship is shown by the curves in figure 1, in which the logarithm of the permeability is plotted with respect to the reciprocal of the absolute temperature.

TABLE 2.—*Permeabilities to hydrogen at 25° C*

Material	Permeability
	$ml\ cm\ cm^{-2}\ min\ ^{-1} \times 10^6$
Rubber	22.8
Perbunan	14.4
Neoprene *G*	5.4
Vistanex	2.6
Thiokol *Dx*	1.9
Pliofilm	0.4

[1] Theron P. Sager and Max Sucher, J. Research NBS **22**, 71 (1939) RP1166.

TABLE 3.—*Variation of permeability with temperature*

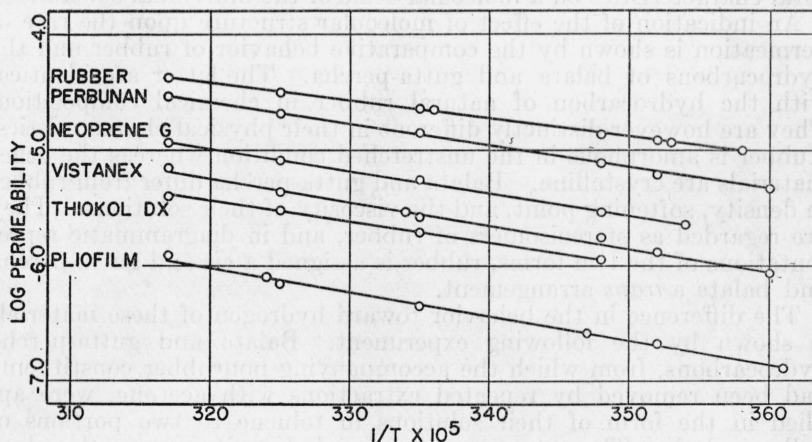| Temperature of test	Permeability to hydrogen at $t°$ C	Temperature of test	Permeability to hydrogen at $t°C$
	RUBBER		**VISTANEX**
$°C$	$ml\ cm\ cm^{-2}min^{-1}\times10^{+6}$	$°C$	$ml\ cm\ cm^{-2}min^{-1}\times10^{+6}$
6.0	9.8	1.0	0.73
10.0	11.8	4.4	.87
11.0	12.3	11.0	1.31
14.0	13.5	14.0	1.75
16.4	15.7	25.0	2.62
24.0	22.8	26.0	2.90
25.5	22.9	34.0	4.30
34.0	31.1	42.0	7.00
42.0	42.0		
	PERBUNAN		**THIOKOL** Dx
		14.0	1.14
4.5	4.61	25.0	1.92
10.9	6.04	34.0	2.97
13.8	7.70	42.0	3.98
25.0	14.4		
34.0	20.5		
42.0	29.0		**PLIOFILM**
	NEOPRENE G		
		3.8	0.13
		10.8	.21
9.0	2.27	14.4	.26
14.0	2.84	25.0	.44
25.0	5.40	34.0	.68
34.0	8.06	35.0	.79
42.0	11.6	42.0	1.26

FIGURE 1.—*Relation between logarithm of permeability and reciprocal of absolute temperature.*

IV. DISCUSSION

The exponential increase in permeability with increasing temperature has been interpreted upon the basis of chemical kinetics. The straight lines obtained in figure 1 are evidence that the velocities of permeation are proportional to the quantity $e^{-E/RT}$, in which E is the activation energy of permeability. In table 4 are shown the values

for E which were computed from the slopes of the curves in figure 1. The values for rubber, chloroprene, and butadiene-acrylonitrile polymer have also been determined by Barrer,[2] with whose results these are in substantial agreement.

TABLE 4.—*Activation energies of permeability for hydrogen*

Material	Activation energy	Material	Activation energy
	cal/mole		*cal/mole*
Rubber	6,800	Vistanex	9,200
Perbunan	8,400	Thiokol *Dz*	8,400
Neoprene *G*	8,900	Pliofilm	9,500

The process of permeation involves the combined action of absorption of the gas by the solid and diffusion or movement of the gas from one point to another in the material. In order for a molecule of gas, located at any point in a solid, to undergo a change of environment, it is necessary that an amount of energy be furnished. Two possible circumstances may govern the consumption of this energy. Energy may be utilized in lessening the binding attraction of the solid for the gas or it may be employed in overcoming the repulsive force encountered as the gas molecule attempts to produce for itself a position or "hole" within the molecular network. In the case of these materials the likelihood of the latter as the predominant factor appears to be the greater. Hence it appears likely that differences in their permeabilities are largely determined by the structural characteristics on a molecular scale of the individual substances.

An indication of the effect of molecular structure upon the rate of permeation is shown by the comparative behavior of rubber and the hydrocarbons of balata and gutta-percha. The latter are identical with the hydrocarbon of natural rubber in chemical composition. They are however distinctly different in their physical characteristics. Rubber is amorphous in the unstretched condition whereas the other materials are crystalline. Balata and gutta-percha differ from rubber in density, softening point, and the viscosity of their solutions. They are regarded as stereoisomers of rubber, and in diagrammatic representations of the two forms, rubber is assigned a *cis* and gutta-percha and balata a *trans* arrangement.

The difference in the behavior toward hydrogen of these materials is shown by the following experiment. Balata and gutta-percha hydrocarbons, from which the accompanying nonrubber constituents had been removed by repeated extractions with acetone, were applied in the form of their solutions in toluene to two portions of balloon cloth. The amounts of material deposited upon the cloth upon evaporation of the solvent were of approximately the same weight per unit of area. A film of a "pure gum" rubber compound was similarly applied to a third portion of the same cloth. The permeabilities to hydrogen of the three fabrics were determined at 25° C. The values obtained and the weights of coatings are shown in table 5. Since the densities of these substances are not appreciably different, the permeabilities obtained on films of about the same weight per unit area are practically comparable.

[2] R. M. Barrer, Trans. Faraday Soc. **35**, 637 (1939).

TABLE 5.—*Comparison of the permeabilities of fabrics coated with rubber, balata, and gutta-percha*

Material	Weight of coating	Permeability to hydrogen
	$g\ m^{-2}$	$Liter\ m^{-2}\ (24\ hr)^{-1}$
Rubber	123.0	13.4
Balata	125.4	1.7
Gutta-percha	98.3	2.2

Results which have been obtained from X-ray and electron diffraction studies of linear polymers [3] indicate that structural differences may exist between natural rubber and synthetic polymers which are similar to those which determine the distinctive characteristics of rubber and substances such as balata, and which may largely account for the differences in the permeability of these materials.

It is obvious that permeability alone does not wholly determine the relative utility of these materials for flexible gas-containing structures. Other factors which equally determine their usefulness are tensile strength, elongation, permanent deformation, resistance to natural aging, continued polymerization or depolymerization, and behavior at extremes of temperature. Most of the properties of the materials which have been considered here are known or are rapidly becoming so. They all possess certain characteristics which render them particularly useful in definite fields for which they were designed. In their present stage of development no one of them represents the ideal in every respect for the construction of gas containers. It has been observed, however, that changes in the physical characteristics of such materials, which are produced through changes in chemical composition, methods of preparation, or the nature and amounts of their compounding ingredients, are frequently not accompanied by any appreciable change in their behavior toward gases. The rate of permeation of uncured rubber, for example, differs but little from that of the fully vulcanized material, despite the extensive changes produced in other properties. The permeability of Neoprene *G* is but slightly higher than that of Neoprene *E*. (See footnote 1.) That of Thiokol *Dx* is of about the same order as that of other types of this material.[4] For this reason materials which are deficient only in certain physical characteristics may be capable of being improved in this respect without serious impairment of their low rates of permeation.

Since it is becoming increasingly evident that neither the property of elastic extensibility nor impedance to the passage of gases is restricted to any sharply defined group of substances, there is the further possibility that some new type of polymer may yield an even more desirable material.

WASHINGTON, June 17, 1940.

[3] C. S. Fuller, Chem. Rev. **26**, 143 (1940).
[4] Theron P. Sager, J. Research NBS **19**, 181 (1937) RP1020.