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PERMEABILITY OF NEOPRENE TO GASES

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ABSTRACT

The specific permeability of Neoprene to hydrogen, helium, and carbon dioxide at 25° C is shown to be about one-fifth to one-sixth that of rubber. Permeability is inversely proportional to the thickness of film. The increase in the rate of permeation of hydrogen with temperature is shown to be exponential since, when log permeability is plotted against reciprocal of absolute temperature, straight lines are obtained. Various factors regarding the behavior of coated fabrics are discussed. Moderate amounts of the usual compounding ingredients do not appreciably affect the rate of permeation. The use of highly volatile solvents in spreading cements tends to produce pinholes. Toluol or its equivalent appears to be the most satisfactory solvent.

CONTENTS

I. INTRODUCTION

The properties most generally associated with Neoprene are its rubber-like character and its resistance to the deteriorative action of mineral oils. To this combination of properties it owes its principal commercial applications. A less generally known characteristic is the relatively low permeability of this material to gases. The most suggestive utilization of this property is in the construction of various forms of gas containers for use in lighter-than-air craft, particularly in view of the fact that the material may be readily applied to cloth as a continuous film having elastic extensibility. The work represented by this report was undertaken as a result of the interest which the Bureau of Aeronautics of the United States Navy Department maintains in all materials which offer promise of application in this field.

Since rubber is the material which has been employed to the greatest extent for gas containers, it is used as the basis for comparison in the present study. Aside from its practical application, the behavior of Neoprene toward gases is of interest because of the relation of its chemical composition to that of other dienes which possess elasticity. The substance used as the base for Neoprene compounds is polymerized chloroprene (2-chloro-1, 3-butadiene). The chemical composition of chloroprene, $CH_2{=}CCl{-}CH{=}CH_2$ differs from that of other conjugated dienes, whose polymers are characterized by elastic extensibility, in that 40 percent of its molecule consists of chlorine.

II. MATERIALS AND METHODS

The Neoprene employed throughout this work was that designated by the manufacturer as type *E*. The compounding materials were all of the type and quality recommended for use with Neoprene. The compounds were prepared in the customary manner, the Neoprene being masticated on a differential-speed mill, the compounding ingredients being added on the mill. The rubber compounds were similarly prepared. In the preparation of cements the thinly sheeted materials were dissolved in toluol which was kept in continuous agitation. The cements were filtered through cloth and stored in tinned containers.

The coated fabrics were prepared by applying a plurality of thin coats to a balloon cloth by means of a small spreading machine equipped with a doctor blade. The cloth was a closely woven cotton fabric weighing 2.05 oz/yd ^{2}, and having a thread count of 120 in both warp and filling directions. The unsupported films were prepared in the same manner except that the base was uncoated Cellophane from which the films, after being cured, could be readily stripped.[1]

Curing in all cases was effected in dry heat. For Neoprene the conditions were a 1-hr rise to 257° F (125° C) followed by 2 hr at 257° to 266° F (125° to 130° C).

Permeability was determined by means of a gas interferometer of the Rayleigh type. The apparatus and conditions of test have been previously described.[2] Except where otherwise noted, all determinations were made under the following standard conditions: The film or fabric is maintained at a temperature of 25° C, with air at atmospheric pressure (760 mm of mercury) on one side of the specimen and the gas whose rate of permeation is being measured at an excess pressure of 30 mm of water on the other side. Permeability is expressed as liters per square meter per 24 hr determined under these standard conditions. The permeabilities in metric units may be converted to their corresponding values in cubic feet per square yard per 24 hr by multiplying the former by the factor 0.0295. Specific permeabilities are expressed as milliliters per square centimeter per centimeter thickness per minute.

III. PERMEABILITY OF UNSUPPORTED FILMS

1. EFFECT OF THICKNESS

In the preparation of unsupported films the following compound was employed:

Compounding ingredient	*Parts by weight*
Neoprene *E*	100
Magnesium oxide	10
Rosin	5
Carbon black (*P-33*)	5
Phenyl-β-naphthylamine (Neozone *D*)	2
Zinc oxide	10

The permeabilities to hydrogen, helium, and carbon dioxide obtained with different thicknesses of films are presented in table 1. The close agreement of the specific permeabilities, calculated from the permeabilities of films of various thickness, indicates that the rate of

[1] T. P. Sager, Ind. Eng. Chem., Anal. Ed. **9**, 156 (1937).
[2] J. D. Edwards and S. F. Pickering, BS Tech. Pap. **11** (1918) T113; BS Sci. Pap. **16**, 327-362 (1920) S387.

TABLE 1.—*Permeabilities of unsupported films of Neoprene*

Thickness of film *cm*	Permeability at 25° C and 1 atm Liters/m²/24 hr			Specific permeability at 25° C and 1 atm ml/cm²/cm/min$\times 10^{+6}$		
	Hydrogen	Helium	Carbon dioxide	Hydrogen	Helium	Carbon dioxide
0.010	6.3	4.1	12.1	4.3	2.8	8.4
.010	6.0	3.7	11.6	4.1	2.5	8.0
.016	3.7	2.5		4.1	2.7	
.017	3.9	2.7	8.3	4.5	3.1	9.7
.022	2.7			4.1		
.029	2.1			4.2		
.035	1.8	1.1	3.6	4.3	2.6	8.7
.039	1.6			4.3		
.068	0.9	0.6	2.0	4.2	2.8	9.4
Average				4.2	2.7	8.8

permeation is inversely proportional to the thickness. This is shown in figure 1, in which is presented the relationship of the gas impedance (reciprocal of permeability) to the thickness of film.

2. RELATIVE PERMEABILITY TO GASES

The average value of the ratio of helium permeability to hydrogen permeability of Neoprene, calculated from the values in table 1, is 0.65, which is the same as the corresponding value for rubber given in the literature. The average of the ratios for carbon dioxide to hydrogen is 2.0, which is somewhat lower than the corresponding values for rubber, which are reported as ranging from 2.46 to 2.91.

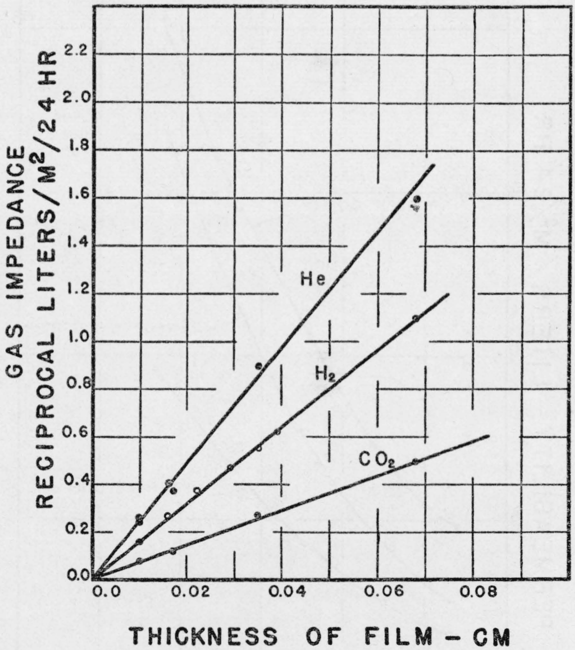

FIGURE 1.—*Relation of Thickness of Neoprene Films to Gas Impedance.*

Values for the specific permeability of rubber to hydrogen, given in the literature, range from about 20×10^{-6} to 27×10^{-6} ml/cm²/min for 1 cm thickness. According to these values, it is apparent that the specific permeability of this Neoprene compound is about one-fifth to one-sixth that of rubber.

3. EFFECT OF TEMPERATURE

For the determination of the effect of temperature on the permeability of Neoprene to hydrogen, the thickness of films chosen was such that convenient values for permeability could be obtained throughout a range of temperatures. For comparison, the permeability of a film of rubber was also measured under the same conditions. The essential data concerning the rubber compound are as follows:

Compounding ingredient	*Parts by weight*
Smoked sheet rubber	100
Sulfur	4
Zinc oxide	5
Zinc stearate	1
Mercaptobenzothiazole (Captax)	1
Phenyl-β-naphthylamine (Neozone D)	1

Cure: Thirty minutes at 288° F.

The values obtained at the various temperatures are given in table 2, and the relations between permeability and temperature are shown in figure 2. In figure 3 are plotted the logarithms of the permeabilities against the reciprocals of the absolute temperatures. The fact that the points fall fairly closely on straight lines indicates, as has been shown in the case of rubber,[3] and in the case of regenerated cellulose and cellulose derivatives,[4] that the increase in permeability with temperature is exponential. The dependence of permeability upon temperature is expressed by means of the equation $Q_m = Ae^{-E/RT}$, in which Q_m is the permeability at the temperature T in moles per square centimeters per second at 1 cm thickness. A is a constant having the same dimensions as Q_m, which bears a relation to the spatial requirements of the reacting molecules. E is the activation energy expressed in calories per mole. R and T are the gas constant and absolute temperature, respectively. When values obtained from figure 3 were employed in this equation the values for E and A which resulted are shown in table 3.

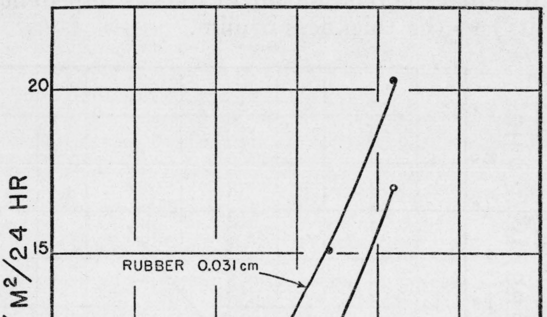

FIGURE 2.—*Relation between permeability to hydrogen and temperature.*

[3] R. M. Barrer, Nature **140**, 106 (1937).
[4] J. H. De Boer and J. D. Fast, Rec. trav. chim. **57**, 317 (1938).

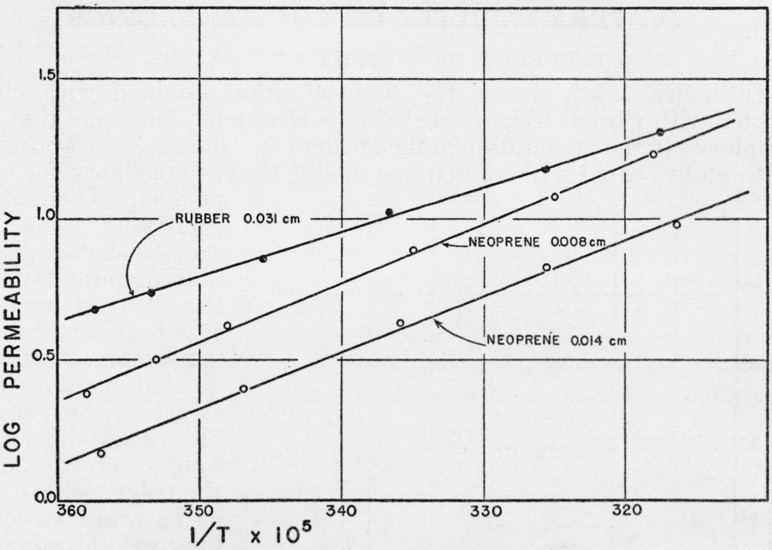

FIGURE 3.—*Relation between log permeability and reciprocal of absolute temperature.*

TABLE 2.—*Variation of permeability with temperature*

Temperature of test	Permeability to hydrogen
Neoprene 0.008 cm thickness	
°*C*	*Liters/m²/24 hr at 1 atm at t °C*
6.0	2.4
11.0	3.2
14.0	4.2
25.5	7.8
34.0	12.1
42.0	17.0
Neoprene 0.014 cm thickness	
7.0	1.5
15.2	2.5
24.7	4.3
34.0	6.7
43.0	9.6
Rubber 0.031 cm thickness	
6.0	4.8
10.0	5.5
16.4	7.3
24.0	10.6
34.0	15.1
42.0	20.3

TABLE 3.—*Values for E and A, in the equation $Q_m = A_e{}^{-E/RT}$, for hydrogen*

Material	Thickness	E	A
	cm	*cal/mole*	*Moles/cm² sec for 1 cm thickness*
Neoprene	0.014	9,376	22.2×10⁻
Do	.008	9,422	24.2
Rubber	.031	6,998	2.2

IV. PERMEABILITY OF COATED FABRICS

1. EFFECT OF WEIGHT OF COATING

In figure 4 are shown the permeabilities obtained with cloth, coated with various weights of the same Neoprene compound that was employed in the preparation of the unsupported films. Values obtained with cloth coated with similar weights of rubber are shown for comparison. The rubber compound was the same as that employed in the determination of the effect of temperature on permeability.

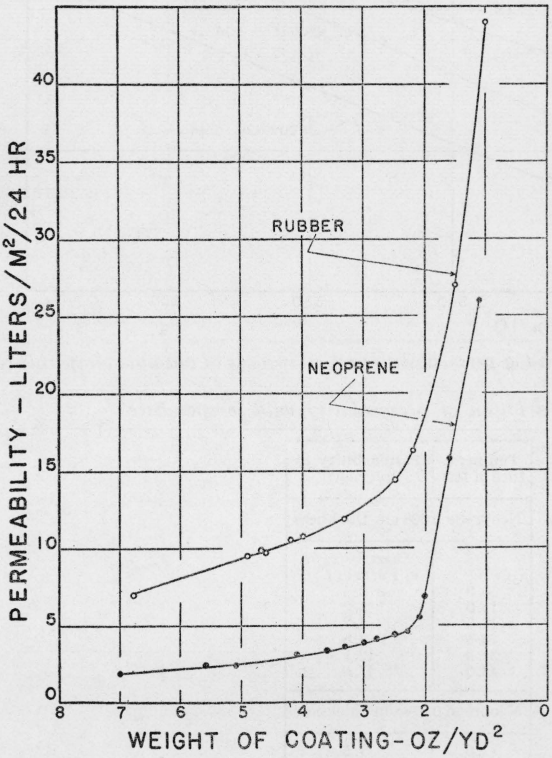

FIGURE 4.—*Comparison of the permeabilities to hydrogen obtained with fabrics coated with various amounts of rubber and Neoprene.*

From the standpoint of airship fabric construction the permeabilities obtained with weights of coating in the neighborhood of 2 oz/yd^2 are of particular interest. It is apparent that within this range the greatest impedance for a unit weight of coating is obtained. Below about 2 oz/yd^2 of coating the permeability changes somewhat more rapidly in the case of Neoprene than of rubber. The specific gravity of the rubber compound is approximately 1.0, while that of the Neoprene compound is between 1.3 and 1.4. The covering power of the latter is consequently less than that of rubber and it becomes increasingly more difficult to obtain a continuous film on the cloth. It is this difference in specific gravities which accounts for the difference between the specific permeabilities and the permeabilities on a weight basis of the two materials. Based on the latter, the permeability of Neoprene is about one-third to one-fourth that of rubber.

In figure 5 a comparison is shown between the permeabilities of Neoprene-coated fabrics and those of unsupported films of the same weights per unit area as the weights of coatings on the fabrics. The difference in permeabilities illustrates a well-known fact that the cloth makes a definite contribution to the gas impedance of a coated fabric. It has been noted that this ratio between the permeabilities of coated fabrics and unsupported films is nearly constant for both Neoprene and rubber within the range shown in figure 5. The effect of the cloth on the permeability doubtless becomes more involved

TABLE 4.—*Characteristics of multiple-ply fabrics*

Construction (order of layers in cross section)	Type of fabric		
	Ballonet	Airtight envelope	Gastight envelope
	Oz/yd^2	Oz/yd^2	Oz/yd^2
Aluminum-pigmented Neoprene	----------	0.7	0.7
Neoprene	0.5	1.0	1.0
Cloth	2.05	2.05	2.05
Neoprene	3.5	1.6	1.6
Cloth	2.05	[a]2.05	[a]2.05
Neoprene	0.5	1.6	3.6
Cloth	----------	2.05	2.05
Neoprene	----------	0.5	0.5
Permeability to hydrogen (liters/m^2/24 hr)	3.8	2.8	1.6

[a] Fabric laid on bias.

when the fabrics are constructed of two or more plies. Typical constructions of such fabrics, employing Neoprene as coatings, and the permeabilities obtained are shown in table 4.

2. EFFECT OF COMPOSITION OF COATINGS

As with rubber, the physical properties of Neoprene compounds vary considerably with the nature and proportions of the compounding ingredients. In table 5 are shown the permeabilities to hydrogen obtained with a number of compounds which were applied to cloth. It was not feasible to attempt to produce fabrics all having the same weight of coating, but since for a given compound the product of the weight of coating and the permeability is nearly constant within the range of weights represented, it was considered permissible, in order to secure a uniform comparison, to express the permeabilities relative to a single weight of coating. A comparison of the permeabilities calculated to a weight of coating of 3.5 oz/yd² is shown in figure 6.

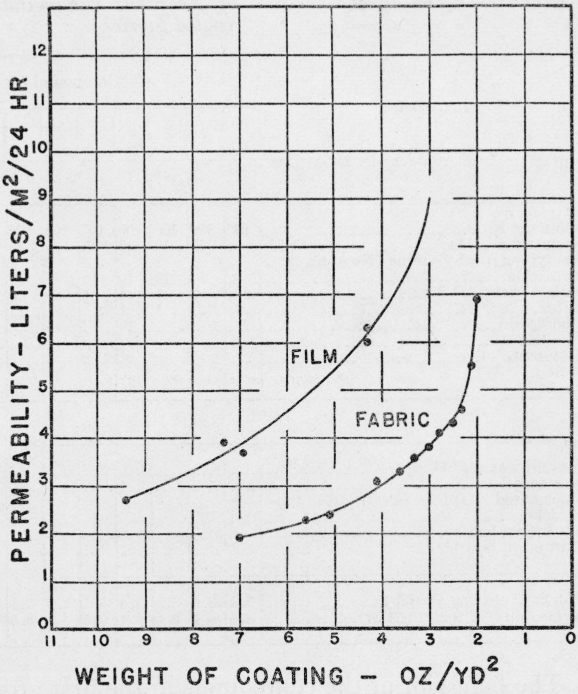

FIGURE 5.—*Comparison of the permeabilities to hydrogen obtained with unsupported film and fabric coated with the same weight of film.*

The compounds comprise two groups. Group 1 includes the conventional compounding materials which are added to secure satisfactory cure, increased flexibility, and similar characteristics. Group 2 contains, in addition, substances which are not usually associated with Neoprene.

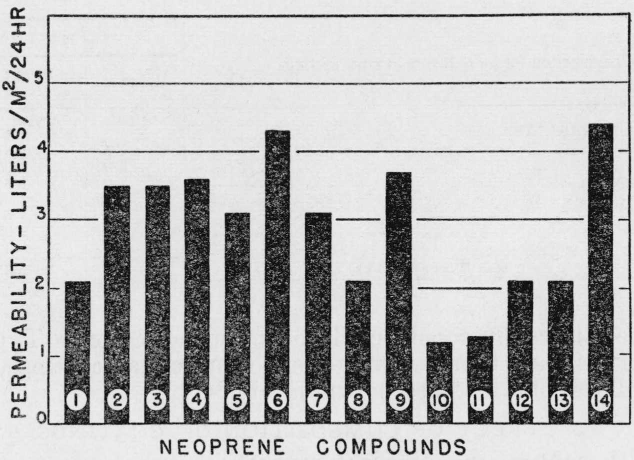

FIGURE 6.—*Comparison of the permeabilities obtained with the compounds given in table 5 calculated to a uniform weight of coating of 3.5 oz/yd².*

TABLE 5.—*Effect of composition of Neoprene compounds upon permeabilities of coated fabrics*

Ingredients	Compound (parts by weight)													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
GROUP 1														
Neoprene *E*	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Magnesium oxide	----	10	10	10	10	10	10	10	10	10	10	10	10	10
Phenyl-β-naphthylamine (Neozone D)	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Zinc oxide	----	10	10	10	10	10	10	10	10	10	10	10	10	10
Carbon black (*P-33*)	----	5	5	5	5	30	5	5	5	5	5	5	5	5
Sulfur	----	----	1	1	----	----	----	----	----	----	----	----	----	----
Wood rosin	----	----	----	10	----	5	5	5	5	5	5	----	5	5
Pine tar	----	----	----	----	10	----	----	----	----	----	----	----	----	----
Cottonseed oil	----	----	----	----	5	10	----	----	10	----	5	----	----	----
Cumar (*P-25*)	----	----	----	----	5	10	----	----	10	----	10	----	----	----
GROUP 2														
Paraffin wax (55° C mp)	----	----	----	----	----	----	5	20	----	----	----	----	----	----
Spermaceti	----	----	----	----	----	----	----	----	----	40	40	----	----	----
Chlorinated naphthalene resin (Arochlor)	----	----	----	----	----	----	----	----	----	----	----	40	----	----
Soft-brown factice	----	----	----	----	----	----	----	----	40	----	----	----	----	----
Aluminum powder	----	----	----	----	----	----	----	----	----	----	----	----	40	80
Weight of coating (oz/yd²)	3.1	3.6	3.5	3.8	3.1	4.0	3.1	3.4	3.4	3.6	3.3	2.7	3.2	3.2
Permeability (liters/m²/24 hr)	2.4	3.4	3.5	3.4	3.5	3.8	3.6	2.2	3.9	1.2	1.4	2.8	2.3	4.9

The behavior of the compounds in the first group indicates that the inclusion of moderate amounts of the orthodox compounding ingredients does not appreciably affect the rate of permeation. This is in agreement with general experience in the behavior of rubber compounds. Of the compounds in the second group the behavior of that containing spermaceti is noteworthy. It should be stated, however, that the relative permeabilities obtained with various compounds are not always reliable indications of their usefulness. Factors connected with the manufacture, and the subsequent ability to withstand handling and exposure, of aircraft fabrics determine their utility to fully as great an extent as their rate of permeation. The behavior of the compounds containing aluminum powder is of interest since the presence of this pigment is of value because of its high reflecting power and opacity. The results obtained with paraffin illustrate the difficulty of employing a compounding material inherently incompatible with Neoprene. Paraffin wax itself is highly impermeable to hydrogen. Balloon cloth impregnated with about 2.4 oz/yd^2 of paraffin wax is permeable to hydrogen to the extent of only 0.5 liter/m^2/24 hr. Its use for aircraft fabrics is limited, for obvious reasons, to its supplementary employment on material such as rubberized fabric. An example of the treatment of a Neoprene-coated fabric in this manner is then of interest. The fabric coated with compound 9 in table 4 was coated on one surface with 0.4 oz/yd^2 of paraffin wax (55° mp). The permeability to hydrogen of the fabric was reduced from 3.5 to 1.0 liters/m/24 hr.

3. EFFECT OF SOLVENTS EMPLOYED IN CEMENTS

Early in the experimental preparation of Neoprene-coated fabrics the formation of pinholes was a matter of considerable concern. Under the conditions of preparation the presence of these did not appear to be related to the nature of the compound nor to the number of coats applied. Furthermore, their persistence was not appreciably affected by the thickness of film built up on the fabric. The method of coating the fabrics was similar to that employed commercially except that the cements contained a higher percentage of solvent. The cement was applied to the cloth, which was under moderate tension, in several successive coats. A source of heat, in the form of heating coils, located beneath the fabric hastened the evaporation of the solvent. It was considered advisable to compare films deposited from several different solvents which were suitable for Neoprene and economically within reason. Fabrics were coated with these cements under conditions of forced evaporation and at room temperature. The coated fabrics were examined, both before and after curing, over a light bank, for the presence of pinholes. No changes, so far as the presence of pinholes was concerned, occurred as the result of the curing. Excessive pinhole formation, as noted by visual inspection, corresponds to the high permeabilities in table 6.

TABLE 6.—*Effect of solvents in cements on pinhole formation*

Solvent	Evaporation at 140° F (60° C)		Evaporation at 78° F (25.5° C)	
	Weight of coating	Permeability to hydrogen	Weight of coating	Permeability to hydrogen
	oz/yd^2	*Liters/m^2/24 hr*	*oz/yd^2*	*Liters/m^2/24 hr*
Carbon tetrachloride	3.1	>50	3.2	>50
Benzol	3.5	23	3.1	4.5
Toluol	3.6	3.1	2.8	4.6
Xylol	2.7	4.6		

Too rapid evaporation of the solvent may not always be the only cause of pinholes, but in extreme cases it would appear to be the most obvious contributing factor. Toluol or its equivalent is the most satisfactory solvent used.

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